DEVELOPMENT OF SOL-GEL CATALYSTS BY USE OF FAST COMBINATORIAL SYNTHESIS AND HIGH THROUGHPUT TESTING TECHNIQUES FOR CATALYTIC OXIDATION OF PROPYLENE TO PROPYLENE OXIDE

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ABSTRACT

DEVELOPMENT OF SOL-GEL CATALYSTS BY USE OF FAST COMBINATORIAL SYNTHESIS AND HIGH THROUGHPUT TESTING TECHNIQUES FOR CATALYTIC OXIDATION OF PROPYLENE TO PROPYLENE OXIDE

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Propylene oxide (PO) is an important raw material for the chemical industry, which is produced commercially by the chlorohydrin process and hydroperoxide process. However the deficiencies in these processes have given rise to considerable interest in the development of a direct route to PO that does not produce by-products or coproducts.

The development of novel, active and selective catalysts for gas phase oxidation of propylene using molecular oxygen were studied via testing a large number of catalysts by high-throughput screening method over combinatorially prepared different catalytic system in this study.

The promoted and un-promoted silver (Ag), copper (Cu), manganese (Mn) mono and bimetallic catalytic system over high and low surface area silica, alumina, titanium oxide and titanium-silicate supports were prepared by single step sol-gel method and by incipient wetness method. The study to determine the most effective catalyst and promoter in the epoxidation reaction with different reaction conditions, showed that potassium (K)-promoted Cu metal supported over high surface area silica favored the PO production at a high reaction temperature (350 °C) and oxygen rich atmosphere ($C_3H_6/O_2=1.0$).

The catalyst showed high and low propylene oxide productivity was investigated by some of the characterization techniques. The highly-dispersed copper particle over silica support was determined by XRD, TEM and XPS techniques. The only change between promoted and un-promoted catalyst was found out in the temperature dependence of propylene consumption and PO production rate. It was inferred that potassium (K) only neutralizes the acid sites of silica.

Keywords: Propylene, Epoxidation, Sol-Gel, High-Throughput Testing

ÖZ

HIZLI KOMBİNASYONAL SENTEZ VE HIZLI KATALİTİK TEST YÖNTEMLERİYLE PROPİLENİN PROPİLEN OKSİTE KATALİTİK OKSİTLENMESİ İÇİN ÇÖZ-PEL KATALİZÖRLERİNİN GELİŞTİRİLMESİ

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Propilen oksit (PO), ticari olarak klorohidrin ve hidroperoksit yöntemiyle üretilen kimya sanayinin önemli bir hammaddesidir. Günümüzde kullanılan bu iki sistemdeki aksaklıklar nedeniyle, propilen oksidin herhangi bir yan ürün ve atık oluşmadan doğrudan sentezlenmesi amacıyla oldukça yoğun çalışmalar yapılmaktadır.

Bu çalışmada, moleküler oksijen kullanarak propilenin gaz fazı oksitlenmesi tepkimesi için yeni, aktif ve yüksek seçiciliğe sahip katalizörlerin geliştirilmesi amacıyla çok sayıda katalizör adayı hazırlanmış ve hızlı sonuç veren katalitik aktivite test sisteminde test edilmiştir. Bu amaçla tekli ve ikili metalik katalizör sistemleri aynı anda yirmi dört katalizör sentezlenmesine olanak sağlayan hızlı sentez reaktöründe çöz-pel yöntemiyle hazırlanmıştır.

Farklı modifiye maddeleri ile modifiye edilen ve edilmeyen gümüş (Ag), bakır (Cu) ve mangan (Mn) tekli ve ikili metallik sistemleri geniş ve düşük yüzey alanlı silikon dioksit (SiO_2), aluminyum oksit (Al_2O_3), titanyum oksit (TiO_2) ve titanyum silikat (TiO_2-SiO_2) destek maddeleri üzerine tek basamaklı çöz-pel ve emdirme yöntemiyle yüklenmiştir. Sentezlenen katalizörler için farklı tepkime değişkenlerinde gerçekleştirilen katalitik aktivite test sonuçları, en yüksek PO verimi gösteren katalizörün potasyum (K) ile modifiye edilmiş Cu içeren yüksek yüzey alanlı silikon dioksit katalizörü olduğunu göstermiştir. En yüksek PO verimine 350 °C tepkime sıcaklığında ve 0.5 propilen/oksijen oranında ulaşılmıştır.

Yüksek ve düşük katalitik aktivite gösteren katalizörler bazı karakterizasyon teknikleri kullanılarak incelenmiştir. Yüksek PO verimi gösteren katalizörler XRD, TEM ve XPS analiz teknikleriyle incelendiğinde, Cu metalinin küçük partiküller halinde silika üzerine çok iyi dağılım gösterdiği görülmüştür. Eklenen potasyumun ise katalizör yüzeyi üzerinde asidik bölgeleri nötralize ederek yüksek propilen dönüşümünü bastırdığı ve PO sentezini arttırdığı belirlenmiştir.

Anahtar Sözcükler: Propilen, Epoksitleştirme, Çöz-Pel, Yüksek-Hızlı Test Yöntemi

To My Family

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INTRODUCTION

1.1. Catalysis

Catalysis plays very important role in societies. The majority of all chemicals and fuels produced in the chemical industry have been in contact one or more catalysts (Chorkendorff and Niemantsverdriet, 2003).

In terms of chemical conversion, catalysts are responsible for the production of over 60% of all chemicals produced and used in over 90% of all chemical processes worldwide. Catalysts manufacturing alone accounts for over $10 billion in sales worldwide and is spread out across four major sectors: refining, chemicals, polymerization, and exhaust emission catalysts (van Santen and Neurock, 2006). However the value derived from catalyst sales, is only a very small fraction of the total value derived from catalysis overall, which includes the value of the products produced, i.e. chemical intermediates, polymers, pesticides, pharmaceuticals, and fuels (van Santen and Neurock, 2006).

Catalysis holds promise of eliminating, or at least substantially reducing, pollution from chemical and petroleum processes, electronics manufacturing, pharmaceutical synthesis, and stationary and vehicular emission sources. Heterogeneous catalysis is at the heart of many of the proposed green chemical processes targeted to reduce emission dramatically. A catalyst, by definition, is used to convert reactants to products without itself being consumed. Catalyst is a substance that changes the velocity of a reaction without itself being altered in the process (Levenspiel, 1972). The aim then is adaptation of the structure of active catalysts to convert reactants directly to product without by-products. Catalysts then provide the elimination of side products, thus elimination most waste by nature (van Santen and Neurock, 2006).

It is clear that catalysis plays prominent role in society today and will be a critical technology for advancing our life.

1.2. Catalysts Type

Catalysts may have different forms, changing from atoms and molecules to large structures such as zeolites or enzymes. In addition they may be employed in various environments: in liquids, gases or at the surface of solids. Preparing a catalyst in the optimum form and studying its exact composition and shape require important specialism (Levenspiel, 1972; Chorkendorff and Niemantsverdriet, 2003).

In catalysis it is ordinary to distinguish the following three subdisciplines: homogenous, heterogeneous and bio catalysis (Chorkendorff and Niemantsverdriet, 2003). In homogeneous catalysis both the catalyst and the reactants are in the same phase. They are frequently metalloorganic molecules or clusters of molecules and find wide and important application in the chemical technologies. Enzymes are nature’s catalysts. They allow biological reactions to occur at the rates necessary to maintain life, such as built up protein and DNA, or breakdown of molecules and the storage of energy in sugars.

Most of the catalysts employed in the chemical technologies are heterogeneous. They are the workhorses of the chemical and petrochemical industry. The chemical reaction takes place on surfaces, and the reactants are introduced as gases or liquids. Catalysts are usually nanometer-sized particles, supported on an inert, porous structure and generally expensive materials (Somorjai, 1994; Chorkendorff and Niemantsverdriet, 2003).

1.3. Heterogeneous Catalysts

There are three major areas of heterogeneous catalysis application at present: automotive, fosil-fuel refining and production of chemicals (Somorjai, 1994). The automotive industry used mostly noble metals (platinum, rhodium and palladium) for catalytic control of car emission: unburned hydrocarbon, CO_x and NO_x. These highly dispersed metals supported on oxide surfaces, and the catalyst system are specially prepared to be active at high space velocities of the exhaust gases and over a wide temperature range. In petroleum refining, zeolites are most widely used for cracking of hydrocarbon in the presence of hydrogen. The important hydrodesulfurization process use mostly sulfides of molybdenum and cobalt on an alumina support. The reforming reactions to produce cyclic and aromatic molecules and isomers from alkanes to improve octane number are carried out mostly over platinum containing bimetallic catalysts, such as Pt-Re and Pt-Sn (Somorjai, 1994).

1.4. Olefins and Oxidation Reactions

Propylene oxide which is also known as PO, methyloxirane or 1,2-epoxypropane, is one of the most important starting materials in the chemical industry. The production of PO consumes 10% of all propylene produced. The main application of PO is in the production of polyether polyols (65%), which are mainly used for the production of (polyurethane) foams. The second and third largest applications are in the production of propylene glycol (30%) and propylene glycol ethers (4%), respectively. Propylene glycols are mainly used in the production of polyesters whereas propylene glycol ethers are primarily used as solvents (Nijhuis et al., 2006).

With a worldwide production capacity of more than 5.8 million tons per year and positive market forecast, PO represents an important chemical intermediate with growing attention. However two unsatisfying routes in liquid phase, the so-called chlorohydrins process and the peroxidation process, are still prevailing in PO production technology. The general disadvantages of both routes are multiple reaction steps and the formation of coupled products in large amounts. In chlorohydrin process, the use of chlorine and hydroxide leads a coupled formation of large amounts of inorganic salts, causing corrosion and environmental problems. The peroxidation process implies a group of routes that employ different organic co-reactants (e.g. ethylbenzene, isobutene). Another separate oxidation to peroxides, these compounds is used as oxygen donors for the propylene epoxidation. Although these co-reactants are subsequently converted to marketable products, process economy of PO synthesis extremely depends on market prices of coupled products (Ananieva and Reitzmann, 2004).

Heterogeneously or homogeneously catalyzed epoxidation technologies in the liquid phase with ex situ and in situ produced hydrogen peroxide as oxidant seem to be most developed. However because of the high H_2O_2 price, the question of profitability still puts this process under debate (Ananieva and Reitzmann, 2004).

Moreover the heterogeneously catalyzed epoxidation of higher alkenes, such as propylene is experimentally challenging, theoretically interesting and technologically highly desirable in the chemical industry. The silver-catalyzed, gas phase epoxidation of ethylene using molecular oxygen is one of the most successful examples of heterogeneous catalysis to date. In 1998, the domestic production of ethylene oxide alone was 3.81 million tons. In spite of the versatility and importance of olefin epoxides in the chemical processing industry, until very recently, no other olefins had been commercially epoxidized using only molecular oxygen as the oxidant. Efforts to directly epoxidize other higher olefins such as propylene to their corresponding epoxides using molecular oxygen in a commercially-viable process have not been as successful. Many explanations have been proposed for the failure to directly epoxidize allylic olefins such as propylene, although the most obvious reason is the reactivity of allylic C-H bonds. For example, while Ag catalysts epoxidize ethylene with selectivity around 80%, propylene epoxidation occurs with 5% selectivity. The electrophilic attack by oxygen and abstraction of one of the allylic C-H bonds in propylene becomes energetically more favorable than electrophilic addition of oxygen across the C=C double bond shown in Figure 1.1. One abstraction of hydrogen occurs, epoxide formation is precluded and leading only to combustion (Monnier, 2001; Cropley et al., 2005).

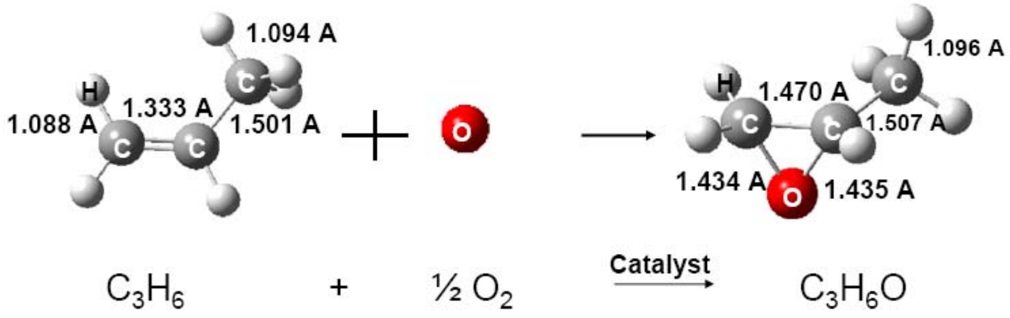


Figure 1.1. Direct propylene epoxidation reaction (Fellah, 2009)

The discovery of any new catalyst or catalytic reaction is always a welcome addition to the general body of scientific knowledge. The three dominant criteria for the development and the design of new catalytic materials are highly active, produced only the desired products and maintain activity for prolonged time (van Santen and Neurock, 2006).

PO requires a new process for its production because of the disadvantages that are encountered with the currently available processes. The research into new catalysts and processes for the propylene epoxidation is not at its end. Improvements are being made continuously and new processes to replace the two existing process are beginning to be applied.

1.5. General Properties of Propylene Oxide

PO is a colorless, low-boiling (34.2°C) organic compound with molecular formula CH_3CHCH_2O (Kirk–Othmer, 1997). It is miscible with most organic solvents but forms a two phases system with water. PO can exits as two optical isomers; the racemic mixture is the commercial product. The physical properties are summarized in Table 1.1. PO forms azeotropes with methylene chloride, ether, and several hydrocarbons. It exhibits a high degree of reactivity, a result of the presence of strained, three-membered oxirane ring.

Table 1.1 Some physical properties of propylene oxide, C_3H_6O (Kirk–Othmer, 1997)

Property	**Value**
Molecular weight	58.08
Boling point at 101.3 kPa, ºC	34.2
Freezing point, °C	-112
Critical pressure, Mpa	4.92
Critical temperature, °C	209.15
Critical volume, cm^3/mol	186
Critical density, g/m^3	0.312
Critical compressibility factor	0.2284
Flash point, Tag closed cup, °C	-37
Heat of fusion, kJ/mol	6.54
Heat of vaporization, 101.3 kPa, kJ/mol	27.8947
Heat of combustion, kJ/mol	1915.6
Specific heat, at 20°C	122.19

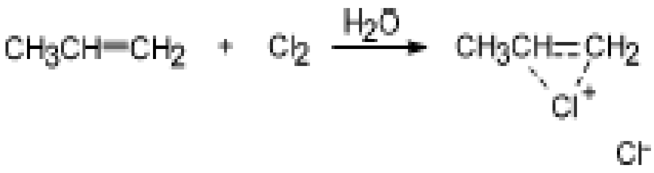
1.6. Current Processes

Propylene oxide is produced by two commercial processes: the chlorohydrin process or the hydroperoxide process (Kirk–Othmer, 1997). Both processes start from propylene. About 4.54 million tons with equal share for two processes was estimated as the 1999 global PO capacity. However the most recently builts plants are all using hydroperoxide process technologies because of the enviromental impacts of the chlorohydrin process (Nijhuis et al., 2006).

1.6.1. Chlorohydrin process

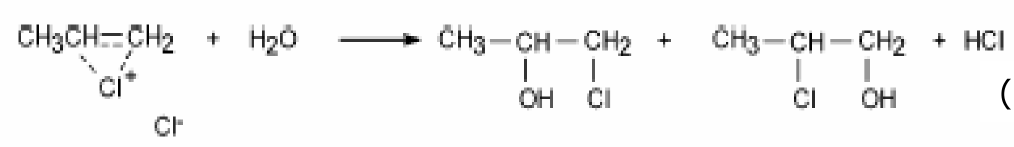
The chlorohydrins process has long been the main process for producing both ethene oxide and PO. In the 1940s, ethane epoxidation started to be phased out, because of the development of a more-efficient direct epoxidation process using a silver catalyst. After that introduction, many ethane epoxidation plants were converted for the epoxidation of propylene.

In the chlorohydrain process, the production of propylene chlorohydrins is the first step (chlorohydrination) and it is started with propylene chloronium complex produced in the first reaction step (Kirk–Othmer, 1997),



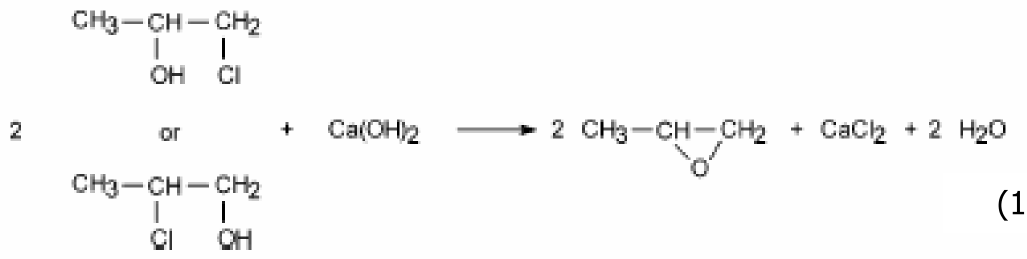
$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow{H_2O} \underset{Cl^+}{CH_3CH{-}CH_2} \quad Cl^- \qquad (1.1)$$

followed by a reaction with water to produce two propylene chlorohydrin isomers.



(1.2)

The selectivity to the chlorohydrin isomers is 90%-95%. Primarily 1,2-dichloropropane and smaller quantities of dichloropropanols, as well as dichloroisopropyl ethers are produced as byproducts. The chlorohydrination is usually performed in a bubble column reactor at a pressure of 1.5 bar and temperature of 50 °C. The use of rubber-, plastic-, or brick-lined equipment is necessary because of the corrosive nature of the reactant mixture. In the epoxidation reactor, the dehydrochlorination of propylene chlorohydrins takes place in the basic condition (usually calcium hydroxide).



(1.3)

Propylene oxide is steam-stripped from this reactor, to prevent base-catalyzed hydrolysis of the product. The dehydrochlorination is performed in the same column where the products are stripped from the wastewater stream (1 bar, 373 K). The chlorinated hydrocarbons that are produced ultimately reside in the PO stream must be removed. The brine leaving the bottom of the reactor contains some propylene glycols, because the hydrolysis of PO cannot be completely avoided. Biologically method is used to remove these glycols and small amounts of other hydrocarbons present. One of the major disadvantages of the process is discharging of brine because of no commercial value and the amount of brine (5% $CaCl_2$) produced is usually 40 times larger than the amount of PO produced. In addition it is extremely difficult to remove all hydrocarbons from this wastewater stream.

Sodium hydroxide can be used instead of calcium hydroxide alternatively. This has an advantage in that the sodium chloride produced can then be used in the production of chlorine, which can be discharged easier or recycled in the first step of the process. The raw PO stream must be purified by distillation from the water and chlorinated hydrocarbons. The relatively large amount of 1,2-dichloropropane (up to 10%) is obtained as a second product from the separation section. Because this compound has very little usage, it not only causes a loss in yield but also creates a disposal problem.

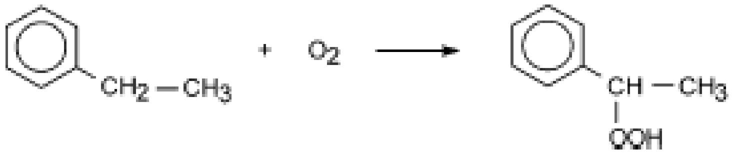
The brine and chlorinated byproducts disposal problems are the main reason that no new chlorohydrin plants are built and old plants are closed down instead of being modernized. Only the large-scale plants (>100 000 tons/yr) are expected to remain operational for a longer period, because they are often integrated with chlorine production plants.

1.6.2. Hydroperoxide processes

The peroxidation of an alkane to an alkyl-hydroperoxide is the basis of hydroperoxide processes. These alkyl-hydroperoxides then react with propylene, producing PO and an alcohol. The production of coproducts beside PO in a fixed ratio, usually 2-4 times the amount of PO produced is the characteristic of hydroperoxide process. Commercially two variants of this process are applied currently. The PO-styrene monomer (PO-SM, also commonly abbreviated as SMPO) process is the first one. In this process, ethylbenzene is oxidized to ethylbenzene hydroperoxide, which reacts with propylene to produce PO and α-phenyl ethanol. The α-phenyl ethanol is then dehydrated to produce styrene. The propylene oxide-*tert*-butyl alcohol (PO-TBA) process is the second process in use. In this process, isobutane is oxidized to *tert*-butyl hydroperoxide (TBHP), which reacts with propylene to produce PO and *tert*-butyl alcohol. This can be dehydrated to isobutene or converted directly with methanol to methyl-*tert*-butyl ether (MTBE).

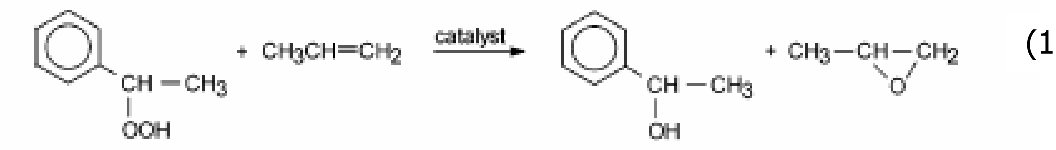
Although there is other combination of processes, no others have been applied so far. Hydroperoxide processes are more selective and produce much less waste than the chlorohydrin process. These are the advantages of the processes. However, the major disadvantage of the hydroperoxide processes is that a fixed amount of coproduct is always produced. Because the markets for PO and the coproducts are not linked, a problem could arise. Since the use of MTBE as a fuel additive is becoming less favorable, the latest plants that have been built using a hydroperoxide process are all of the PO-SM type.

The essential principle of the PO-TBA process is similar to that of the PO-SM process, the ethylbenzene or isobutene noncatalytically is first converted to its corresponding hydroperoxide by direct liquid-phase oxidation, in oxygen or air atmosphere. The oxidation is usually performed in a bubble column at 400 K and 30 bar when isobutane is used, or 423 K and 2 bar in the case of ethylbenzene. The reaction equation is,



(1.4)

A relatively large amount of the TBHP is produced using isobutane but decomposition of TBHP to TBA immediately is the disadvantage of this process. Beside decomposition of TBHP reduces the ratio of PO to coproduct. The unreacted hydrocarbons are removed and recycled. The hydroperoxide stream is sent to a second reactor, where it catalytically reacts with propylene to produce PO and an alcohol. The temperature in this reactor is 373 K at 30 bar pressure. The reactor used for the epoxidation is usually divided up into compartments reactor with staged propylene feeding. The total conversion in the reactors is >95% (of the hydroperoxide) at >95% selectivity to PO, and the only byproduct produced is acetone.



(1.6)

Homogeneous tungsten, molybdenum, or vanadium catalyst or a heterogeneous titanium-based catalyst to catalyze the epoxidation reaction were used for most processes. A waste/separation problem arises because of the disposal of a homogeneous catalyst. After the reactor, the propylene and PO are separated sequentially from the liquid stream. In case of the PO-SM process, some unreacted ethylbenzene in the remaining stream is removed and recycled. The dehydration process is carried out to produce styrene or isobutene from alcohol stream or the *tert*-butyl alcohol can be used directly for the PO-TBA process. However during the dehydration reaction an important side reaction can occur by oligomerization of the styrene produced. This results in a loss of catalyst activity and reduces the catalyst lifetime.

1.6.3. Epoxidation using nitrous oxide

Nitrous oxide (N_2O) has been investigated extensively as an alternative oxidizing agent for the epoxidation of propylene. Especially this oxidant has received much attention for many different oxidation reactions after the discovery of Fe-ZSM-5 zeolite, in which selective oxidations could be performed using nitrous oxide. PO selectivity of up to 80% has been obtained at conversions of up to 5%, which would be sufficient to run a propylene epoxidation process over potassium-promoted iron oxide on SBA-15 catalyst. However deficiency of nitrous oxide commercially in large quantities is a main disadvantage of an oxidation process using nitrous oxide.

1.6.4. Epoxidation using molten salts

A process for the epoxidation of propylene using molten alkali-nitrate salts was developed by Olin. In this process PO selectivity of 65% at 15% propylene conversion is reported when a propylene-air mixture flow through a molten alkali-nitrate salt mixture at a pressure of 20 bar and a temperature of 473 K. Aldehydes, carbon monoxide, and carbon dioxide are the major byproducts of the reaction. Recirculation of the aldehydes caused an increase in selectivity. When a supported palladium co-catalyst is used or when sodium hydroxide is added into the molten salt, higher selectivity has been reached. Using the same molten salt systems, it has also been reported that propane can be directly epoxidized to PO. However the reported selectivities for the epoxidation of propane are low (<15%). Note that the reported high PO productivity (selectivity of 65% with a propylene conversion of 15%) should be sufficiently enough to operate a productive direct epoxidation process.

The disadvantage of performing the propylene epoxidation in a homogeneous gas-phase reaction is that it is extremely sensitive to the reactor and operation conditions. So very different conversions and selectivities have been obtained. Furthermore, the large amount of side products produced makes the separation expensive.

1.6.5. Homogeneous catalysts

Although a large number of homogeneous catalytic systems are available to epoxidize alkenes, almost all of these catalysts only use hydroperoxides as oxidant. Using these hydroperoxides, high selectivities (>90%) at moderate propylene conversions (10%) can be obtained. When (di)oxygen is used as an oxidant, the selectivities to epoxidation are usually lower (<15%), but higher selectivities (up to 50% at 12% conversion) are also reported (Baer and Ralek, 1983). A main problem of more selective homogeneous catalysts is the consumption of catalyst during the reaction. Two reasons can clarify the consumption of catalyst. First, catalyst cannot be reoxidized by molecular oxygen after it oxidizes propylene. Second, when the catalyst absorbs a molecular oxygen (O_2), it epoxidizes propylene with one of these oxygen atoms. The unreacted oxygen atom remains bonded to the catalyst. This oxygen atom is not active in the epoxidation reaction so active sites of the catalyst decreases. The catalyst can be used again by reduction in a second reactor.

Even though some of the homogeneous catalysts found so far are performing better than most heterogeneous systems, no processes based on these homogeneous catalysts are applied. Because homogeneous catalytic systems have some disadvantages when compared with heterogeneous systems: an extra separation of the catalyst from the liquid stream leaving the reactor is necessary and there is the loss of catalyst and/or ligand(s) during separation process. The solvent for the reaction will also be necessary because of a high vapor pressure of propylene, if the process is not operated at a high pressure. Because PO is a cheap bulk chemical, these extra separation and pressure costs can make a homogeneous process expensive. Still, homogeneous processes is valuable to consider, because they are successfully applied in other selective oxidation processes.

1.7. Catalyst Preparation Methods

It is well proved that catalyst particle size and shape as well as the support on which metal sit can significantly influence catalytic performance for structure sensitive reactions. In order to provide an aspect of the physical chemistry of supported clusters, first brief overview of basic catalysts preparation methods must be provided. These methods finally determine the surface composition of the support, and thus control the size, shape, morphology and connection of the metal-support interface that form on the support. For this reason, an improvement in the preparation of heterogeneous catalysts is based on the understanding of the chemistry that occurs at the metal-support interface. The goal of catalysts synthesis is mostly to produce a catalyst containing highly disperse small particle size that considered as catalytically active site (van Santen and Neurock, 2006).

The surface structure of the metal particles loaded into the support can often be controlled by the preparation method. There are various ways to make supported catalysts. These are summarized below:

1.7.1. Coprecipitation

In this method catalytically active metal salts solutions and the support material salts solution are mixed and a precipitating agent such as NaOH or $NaHCO_3$ is added into mixture. After a time hydroxides or hydroxyl salts start to precipitate and form a homogeneous mixture that is filtered off. CO_2 and water into the structure are removed during drying and calcinations period, and oxygen flow during these step ensure the formation of porous catalyst. The control of this process is difficult. It is essential to retain the mixture solution homogeneous to provide the two components to precipitate simultaneously and pH variations through the solution should be prevented (Chorkendroff and Niemantsverdriet, 2003).

1.7.2. Impregnation, adsorption and ion-exchange

The simplest way to insert an active material into the support is the filling the pores of the support with a solution of the catalytically active elements and after that removes the solvent by drying. Nevertheless, in this process several interactions possibly take place between the dissolved catalyst precursor and the support surface. This property can be used to provide a good dispersion of the active component over the support. The importance of such interactions can be understood by taking closer look at the surface chemistry of hydroxylated oxides in solution (Chorkendroff and Niemantsverdriet 2003).

1.7.3. Deposition precipitation

The basis of this method is heterogeneous nucleation of the small crystallites of metal hydroxide or carbonate by precipitation from solution at the interface between liquid and support. To provide this, the powder of support is suspended in the metal salts solution, and the pH of the slurry is increased by addition of base. Effective stirring is necessary to provide homogenous pH through the mixture. However providing the same pH value throughout the slurry is problem if large volumes also porous systems available in the system. This method has been applied effectively to prepare supported vanadium, molybdenum, manganese, iron, nickel and copper catalysts with a homogenous distribution throughout the entire support. The precipitation step is followed by filtration of solid, washing with deionized water or metal containing solution, drying and shaping. Finally, the prepared catalyst is calcined and further activated by reduction or sulfidation if necessary (Chorkendroff and Niemantsverdriet, 2003).

1.7.4. Sol-gel technology

Among the various catalyst preparation methods, sol-gel methods are the most promising and thus have been widely investigated method because the method allows to preparation of high purity and high specific surface area solids (Dumeignil et al., 2003).

1.7.4.1. Sol-gel technology

The sol–gel process has a potentially high technological value and permits synthesis of materials having unique structures and properties rarely obtained by other preparation methods to be produced. Materials synthesized by sol–gel method are of very high purity and homogeneity, having controlled multiphase microstructures, net-shape forming, and as-cast surface features made at lower temperatures than those used for other processes. In the synthesis of nanometric materials, metal alkoxides with high purity are employed as precursors that spread in a liquid media or sol that finally forms a gel. The gel nanostructure can be made feasible by changing the chemical reactions taking place between the precursors.

The films, fibers, powders, monoliths, porous media, and composites are the form of sol-gel synthesized materials that find various applications area. In catalysis science, sol-gel technique provides a homogeneously well-dispersed metal catalyst at least up to the calcinations stage. The sol–gel method also enables uniform fixed metal crystallite size and pore size distribution regardless of metal loading. The growth and enlargement of metal clusters during sintering process can be prevented effectively by sol-gel preparation method. A lot of studies in the literature stated the importance of sol-gel method in a catalyst preparation technique to obtain an homogeneous metal-support interaction effect (Kırk-Othmer, 1997).

In sol–gel technology, first precursors are mixed to form a colloidal suspension, and then the low viscosity sol is introduced in molds for casting operation. The precursors to prepare a colloid solution in the sol-gel process consist of a metal or metalloid elements surrounded by various ligands. The inorganic salts such as $Al(NO_3)_3$ and organic compounds such as $Al(OC_4H_9)_3$ are the common precursors used in this method. $Al(OC_4H_9)_3$ is an example of an alkoxide which widely used the class of precursor in sol-gel research. Metal alkoxides react easily with water therefore they are very popular precursors. The first step in the reaction between water and alkoxide is the attack of one hydroxyl group of water to the metal which is called hydrolysis, as in the following reaction:

$$Si(OR)_4 + H_2O \longrightarrow OH\text{-}Si(OR)_3 + ROH \qquad (1.7)$$

The R can be a proton or other ligand, if R is an alkyl, then **.**OR is an alkoxy group, and ROH is an alcohol. Complete hydrolysis reaction depends on the water amount and catalyst used in the reaction, so that all of the OR groups are replaced by OH,

$$Si(OR)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4ROH \qquad (1.8)$$

or only partially hydrolysis of metal occurs and $Si(OR)_{4-n}(OH)_n$ molecules form.

In the following condensation reaction two partially hydrolyzed molecules can connect together, such as

$$(OR)_3Si\text{-}OH + HO\text{-}Si(OR)_3 \longrightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O \qquad (1.9)$$

or

$$(OR)_3Si\text{-}OR + HO\text{-}Si(OR)_3 \longrightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH \qquad (1.10)$$

A small molecule, such as water or alcohol is released during the condensation reaction. This reaction continues with the formation of larger silicon containing molecules by the polymerization process (Brinker, 1990).

The kinetics of hydrolysis and condensation reactions is affected by many factors because both processes often occur at the same time. Temperature, nature and concentration of electrolyte, solvents type, and nature of alkoxide precursor are the most important variables. The gelation process is also influenced by pressure (Kırk-Othmer, 1997).

After a while the colloidal particles and condensed silica species link together to become a three-dimensional network. The physical characteristics of the gel network depend extremely on the particles size and extent of cross-linking before gelation. At gelation point, the viscosity of the clear solution increases sharply and a solid material ends up with the shape of the mold. Particles having shaped morphology and structure can be formed through gelation. After the gel point, the structure and properties of a gel in liquid phase continuous to change and this process is called as aging. The shrinkage of the gel and the expulsion of liquid from the pores during aging is called syneresis. During aging, polycondensation reaction continues along with available solution and reprecipitation of the gel network. This increases the thickness of interparticle necks while decreases the porosity. The strength of the gel thus increases with aging. An aged gel must be strength enough to resist cracking during drying. The liquid evaporates from the interconnected pore network during drying step. A chemically stable ultraporous solid can be obtained by the removal of surface hydroxyl bonds from the pore network during dehydration or chemical stabilization step. Densification is the last step. Heating the porous gel at elevated temperature results in densification.

1.8. Combinatorial Method

In order to develop a sustainable chemical processes, the following points have to be taken into consideration: (i) the process has to be atom efficient, which means that ideally large excesses, auxiliary reagents, protecting groups and solvents etc. have to be avoided, (ii) the process should be environmentally friendly, so that ideally no side products are produced or such compounds can be used in an integrated process, (iii) chemical engineering considerations play an important role to scale-up a process from the laboratory bench to a multi-ton process, and (iv) the process should be economical efficient. All these points are related to each other and their common denominator is the energy expense. Therefore, the aim is to find direct chemical conversions under normal conditions, which can be only achieved by using highly efficient and selective catalysts for most processes (Hagemeyer et al., 2001; Trapp, 2008).

In the heterogeneous catalysis area, the development of novel multi-component catalytic materials takes places mainly by an empirical approach since basic principles which allow the prediction of catalytic activity of complex solids are not generally available. Considering the high time effort for synthesizing and screening potential solid catalysts, the developments of new methods which show a higher efficiency arouse interest (Wolf et al., 2000).

Over the past decade, the conventional approach to catalyst testing has been displaced by more modern and sophisticated methodologies where catalyst synthesis and reactivity evaluation are integrated using special-purpose devices designed for high-throughput experimentation (HTE) or combinatorial catalysis. The development and application of special-purpose methods for HTE that are driving innovation in various technology have been subjected of various recent reviews in heterogeneous catalysis, homogeneous catalysis, fine chemicals, asymmetric catalysis, nanomaterials, microporous materials, pharmaceutical and drug discovery, advanced electronics materials, and polymers. Although HTE has gained increasing attention in academic laboratories, new evidence suggest that it is also becoming a key core competency for invention of industrial catalysts. The ability to perform HTE with increased efficiency has also driven the development of various key supporting technologies, such as automated methods for catalysts library design, data informatics, kinetics data modeling, catalysis knowledge extraction, microfluidics, fluidic microdispensing. The impact of HTE on reaction engineering is still evolving, but it will likely derive the accelerated development of new processes and process concepts in the technology (Mills and Nicole, 2004; Bricker et al., 2004).

Heterogeneous catalysis, where compositional and structural change of the material greatly influences its activity and selectivity, is also poised to benefit from this new technology. In the combinatorial approach, large diversities of distinct catalytic materials are prepared, processed and tested in parallel using specialized reactors and requisite instruments. The advantages of these high-throughput techniques are obvious: results obtained under same reaction conditions are comparable and more meaningful than single batch experiments, automation and measurement under defined conditions is highly reproducible, and a reference standard can be measured under same conditions and used for calibration. Although the concept of parallel testing of catalytic materials is not new, it is only recently that such approaches became viable due to advances made in laboratory instrumentation, automation, robotics, computers and software (Miyazaki et al., 2003; Trapp, 2008).

The discovery of heterogeneous catalysts is a great challenge because unlike superconductivity, magneto resistivity, and electrochemical reactions, which can be tested by contact probes, or non-specific luminescence/fluorescence, the screening of heterogeneous catalysts requires the unambiguous detection of a specific molecule (i.e., a product) in the vicinity of small catalyst sites. To date several methods have been proposed to screen heterogeneous catalyst libraries (Senkan and Sukru, 1999):

Optical Methods: Perhaps the simplest optical screening is the color indicator method, which is applicable to liquid-phase reactions. This technique was applied first to determine the relative activity of a series of conventional hydrosilation catalysts.

Infrared (IR) Techniques: Among the optical methods, infrared (IR) thermography is most widely used to screen the activities of libraries of catalytic materials because of its ease of applicability. Fourier transform infrared (FTIR) spectrometry can also be used to screen libraries of solid-state catalytic materials.

Laser Induced Fluorescence Imaging (LIFI): This technique exploits the alteration of fluorescence properties of molecules as a consequence of the breakage and formation of chemical bonds. However, as evident from its name, LIFI is only for the detection of fluorescent species, and this limits the use of this technique.

Resonance-Enhanced Multiphoton Ionization (REMPI): A broadly applicable optical screening technique that provides specific product information on gas-phase species. The approach is based on the in situ ionization of reaction products by UV lasers, followed by the detection of the photo ions or electrons by spatially addressable microelectrodes placed in the vicinity of the laser beam.

Photothermal Deflection (PTD): Additional optical techniques will probably be developed and applied to screen libraries of catalytic materials on a case-by-case basis. For example, a photothermal deflection (PTD) method has recently been reported to provide a highly sensitive and selective detection of ethylene in an ethane background.

Mass Spectrometry Methods: Mass spectrometry is a mature and widely used detection technology and can readily be applied to analyze complex gaseous mixtures. Recently, a quadrupole mass spectrometer (QMS) based system to screen heterogeneous catalyst libraries in a sequential fashion were reported by many groups (Senkan, 2001).

Gas Chromatography Method (GC): Complex mixtures require chromatographic separations for a quantitative analysis; however chromatographic separations are often the time limiting step in high-throughput screening. Approaches using off-line gas chromatographic analysis as well as on-line gas chromatographic analysis covering chromatography has been studied to provide strategies for an ideal work flow which should enable to analyze reaction mixtures and evaluate data in real-time (Trapp, 2008).

With recent advances in experimental methods (both library preparation and screening) together with data management and numerical optimization tools, combinatorial catalysis is poised to make a significant impact on the pace of research leading to the discovery and optimization of new generations of superior heterogeneous catalysts. By a suitable combination of methods, it is now feasible to prepare, process, and test thousands of potentially catalytic materials in a day. New catalyst discoveries are routinely occurring now in a number of laboratories in time scales of the order of days and weeks as opposed to the months and years required by traditional methods. In the next few years, the intensified activities in all aspects of combinatorial catalysis as well as the commercialization of new discoveries should be seen. All of this should spur further interest in combinatorial catalysis as the new paradigm in catalyst research and development (Senkan, 2001).

1.9. The Objective of the Study

Propylene oxide is a significant organic chemical and currently produced by two major industrial processes. However direct epoxidation of propylene to PO by molecular oxygen in the presence of a heterogeneous catalyst would be the most desirable in view of environmental friendliness and operating costs.

The aim of the study is to investigate a large number of catalysts with combinatorial approach for the development of novel, active and selective catalysts for direct oxidation of propylene to PO with molecular oxygen at atmospheric pressure. A large number of catalyst candidates including Ag, Cu, Mn mono and bimetallic catalytic systems supported over silica, alumina and titanium dioxide and combination of these oxide were synthesized in a much faster combinatorial fashion with a sol-gel method. The prepared oxide-based metal catalysts were tested and ranked in macro amounts in a high throughput activity and selectivity testing apparatus at different experimental conditions such as reaction temperature and reactant gas ratio. The catalysts gave relatively high PO productivity were then modified with different promoters to enhance the catalytic activity further in epoxidation reaction.

These catalysts were also structurally characterized before the reaction by means of X-ray diffraction (XRD), N_2-adsorption method, X-ray photonelectron spectroscopy (XPS), scanning electron microscopy-energy dispersive X-ray (SEM-EDX) and transition electron microscopy (TEM) techniques in order to draw meaningful correlations between catalytic activity and physico-chemical structure of catalysts. XPS analysis technique especially was performed to investigate the change in the oxidation state of supported metal after and before modification with a promoter.

CHAPTER 2

LITERATURE SURVEY

The heterogeneous epoxidation of alkenes, especially ethene and propylene, is a topic of enduring interest, both from the point of view of fundamental chemistry, and with respect to the importance of these processes in modern chemical technology. The reactions taking place are mechanistically interesting and both epoxides are commercially valuable intermediates (Lambert and Williams, 2005). In spite of the versatility and importance of olefins epoxides in the chemical processing industry, no olefins except ethylene had been commercially epoxidized using only molecular oxygen as the oxidant (Monnier, 2001).

Propene epoxide is in fact more valuable product than ethene epoxide: It is a strategically important and finds more application area as a chemical intermediate. However, direct gas phase epoxidation of propene is a much difficult problem to solve: Ag catalysts are used effectively in the ethylene oxide production but they catalyze propylene with very low selectivity over various reaction conditions and formulations of catalyst. Eventually, propylene epoxide is produced currently by the old chlorohydrin process or hydroperoxide process. However chlorohydrin process is environmentally unfriendly because chlorine is used in the process and hydroperoxide route involves co-production of propene epoxide and styrene (Lambert and Williams, 2005).

So a major research effort has been made in the development of alternative direct synthesis of PO by oxygen or air in the gas-phase, which is mainly focused on Au and Ag catalysts at ambient pressure (Nijhuis et al., 2006).

Haruta and coworkers (Hayashi et al., 1998) were the first group that reported gold containing titanium catalysts as highly selective catalysts for the direct epoxidation of propene. The largest advantage of these catalysts for the propene epoxidation is that they are capable of epoxidizing propene very selectively (~99%) under mild conditions. The fact that this oxidation reaction requires hydrogen to be present with oxygen, as well as the fact that propene can be epoxidized very selectively by hydrogen peroxide over titania, creates the common assumption that the reaction mechanism involves a peroxide species that would be produced by gold. Although theoretical calculations have shown that hydrogen peroxide can be produced on small gold particles, there is no experimental evidence exists that this is also occurring during the propene epoxidation, which makes this peroxide mechanism speculative. Both a higher conversion level to propene oxide and the higher efficiency will be needed for profiting process economics, because otherwise the costs of both the hydrogen and the separations will be too high (Nijhuis et al., 2006).

Great efforts have been performed to enhance the efficiency of the supported Au catalyst in the epoxidation of the propylene to PO by many academic and industrial groups. Some studies on the efficiency of supported Au catalysts were given below:

Hayashi et al. investigated Au catalysts supported on the different support materials by different preparation method. They prepared Au catalysts on different support material (TiO_2, γ-Al_2O_3, Fe_2O_3, Co_3O_4, ZnO, ZrO_2 and SiO_2).

Among all the catalysts, they obtained 90% PO selectivity with 1.1-0.3% conversion for Au/TiO_2 catalyst. However Au/TiO_2 catalysts prepared by the conventional impregnation method have spherical Au particle simply loaded on the TiO_2 support and with diameters above 10 nm and there was no PO formation on it. When the TiO_2 support replaced with TiO_2 deposited on SiO_2, the reaction temperature is shifted toward higher temperature and they obtained 93% PO selectivity at 2.5% C_3H_6 conversion at 393 K (Hayashi et al., 1998).

Sinha et al. studied with Au particle on mesoporous Ti-MCM-41, Ti-MCM-48, three dimensional sponge-like mesoporous titanium silicates (TiO-SiO), Ti-HMM (highly ordered Ti-containing mesoporous hybrid silsequioxane), Ti-containing non-porous silica support according to their previous study reported by Hayashi et al., 1998. In the titanosilicates, an increase in PO yield is observed with an increase in pore diameter of 0.55 nm in TS-1 (~1% conversion with PO selectivity >90%) to about 3-10 nm in mesoporous titanosilicates (4-5% conversion with PO selectivity >90%) especially for sol-gel prepared sponge-like titanosilicate with three-dimensional mesoporosity (TiO-SiO). Enhanced propene conversion and PO selectivity was attributed to larger pore size and three dimensional mesoporosity because of easy diffusion of reactants and products. In addition, better synergism between Au and Ti sites both on the surface as well as inside the mesopores (due to large, >70 Å pore size) was evaluated as favors for the epoxidation reaction in this reaction (Sinha et al., 2004).

The deactivation with time-on-stream observed for all gold catalysts is considered due to accumulation of PO and other successively oxidized products on the catalyst surfaces. Qi and his co-workers at the head of Haruta made an attempt to use non-porous but relatively high surface area

SiO_2 (77 m^2/g) as a carrier for Au catalysts because of the expectation of the smooth surface of non-porous silica may facilitate desorption of PO. They prepared Ti/SiO_2 by incipient wetness method and calcined at different calcination temperature. Gold was deposited on the prepared support by deposition-precipitation method and calcined at 300 °C. The catalytic performance tests were also performed at different reaction temperature (60-150 °C). They obtained maximum PO selectivity as 99% (0.08% conv.) at a reaction temperature of 60 °C and a calcination temperature of 800°C whereas propylene conversion showed maximum value as 0.68% (with 4.5% select.) at 150 °C reaction temperature and 300 °C calcination temperature. They concluded that PO yield and selectivity were improved with preheating temperature of support materials. From IR and HRTEM analysis, the interaction between titanium oxide and non-porous silica was intensified and formed many isolated tetrahedrally coordinated TiO_4 unit on the surface with an increased in calcination temperature. And they stated that isolated TiO_4 sites can be considered to be important for PO production as well as deposition of Au particles (Qi et al., 2001).

Haruta and his co-workers have continued their studies on the different type of promoter for Au/titanosilicate catalysts. Chowdhury et al. reported that the effect of presence of extremely low concentrations of (10-20 ppm) trimetylamine (TMA) in the reactant gas, a strong base with a pK_a value of 9.9, on catalyst life time, catalyst regeneration, PO selectivity and H_2 efficiency. They investigated the effect of TMA on $Ba(NO_3)$-promoted Au/titanosilicate (Ti/Si=3/100) catalysts in the presence of 13-15 ppm TMA as a gaseous promoter. They obtained propylene conversion up to 8.5% and PO selectivity of 91% at 423 K and atmospheric pressure. According to these results they claimed that the PO yield (1.1-1.4x10^{-3} mol/h g cat.) is close to that of ethylene in the current industrial process. UV-Vis method showed that

TMA is partially absorbed on the Au surfaces and depress direct H_2O formation and inhibit PO adsorption (Chowdhury et al., 2006).

Nijhuis at al. after Haruta and his group investigated gold titanium catalysts prepared by deposition-precipitation method on different titanium-containing supports. The standard supports used in their study were TiO_2, TS-1, TiO_2 on SiO_2, SiO_2, γ-Al_2O_3, gold sponge, titanium without gold. Among this catalysts, only dispersed gold-on-titanium catalysts showed activity for epoxidizing of propene using a mixture of hydrogen and oxygen at low temperature. The use of dispersed titanium-containing support material, such as TS-1 or TiO_2 dispersed on SiO_2, instead of pure titania resulted in a catalyst more resistant to deactivation and able to obtain slightly higher propene oxide yields. At low temperature (<350 K), they observed that the titanium supported catalysts are most active (99% selectivity at 0.8-1.3% conversion). When the temperature is increased, they obtained that dispersed titanium on silica catalysts gave higher activities without a loss in selectivity (0.3-0.8% conversion with 99% of PO selectivity until 398 K, and ~ 2% conversion with 50% of PO selectivity at 473 K). The investigation of the deactivation of catalyst with TGA analysis showed that there was a combustion peak for Au/TiO_2 whereas silica supported titanium did not show this combustion peak. So they explained that deactivation occurs by oligomerization of molecules adsorbed on titanium sites. For both support materials they obtained the maximum PO yield less than 2% like Haruta group (Nijhuis et al., 1999).

The other study on the catalytic performance of the Au/TiO_2 catalysts prepared by different method was performed by Stangland and coworkers. They prepared Au-Ti and silica supported Au-Ti nanocluster with controlled composition by variety of techniques. The best catalysts detected in the study were titanium-modified silica catalysts prepared by DP method and Au-Ti bimetallic cluster catalyst produced in the aerosol reactor. They obtained 0.0164 s^{-1} of TOF and 90.8% of PO selectivity for Au/Ti-Si catalyst at 413 K. For DACS cluster at three intermediate Au-Ti ratio gave high activity (0.0033 s^{-1} TOF) and above 80% selectivity at 373 K. Other catalysts generally gave low PO selectivity. They observed that the largest loss in PO selectivity with increasing temperature was to the oxidative cracking products to ethanol and CO_2. They concluded that catalysts that have isolated Ti atoms, such as the silica supported Au-Ti catalyst nonoclusters, generally maintain a higher selectivity to PO (Stangland et al., 2000).

The studies on the supported Au catalysts for epoxidation of propylene had been performed at the presence of both H_2 and O_2 mostly. However Suo and co-workers prepared Au catalysts supported on SiO_2, TiO_2, TiO_2-SiO_2, ZrO_2-SiO_2 by impregnation method and tested with only air as an oxidant. When they evaluate the overall test results according to the oxygenated products, they concluded that Au/SiO_2 is probably good catalyst to produce especially acrolein and washing the catalysts with water and magnesium citrate can markedly enhance the dispersion of Au particle on the support surface and improve PO selectivity. They obtained 17.9% PO selectivity at 0.9% conversion at the initial stages of the reaction (10 min). After the reaction 60 min, the propylene conversion increased to 1.4% but the PO selectivity decreased to 8.9% and the main product was AC (72%). The higher selectivity of PO at low propylene conversion (48.5% PO & 0.47%) was obtained for Au/ZrO_2-SiO_2 catalyst washed with magnesium citrate solution prior to calcination. They concluded that Au and Ti are both necessary under oxygen and hydrogen atmosphere for high PO selectivity as stated in previous reports (Suo et al., 2008).

Beside experimental study, some theoretical studies were reported for Au catalysts. Joshi and coworkers (Joshi et al., 2006) studied partial oxidation of propylene to PO using H_2 and O_2 on a neutral Au_3 cluster by using DFT. They reported that the O_2 adsorbed on Au_3 facilitates the dissociative adsorption of H_2 to form a OOH intermediate, which remains adsorbed on the Au_3. The activation barrier for this step is only 2.2 kcal/mol. The activation barrier for propylene epoxidation step is 19.6 kcal/mol. The PO interacting with the Au_3 requires about 11.5 kcal/mol to desorb. They staded that this activation barrier is comparable to the barriers reported (15-20 kcal/mol) in several other olefin epoxidation mechanisms on Ti sites in the absence of Au. Therefore they advance the possibility of the Au playing a important role than the mere production of the oxidizing agent from the H_2 and O_2 by offering a competitive epoxidation channel to that occurring on Ti.

Chretien and coworkers had studied on the interaction between gold and silver clusters and propene by using DFT method. They reported that for a given cluster size, the electron affinities of the Ag clusters are smaller than the ones of the Au clusters. An electron affinity is a measure of the tendency of the cluster to accept an electron. They predicted that propene will bind more weakly to Ag_n than Au_n. The electron affinities of the mixed Au/Ag clusters are in between the ones of the pure Au and Ag clusters (Chretien et al., 2004a; 2004b; 2004c).

Although high PO selectivity obtained on Au catalysts, the main hurdles for the industrial application of this catalyst are its fast deactivation caused by the accumulation of oligomerized and oxidized PO by-products around the gold nanoparticles, the lower activity of the successively regenerated catalysts, and its low H_2 efficiency. However the direct epoxidation of propene with hydrogen and oxygen has still attracted a considerable academic and industrial interest.

The heterogeneous selective oxidation of ethene to ethene oxide (EO) is a mature technology based on Ag/α-alumina as the catalyst with O_2 as an oxidant. The molecular mechanisms involved in EO catalysis over Ag are relatively well understood; the same is true of the mode of action of various promoters, including chlorine, alkalis and NO_x. An addition of these promoters increases EO selectivity approaching 90%. On the other hand propene epoxidation over Ag/α-alumina is notably unsuccessful, yielding propene epoxide selectivity in the order of only a few percent. As a result, the efficient heterogeneous selective oxidation of propene to PO is a key technological goal that remains to be realized.

The main reason for the low selectivity is that the allylic hydrogen. It easily reacts with the nucleophilic oxygen species adsorbed on the Ag surface, which results in the by-products and final production of CO_2. However, it is also noteworthy that, if the silver catalyst is well modified, which would result in the adsorbed oxygen species with proper electronic properties, it could be also possible that the catalyst may be effective for the epoxidation of propylene. Therefore many groups have investigated the effectiveness of modified and unmodified Ag catalysts in the direct epoxidation of propylene to PO.

Yao and coworkers (Yao et al., 2007) investigated the effect of rare earth, alkali and alkaline earth metal oxide ($Y(NO_3)_3$, KNO_3, $Ba(NO_3)_2$ or $Ca(NO_3)_2$) promoter on the catalytic performance and physicochemical properties of Ag/α-Al_2O_3 catalysts efficiency. To observe the effect of support material on the performance of Ag catalyst, alumina with different surface area and pore diameter distribution were used. As a result of first screening test, they observed that 20%Ag/α-Al_2O_3 and modified with single metal oxide catalysts gave low PO selectivity (0-4.3%) at 2.5-8% propylene conversion. When 0.1%Y was added into 20%Ag/K_2O/α-Al_2O_3 catalyst, the selectivity to PO increased from 4.3% to 46.8% with a decrease in the conversion (from 8% to 4%). Barium (Ba) and Ca modified catalysts gave approximately the same results. After determining the best promoter, the reaction temperature between 205 to 300 °C with a temperature interval of 20 °C was screened and the maximum performance was reached at 245 °C. Also they changed calcination temperature from 400 to 800 °C and obtained the highest selectivity and conversion at 550 °C. Above 550°C particle size of silver metal and pore diameter increased but the surface area decreased. SEM analysis of catalysts showed that Ag particle with small (0.05-0.1 µm) and large (0.3-0.6 µm) particle sizes exit simultaneously for K modified catalyst. However on the surface of K_2O-Y_2O_3/α-Al_2O_3 catalyst calcined at 550°C, there is some nearly spherical particle (0.1-0.2 µm). They explained that Y_2O_3 could effectively regulate the size of Ag crystallite to restrain agglomeration. They also investigated the basicity of catalysts by CO_2-TPD method. For support material and Ag catalyst there is no desorption peak. After modification with alkali metal oxide there is strong surface basic sites. However addition of Y_2O_3 to K_2O-modified catalysts caused a decrease in the strong basic sites. And they claimed from these results that the suitable basic sites are necessary to a highly effective Ag catalyst for the epoxidation of propylene.

Lu and coworkers (Lu et al, 2002a) studied with NaCl-modified silver (NaCl/Ag) catalysts to determine the effects of NaCl loadings, propylene to oxygen ratio, and the reaction time on the catalytic performance. They compared different Ag catalysts and stated that Ag_2O, Ag and AgCl cannot be the right phase for epoxidation of propylene. When NaCl was added, they obtained the selectivity to PO up to 29.1% for NaCl/Ag (5 wt%) catalyst at 11.2% propylene conversion. But for Ag catalyst, PO selectivity was only 0.35% at 32.5% propylene conversion. The types of promoter on the performance of catalysts were investigated with the different Na and K salts (Cl, Br and F salts). And they obtained the highest selectivity to PO for NaCl. When they modified Ag with 10 wt% NaCl, 12.4% conversion of propylene and 31.6% selectivity to PO were obtained. They concluded that the AgCl formed in the preparation stage change the electronic property of silver catalysts, thus inducing the adsorbed oxygen species to become electrophilic. They also investigated the effect of C_3H_6:O_2 ratio on the reaction at different value. When the ratio of propylene to oxygen is 0.25, the conversions of propylene and the selectivity to PO are 38.1% and 8.6%. When the ratio is 0.5, the conversion of propylene is 12.4% and the selectivity to PO reaches 31.6%. With further increase of propylene content in the feedstock, both activity and selectivity of the catalyst decrease. They concluded from the results that C_3H_6:O_2=0.5 in the feed gas is the proper ratio in order to obtain a high selectivity. They reported in this study suitable promoter and its proper amount, and gas ratio for unsupported Ag catalyst.

Among the promoted Ag catalysts supported on different oxide materials, Ag/$CaCO_3$ attracted most attention by both academic and industrial laboratories. Palermo and his group at head of Lambert examined supported Ag catalysts on different oxide (α-alumina, K promoted β-alumina and $CaCO_3$) and the effect of K, NO, Cl and combinations of these modifier. Among these modifiers, only K is good for PO production despite of low PO selectivity and propylene conversion. Beside of this, they obtained $CaCO_3$ as the most effective support material for epoxidation of propylene (Palermo et al., 2002).

Zemichael and coworkers tried to solve why alkali-promoted Ag/$CaCO_3$ are substantially more selective towards propene epoxidation than Ag/α-alumina as a regards to Palerm`s report. They prepared 45 w/w% Ag/$CaCO_3$ with K loadings of zero, 1.7%, 2.5% and 4.2% catalysts and tested at atmospheric pressure with a C_3H_6:O_2:1:2 feed composition. The obtained results showed that un-promoted catalysts gave the lowest selectivity (3.7%) whereas catalysts containing 1.7% K was the best of all, delivering 15.2% PO at propene conversion of ~6%. They found that there is a correlation between K loading and Ag particle sizes, and addition of 1.7%K caused Ag particle dimensions in the range of 20-40 nm. They stated that Ag particles that are either much larger or much smaller than this are less selective to PO (Zemichael et al., 2002).

The other study performed on the modified supported-Ag catalyst is reported again by Lu et al. who is a member of Oyama group. The effect of particle size of metal on ethylene and propylene epoxidation was investigated on a series of silver catalysts supported on $CaCO_3$ with loading levels of 0.5-56 wt%. They observed that large particle favor ethylene epoxidation by 3-5 fold at 473-493 K, whereas particle size has not large effect on propylene epoxidation. They determined from XRD and UV-vis spectroscopy that the bulk of the particles consist of silver in a metallic state, but small particles have silver in Ag^+ state and the ratio of Ag^+/Ag^o increased with lower silver loading. They concluded that the small particles are probably covered by a layer of Ag_2O which results in lower selectivity for epoxidation for both propylene and ethylene oxidation in the small size regime (Lu et al., 2005).

After that they investigated the effect of the different support materials on the activity and selectivity of Ag catalysts. It was reported that medium surface area support such as α-Al_2O_3, CeO_2 and low surface area supports such as $CaCO_3$ gave high TOF values for PO formation. They concluded that large silver particles are favorable for PO formation. However in the previous study they stated particle size does not have large effect on propylene epoxidation. Then they tried various promoters on the 56% Ag/$CaCO_3$ catalysts, and found that NaCl was to be an effective promoter for propylene epoxidation. The un-promoted catalysts had very high propylene conversion (60%), but low PO selectivity (< 2%) at 260 °C. Addition of NaCl resulted in a dramatic decline in propylene conversion (from 60 to 1-3%) but PO selectivity passed through a maximum (39.2%) at a NaCl loading of 1wt%, then decreased with further addition of NaCl. They explained the NaCl effect is due to changes in the electronic properties of the catalysts surface, including the adsorbed oxygen species to be more electrophilic and increased the Ag size. For the 56%Ag/$CaCO_3$ sample, the maximum in the distribution was at 370 nm, while for the 56%Ag-1%NaCl/$CaCO_3$ sample, the maximum was at 800 nm with more regular in shape (Lu et al., 2006). However Zemichael and coworkers reported that the particle size in the range of 20–40 nm for 45%Ag–1.7%K/$CaCO_3$ catalyst is effective for high PO selectivity (Zemichael et al., 2002).

In the Lu and coworkers study, they tried CeO_2 support material because of its known ability to store and release oxygen but they did not obtain better results than $CaCO_3$. Dibenedetto and co-workers investigated reticular oxygen of Al_2O_3 and CeO_x supported Al_2O_3 and obtained the selectivity of PO as equal to 30% for CeO_2 and 40% for Al in the reaction carried out at propene/oxygen atmosphere. Conversely, if the Al and CeO_x-Al catalysts were first reacted with O_2 at 750 K and the oxidized form of catalyst was allowed to react with propene in absence of O_2, PO formed with selectivity ranging from 70 to 100% depending on the reaction time at low conversion (2-4%). They performed XPS analysis before and after reaction and showed that there is a decrease of the signals of Al(III) or Ce(III) or Ce(IV) after running the catalytic reaction and suggested that Al_2O_3 or CeO_2/Al_2O_3 involve directly in the formation of PO using reticular oxygen with high selectivity towards PO (Dibenedetto et al., 2006).

Generally titanium siliate (TS) are used as a support material under oxygen and hydrogen atmosphere to produce peroxide for Au catalysts. However Wang et al. studied on Ag/TS-1 catalyst to observe the efficiency of Ag loading, Si/Ti ratio of TS-1, and calcination temperature and calcination method on propylene epoxidation. They obtained the propylene conversion and the selectivity to PO as 0.58% and 86.87% respectively when the amount of Ag loading is 2.0 wt%. To observe the effect of support material, they used TiO_2, SiO_2, HZSM-5 and TS-1. Among the support materials, TS-1 was determined as the best support and when Si/Ti ratio was 64, catalyst exhibited optimum performance (0.92% propylene conversion and 91.21% PO selectivity). However when the Si/Ti ratio was increased, the propylene conversion decreased and no PO was detected in the product. They also investigated the effect of calcination temperature and calcination method. The catalysts calcined in air at 450 ^{o}C exhibited the optimum activity. The ESR spectra of catalyst showed that there is no signal belongs to Ag^{o} for catalysts calcined in air or N_2. TEM shows that Ag/TS-1 particle become very small, only about 2-4 nm, and a few larger particles are about 30 nm. Combined with the reaction results, they concluded that neither big nor small metal silver particles is beneficial to the formation of PO (Wang et al., 2003;2004).

Guo and coworkers (Guo et al., 2004) investigated the effects of preparation methods and reported that the catalysts prepared by both DP and IMP methods exhibit catalytic activity and selectivity. 0.48% propylene conversion with 57.88% selectivity to PO was obtained over Ag/TS-1 catalyst prepared by IMP method. However, DP method showed the optimum (94.85% PO selectivity at 0.37% conversion). Beside alkaline carbonate and nitrate were used to determine a suitable precipitator for epoxidation reaction. The catalyst exhibited high selectivity and activity when K_2CO_3 was used as a precipitator and the stability of the catalyst was improved by using Cs_2CO_3 as the precipitator. They obtained the propylene conversion and PO selectivity for these catalysts as 1.28% and 84.12%, 1.11% and 85.41% respectively at 31 and 54 min respectively. However catalysts prepared using K_2CO_3, an increase in the reaction time caused a decrease in the conversion (from 0.77 to 0.44) during an increase in PO selectivity (90.22% to 100%). From these results they stated that alkali metal carbonate is more suitable precursor than nitrate for Ag/TS-1 catalyst.

The study on the silver catalysts is not restricted with the effect of different support materials and alkali and alkali earth metal as promoters. Beside these, the effect of transition metal as a promoter has been studied to observe the performance of silver catalysts for EO and PO.

The study on the ethylene oxide (EO) formation has been performed on the different metallic system, unimetallic and bimetallic system, by many groups. Jankowiak et al. reported a detailed investigation of the performance of monolith-supported Ag and Cu-Ag bimetallic catalysts at different reaction conditions and showed that Cu-Ag bimetallic catalysts decrease activation energy by 1-2 kcal/mol relative to pure Ag catalysts. In their latter study, they investigated catalytic performance of the Ag and Cu-Ag bimetallic catalysts when conventional promoters such as cesium (Ce) and chlorine (Cl) are used as a promoter. They obtained 15% higher selectivity for promoted bimetallic catalysts than those obtained for promoted silver catalysts at comparable conversion (Jankowaik and Barteau, 2005a and b).

Bimetallic catalytic systems have been investigated to improve selective epoxidation of propylene to PO like EO. The effect of adding 3d transition-metals on Ag-based catalysis was investigated by Takahashi and coworkers. They prepared Ag-based catalysts containing Mn, Fe, Co and Ni by co-precipitation and showed that the addition of Ni afforded the highest yield of PO at similar values for the conversion of propylene (4-6%). They obtained the highest PO selectivity for 33 mol% Ni (11.8% at 6.5% conversion) as four times that obtained with the Ag single catalyst (2.5% at 7.9% conversion). They performed XRD and TEM analysis and showed that dispersion of Ag particle in the Ag-Ni catalysts increased with increasing Ni content, which suggests that Ni atoms controlled the Ag particle size approximately 80 nm. As a result of the study, they suggested that oxygen species on the terrace sites (nucleophilic) and defect sites (electrophilic) on the Ag surface worked cooperatively to catalyze propylene epoxidation and Ni played an important role in controlling the particle size of Ag by acting as a spacer to isolate Ag particle (Takahashi et al., 2005).

Direct gas-phase epoxidation of propylene was studied over the MoO_3-modified supported Ag catalyst prepared with different methods by Jin and coworkers (Jin et al., 2004;2005). Firstly they investigated the performance of unsupported Ag-MoO_3 catalyst as a function of the MoO_3 loading. Over the MoO_3-free Ag catalyst, the O_2 conversion of 58.9% was obtained with the PO selectivity of 0.8%. Over the 50%Ag-50% MoO_3 catalyst, the conversion of the oxygen and the selectivity to PO was 7.1 and 34.3% respectively. Among the $CaCO_3$, CaF_2, SiO_2, TiO_2, ZrO_2, TiO_2-ZrO_2 and TiO_2-SiO_2 support materials, maximum selectivity to PO was achieved for ZrO_2. After determining the most effective supports, the effect of reaction temperature, space velocity on the performance was investigated over 20%Ag-4%MoO_3/ZrO_2 catalyst. According to the textural properties of support material, they inference that suitable low surface area and large pores are in favors of a diffusion of PO out of the catalysts. The presence of support is also available to control the size of the Ag-MoO_3 particle and pore channels of catalyst. The catalysts having the larger particle size of Ag-MoO_3 (300-500 nm) showed higher performance for the epoxidation of propylene.

After these studies, they investigated the adsorption and reaction behavior of propylene, propylene oxide and the gaseous mixture of propylene and oxygen on the surface of Ag and Ag-MoO_3 catalysts by in situ FT-IR technology to better understand the mechanism over different surface. They prepared Ag and 50%(wt)Ag-50%(wt)MoO_3 catalysts and observed that the open-ring reaction and polymerization of open ring products to form coke occurred at a higher temperature over Mo modified Ag catalyst than Ag catalyst which leads to an increase in the selectivity to PO (Jin et al., 2006).

Generally it is reported that larger or proper size of Ag particle (20-40 nm) is necessary for high PO formation to day (Lu et al., 2005;2006; Zemichael et al., 2002; Jin et al., 2004;2005;2006). However Lei et al. reported that unpromoted size-selected Ag_3 clusters and ~3.5 nm Ag nanoparticles on alumina supports gave much higher PO formation rate with negligible amount of CO_2 than reported for any Ag catalysts. In addition they showed that oxidized silver trimers are more active and selective for oxidation than extended silver surface with density functional calculation (Lei et al., 2010).

The effectiveness of Cu containing catalyst was investigated after determining Cu is more selective than Ag catalysts for alkene epoxidation (Cowell et al., 2000).

Lu et al. investigated the catalytic performance of Cu to find a new approach to catalysts other than silver and Au supported on Ti-silicates for propylene oxidation. They studied on NaCl-modified VCe_xCu_{1-x} (x=0-1) catalysts. They observed that VCe-NaCl(20) is not active for the epoxidation reaction and produced little amount of CO_x. For the VCe_xCu_{1-x}-NaCl(20) family, they found that catalytic performance is strongly dependent on the Cu content in the catalysts. When they loaded different amount of Cu into catalysts, PO selectivity reached its maximum (43.4%) at 0.19% conversion for $VCe_{0.2}Cu_{0.8}$-NaCl(20). CeCu-NaCl(20) catalyst also showed activity to the propylene epoxidation but with low selectivity (6.5%) due to total oxidation of propylene on CeO_2. From XPS analysis they inferred that intermediate state of Cu is required for high PO performance (Lu et al., 2002b).

Vaughan and co-worker studied on 1 and 5% copper containing silica catalysts to observe the effect of Cu amount and reaction temperature on activity. At 225 °C, they obtained maximum PO selectivity (53% selectivity and 0.25% propylene conversion) and it declined rapidly to a negligible value at 275 ^oC (1.26% of propene conversion) correlated with increase in selectivity to acrolein for 1%Cu/SiO_2. The behavior of the 5%Cu/SiO_2 catalyst is broadly similar to that of catalysts containing 1% Cu, although PO selectivity is significantly lower (~15% selectivity and 0.24% conversion at 225 ^oC). They finally investigated the effect of a range of alkali and chlorine additives on 5%Cu/SiO_2 catalyst. 5 wt% NaCl-modified and 5wt% Cl-modified catalysts prepared with by impregnating method showed that all additives had a detrimental effect on the selectivity toward PO formation.

They investigated the catalysts with XPS and Auger spectroscopy techniques and stated that the active form of copper is Cu^0 species in highly dispersed atomic like form (Vaughan et al., 2005).

Lambert and his group also tried to find the answer of why copper is much more selective than silver. They examined the oxidation chemistry of allylbenzene, trans-methyl stryrene and α-methyl stryrene on single crystal surface of copper and silver and revealed the difference in their oxidative behavior on Cu and Ag surfaces. When allylic hydrogen atoms are present, Cu surface continues to catalyze selective oxidation effectively, whereas Ag simply burns these alkenes. The proximity of the C=C bond to the Cu surface is critically important in determining the degree to which epoxidation occurs (Lambert et al., 2005).

In a latter study, DFT quantum chemical calculation method on Cu(111) and Ag(111) surfaces was used to determine the thermochemistry and activation-energy barriers that determine selectivity in propylene epoxidation by Torres and coworkers. Periodic slab calculation results imply that propylene epoxidation on silver is strongly disfavored by the markedly basic character of adsorbed oxygen which leads to allylic hydrogen stripping and combustion. In contrast, the lower basicity of copper favors metallacycle formation then epoxide production (Torres et al., 2007).

Chu and his coworkers (Chu et al., 2006) studied on the halogen-free K^+–modified CuO_x/SBA-15 catalysts and claimed that this catalyst exhibited better catalytic performance that other Cu-based catalysts at oxygen-rich atmosphere reported so far. They prepared CuO_x/SBA-15 catalysts and compared its catalytic performance after modified with K at the K/Cu=0.7. Without K^+ modification, propylene conversion was higher but PO selectivity was lower (9.9% at a conversion of 0.77% at 498 K) and main partial oxidation product was acrolein. After the modification, PO became the main product and its selectivity was 59% at 498 K (0.40% conversion) and 46% at 523 K (0.95% conversion).

Wang and coworkers (Wang et al., 2008) used NH_3-TPD measurements and showed that the strength and the amount of the acid sites decreased with K^+ amount. From these and XPS results they concluded that Cu is in oxidized state (Cu^I or Cu^{II}) and its responsible for the epoxidation of C_3H_6 by O_2 not metallic Cu stated by Lu and Vaughan et al (Lu et al., 2002b;Vaughan et al., 2005).

After determining the effect of the K on the Cu metal, they continued their study to understand clearly the exact state of Cu. For this purpose, FT-IR studies of absorbed CO combined with XRD measurement was performed over K^+-5wt%CuO_x-SiO_2 (K/Cu=0.2) catalyst. From in-situ XRD and FT-IR measurements, they concluded that Cu(I) is the active site for the activation of propylene by oxygen (Zhu et al., 2008).

The active oxidation state of Cu in epoxidation reaction is investigated by many groups but there is still a lack of agreement. Vaughan et al. stated that the active form of copper is Cu^0 species in highly dispersed atomic like form while Zhu et al. stated that Cu^I is active form. In addition to this, Su et al. concluded that both form of Cu (Cu^0 and Cu^I) especially Cu^0 form in the small oxide cluster are necessary for propene epoxidation. And it was reported that the best modifier for Cu is halogen-free K for Cu containing silica system at different reaction conditions (Vaughan et al., 2005; Zhu et al., 2008; Su et al., 2009).

Beside Cu catalyst modified with alkali promoter, the bimetallic system was also investigated. Khan and coworkers (Kahn et al., 2010) prepared silica supported 35 metals by high throughput pulsed laser ablation method and determined Cr, Mn, Cu, Ru, Pd, Ag, Sn, and Ir were the most promising metals for PO synthesis. However PO yield was still low. Therefore to increase the PO production rate while also increasing PO selectivity, binary combinations of the metal was tried. First Mn+Cu bimetallic system was investigated. Mn+Cu bimetallic catalysts were prepared by the sequential deposition process. They obtained the most remarkable result for Cu-on-Mn/SiO_2 catalyst. The PO formation rate for Cu-on-Mn/SiO_2 catalyst was higher by a factor of 5 than the corresponding unimetallic catalysts (from 17% for Cu/SiO_2 and 8% for Mn/SiO_2 to 22% for Cu-on-Mn/SiO_2).

Another approach used to improve the yield of PO is the production of the radical by surface initiate gas-phase reaction. The application of radicals on epoxidation of propylene was first performed by Mimura and co-workers. They prepared Ti oxide clusters supported on the SiO_2 with the different Ti precursors and tested in the post-catalytic-bed volume (25 ml) of the reactor with and without quartz sand at 3.5 atm and 568-573 K. TiO_2(2%)/SiO_2 catalyst gave 9.2% conversion and 35% PO selectivity, TiO_2(15%)/SiO_2 catalyst gave 22% propylene conversion and 21% PO selectivity. TiO_2(2%)/SiO_2 catalyst in which the post-catalytic-bed volume was filled with quartz sand gave low conversion (0.2%) and PO selectivity (1.6%). They concluded from these two results that the post-catalytic-bed volume without quartz sand is essential for PO production because of radicals generation. And the surface-initiated gas-phase radical generation at the remarkably low temperature is probably a consequence of the unique properties of the Ti dimer complex which has suitable structure for generating the radical (Mimura et al., 2006). They continued their study with screening different metals and supports in post catalytic bed volume reactor and reached 43.6% PO selectivity at 17.6% propene conversion over Mo/SiO_2 catalysts under again a relatively higher pressure of 5 atm (Song et al. 2007).

After these studies, DFT calculation reported by Kizilkaya et al. showed that the activation barrier for PO production is lower than that for acrolein formation and combustion reaction for gas-phase radical chain reactions (Kizilkaya et al, 2010).

In the direct production of PO from propylene over silicate with low and medium surface area has been investigated by many groups. Nevertheless mesoporous materials with high surface area have been tested only a few groups. Murata and co-workers reported the activity test results of Ti- and Al- containing MCM-41 and MCM-22 catalysts in the vapor phase. They prepared catalysts with different Al/Si ratio and different Si source such as water glass and $Si(OEt)_4$. The investigation of the synthesized catalysts with XRD and BET showed that the pore distribution was narrow, characteristic of mesoporous material with uniform size and regularity of samples were not high. Catalysts prepared from $Si(OEt)_4$, showed a 1.09% conversion with PO selectivity of 68.8% while there is no oxygenated product over catalyst prepared with water glass. They observed that the conversion of propylene increased with an increase in Si/Al ratio of 150-250 and the highest value of 3% with PO selectivity of 46.5% was achieved at Si/Al=250 and then decreased with a further increasing in ratio of Si/Al.

After that they tested Ti- containing Al-MCM-41 catalysts. In the presence of Ti, the conversion was higher than without Ti, while PO selectivity was a little lower. They obtained maximum PO yield of 2.99% at Si/Al=150 (35.3% PO selectivity at 8.45% conversion) at constant Si/Ti ratio. In the case of MCM-

22 modified with Na (Si/Al=30), they obtained higher catalytic activity than those of Al-Ti-MCM-41. The conversion was above 40% even at 523 K, and it reached to 90% at 623 K. The maximum PO yield was 11.5% (12.5% PO selectivity at 90.4% conversion) at 573 K. As a conclusion, they stated that Al-Ti-MCM-41 is more effective than Al-MCM-41 because of synergetic mechanism between Ti and acid site may be responsible for the formation of PO. MCM-22 alone with Si/Al_2 ratio of 30 with Na is also active and gives the highest PO yield of 11.3% because of high propylene conversion (Murata et al., 2003).

After these studies, they synthesized hexagonal mesoporous silica (HMS) containing again Ti and Al with dodecylamine as a template at room temperature. The acidic amount of HMS and Ti-HMS determined by NH_3-TPD method were very weak and addition of Al into the catalysts increased the acidic strength and amount directly proportional with the loading. HMS gave a low propylene conversion of 0.5% and did not produce any oxygenated products. Ti-Al-HMS with 4/1/100 molar ratio showed a propylene conversion of 47.8% which is higher than those over Ti-HMS (3.7%) and Al-HMS (13.5%) at the same reaction condition. They obtained the highest PO selectivity for Ti-HMS as 34.5% with low conversion while 6.6% PO selectivity for Al-HMS due to the formation of large amounts of hydrocarbons. Furthermore Ti-Al-HMS gave 30.6% PO selectivity with high propylene conversion and they concluded from these results that the simultaneous existence of Ti and Al in HMS framework is very important for improving the yield of PO. When they compared the activity of catalysts prepared by impregnation and sol-gel method, they observed that sol-gel method (yield of 14.6%) was more effective than impregnation method (yield of 5.3%) (Murata et al., 2004).

In the study, they also investigated the effect of various additives (KNO_3, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Ba(NO_3)_2$, $CaCl_2$, $LiNO_3$, NaCl) alone or binary on Ti-Al-HMS catalyst. Among these additives, the co-existence of K and Ca ions improved the PO yield more effectively than other additives (yield from 14.6% to 19%). Despite they obtained high PO yield, Ti-Al-HMS deactivated quickly for propylene oxidation due to carbonaceous deposit on the catalyst surface. However addition of a little amount of H_2 in the feed gases greatly decreased the speed of activation but did not completely suppress catalysts activation (Liu et al., 2006).

Another alternative oxidizing agent for the epoxidation of propene that has been extensively investigated is nitrous oxide (N_2O). The first group who used N_2O as an oxidant in the epoxidation of propene to PO in the vapor phase was Duma and co-workers (Duma and Dieter, 2000). After Duma et al. report, some experimental investigations were performed to understand the course of the reaction and to elucidate the reaction network including parallel and consecutive reactions. The kinetic importance of each reaction pathway in the network dependent on the catalyst properties and feed composition has been investigated by other groups (Ananieva and Reitzmann, 2004).

However N_2O is not commercially available in large quantities. So this is the major disadvantage of using nitrous oxide in oxidation process. Virtually all N_2O is produced as byproduct of the adapic acid plant. If one were to produce PO using N_2O, it would be necessary to place the production facility close to an adapic acid plant. Although these adapic acid processes can produce N_2O in equimolar amounts, the amount of PO as a coproduct next to adapic acid is only a very small-scale production of PO. If one were to envision this process as a way of disposing of the harmful N_2O this could be a moderately profitable process (Nijhuis et al., 2006).

In the field of heterogeneous catalysis the development of new multi-component catalytic materials occurs mainly by an empirical approach since general principles which allow the prediction of catalytic activity of complex solids are not available. Considering the high time effort for synthesizing and screening potential solid catalysts, the development of methods which lead to a higher efficiency is of interest (Wolf et al., 2000). In the conventional approach, a single or a few catalyst compositions are evaluated over a pre-defined range of reaction conditions using a dedicated bench-type reactor system. Over the past decade, this approach to catalyst testing has been displaced by more modern and sophisticated methodologies where catalyst synthesis and reactivity evaluation are closely integrated using special purpose devices designed for high-throughout experimentation (HTE). The development and application of special-purpose methods for HTE that are driving innovation in various technologies has been the subject of various recent reviews in heterogeneous catalysis and area.

The application of combinatorial method in the discovery of heterogeneous catalysts has been investigated by many groups. Senkan and co-workers first used this technique to observe the activity of commercial Pt and Pd catalysts in dehydration of cyclohexane into benzene by resonance-enhanced multiphoton ionization (REMPI) detection method. Then they continued their studies with catalysts containing Pt, Pd and In metals prepared by impregnation method in dehydration of cyclohexane into benzene by REMPI and quadrupole mass spectroscopy (QMS). They determined benzene signal by these two methods to show the effectiveness of the combinatorial method to determine the performance of catalysts in a short time (Senkan, 1998; Senkan and Ozturk, 1999).

After these studies, Miyazaki and coworkers (Miyazaki et al., 2003) used combinatorial methodology to determine active catalyst for direct epoxidation of propylene to PO in the presence of only oxygen as oxidation agent. In the study, they investigated the catalytic performance of single metals (34 metals) as well as their binary combinations on γ-Al_2O_3. Among 34 elements and three metal loading levels (0.1, 1 and 10wt%) the maximum PO level observed was as 1000 ppm at 1.0%Rh at 1% conversion of C_3H_6. For binary system, Rh-based binary catalysts reached maximum levels as 2000 ppm at again 1% conversion. They obtained superior binary combinations that exhibited superior PO production levels were Rh-V, Rh-Cr, Rh-Sn, Rh-In, Rh-Mo and Rh-Sm albeit substantial CO_2 formation. On the other hand Rh-Ag, Rh-Zn and Rh-Cr combinations were significant leads with regard to high PO and low CO_2 products.

Senkan and coworkers (Senkan et al., 2006) used a high-throughput laser ablation (HT-PLA) method to prepare catalytic materials containing again Rh, bimetallic Rh/Pt and trimetallic Ph/Pt/Au nano-particle in the latter study. They prepared over 40 catalytic materials of nano-particles on γ-Al_2O_3, CeO_2, TiO_2, SiO_2 and γ-ZrO_2 in a short time with different particle size and loading by changing distance of the ablation plume and pulse number. They obtained the highest PO plus acetone (AT) yield (13%) for TiO_2 supported single Rh nanoparticles at 100 pulse loading at 275 °C and C_3H_6/O_2 gas ratio of 1. The conversion at these conditions was 16.9% and PO+AT selectivity was 77.2%. And they stated that HT-PLA in conjunction with high-throughput catalysts screening method increase the tempo of research for the discovery and optimization of new catalytic system. However when they used micro-GC with thermal conductivity detector (TCD) for qualification of reaction products, they declared that Rh/TiO_2 catalyst only gave propionaldehyde (PaL) and acetone not PO as reported in previous study (Duan et al., 2007).

CHAPTER 3

EXPERIMENTAL

A large number of catalysts were synthesized by sol-gel method in a combinatorial fashion. In order to be able to synthesize catalysts in a combinatorial fashion, a commercial synthesis apparatus was adapted to prepare catalysts in the laboratory. The synthesis apparatus used for this purpose contains 24 cells where catalysts can be simultaneously synthesized as shown in Figure 3.1. The synthesis reactor block has a capability for reflux by circulating cold water. Magnetic stirring is also provided for each cell where a catalyst is synthesized. Reflux capability is an advantage during synthesis of the catalysts, such as silica and alumina that require high temperature conditions. Besides, inert gas could be used if required during catalyst synthesis.

Figure 3.1 The synthesis reactor block used in this study

The general procedures applied for synthesis of the catalysts were as follow:

3.1. Synthesis Procedure for Silica Supported Catalysts

The materials used in synthesis of silica were tetraethyl orthosilicate (TEOS) with 99% purity supplied from Fluka, 1 M of nitric acid (HNO_3) solution, 0.5 M of ammonium hydroxide (NH_4OH) solution, ethanol (EtOH) with 99.8% purity, metal nitrates (silver (Ag), copper (Cu), manganese (Mn), potassium (K), lithium (Li), yttrium (Y), cerium (Ce)) and water. The molar ratios of chemicals with respect to Si are shown in Table 3.1.

Table 3.1 The molar ratios of chemicals with respect to Si

Material	**Ratio**
EtOH/Si	10, 20, 30
HNO_3/Si	$7.9x10^{-4}$
NH_4OH/Si	$2.5x10^{-3}$
H_2O/Si	12.8
Metal	1-20 w/w

The basis for preparing of silica catalysts containing metal particle was taken as 1 g SiO_2 and amount of chemicals were determined on this basis.

TEOS, HNO_3, ethanol and water were put together in the glass tube at room temperature and heated to temperature of 80-85 °C. During heating, the solution was stirred by a magnetic stirrer under reflux condition. The solution was kept at this temperature for 2 h. After 2 h, the necessary amount of metal nitrate was added into the mixture and continued to stir for 1 h. If the catalyst was promoted with metal like K, Li etc., the metal nitrate salts were added after another 1 h. To obtain gel, NH_4OH was added into the metal containing solution. After aging during a day, silica supported metal catalysts were dried at 120 ^{o}C to obtain homogeneous solid catalysts and calcined at 550°C for 5 h. Calcination temperature of samples were decided according to the TGA-DTA analysis given in Figure A.1.

3.2. Synthesis Procedure for Alumina-Supported Catalysts

The materials used in synthesis of alumina were aluminium isopropoxide (AIP) supplied from Aldrich, water, metal nitrates (Ag, Cu) and 15.8 M of stock HNO_3 solution. The molar ratios of chemicals with respect to AIP are shown in Table 3.2.

Table 3.2 The molar ratio of chemicals with respect to AIP

Material	Ratio
H_2O/AIP	10, 15, 20 ml/g
HNO_3 /AIP	0.195 mol/mol
Metal/AIP	1-20 w/w

The amount of all chemicals were calculated according to 1 g of alumina.

The necessary amount of deionized water was heated to 85 °C. Then, corresponding amount of AIP was added into the water at this temperature under vigorous stirring. After that, the mouth of the tubes was closed to prevent evaporation with the refluxing condenser and kept the slurry stirred at 85 °C for 1 h. The necessary amount of HNO_3 was added to the solution that was kept stirring for 1 h under reflux. The required amount of metal precursor was added into the solution and continued stirring at 85 °C for 1 h. Then the heater was switched off and the solution was kept to stir for 24 h. The solution was transferred into a large beaker and let the solvent evaporating at temperature of 60 to 70 °C without stirring. When the gel formed, the heater was switch off. The gel was aged for a certain time and dried at 100 °C for approximately 20 h. The dried gel was calcined at 450 °C for 4 h. Calcination temperature of samples were decided according to the TGA-DTA analysis given in Figure A.2.

3.3. Synthesis Procedure for Titanium Oxide

The materials used in synthesis of titanium oxide were tetrabutylortotitanate (TBOT) supplied from Fluka, EtOH, water, 15.8 M of stock HNO_3 solution and metal nitrate (Ag, Cu, Mn). The molar ratios of chemicals with respect to TBOT are shown in Table 3.3.

Table 3.3 The molar ratios of chemicals with respect to TBOT

Material	**Ratio**
H_2O/TBOT	5
HNO_3/TBOT	0.3
EtOH/TBOT	4
Metal/TBOT	1-20 w/w

1 g of TiO_2 was taken as basis.

Ethanol was put in a tube, the corresponding amount of TBOT was added to EtOH and started to stir at room temperature. The necessary amount of HNO_3 acid and then aqueous solutions of metal nitrates were added into the clear mixture of TBOT and EtOH. The solution was kept until the gel was obtained. The obtained gel was dried at 100 ^oC then calcined at 400 ^oC for 2 h. Calcination temperature of samples were decided according to the TGA-DTA analysis given in Figure A.3.

3.4. Synthesis Procedure for Metal Containing Mesoporus Silica

The materials used in synthesis of mesoporus silica were: TEOS, 15.8 M of stock HNO_3 solution, dodecylamine (DDA) supplied from Fluka, EtOH, water, and metal nitrates (Ag, Cu, and Mn). The molar ratios of chemicals with respect to Si are shown in Table 3.4.

Table 3.4. The molar ratios of chemicals with respect to Si

Material	**Ratio**
EtOH/Si	6.54
$H(NO_3)$ /Si	0.02
H_2O/Si	36.3
DDA/Si	0.27
Metal/Si	0.5-20 %

The necessary amount of metal precursor was put into the tube and dissolved with water. Then DDA with HNO_3 were added into the solution. The mixture was stirred for 1 h. The clear solution of TEOS and EtOH were added to the above mixture. The mixture was continued to stir during 4 h at room temperature. After that the magnetic stirrer was closed and allowed the mixture to age for 18 h at room temperature. The resultant product was filtered, dried at 70 ^{o}C during a day to prevent ignition of filter paper and calcined at 650 ^{o}C for 3 h. Calcination temperature of samples were decided according to the TGA-DTA analysis given in Figure A.4.

3.5. Synthesis Procedure for Metal Containing Mesoporus Titanium Silicate

The materials used in synthesis of mesoporus titanium silicate were TEOS, TBOT, buthyl alcohol (BA), 15.8 M of stock HNO_3 solution, DDA, EtOH, water and metal nitrates (Mn and Cu). The molar ratios of chemicals with respect to Si are shown in Table 3.5.

Table 3.5. The molar ratios of chemicals with respect to Si

Material	**Ratio**
EtOH&BA/Si	6.54
DDA/Si	0.27
HNO_3 /Si	0.02
H2O/Si	36.3
TBOT/Si (molar ratio)	2, 4
Metal/Si	0.5-20%

The necessary amount of metal precursor was put into the tube and dissolved with water. Then DDA with HNO_3 were added into the solution. The mixture was started to stir for 1 h. The clear solution of TEOS, TBOT, BA and EtOH were added to the above mixture. The mixture was continued to stir for 4 h. After that the magnetic stirrer was turned off. The mixture was allowed to age for 18 h at room temperature. The resultant product was filtered, dried at 70 ^{o}C for a day and calcined at 650 ^{o}C for 3 h.

The general flow sheet for the experimental procedure was given in Appendix B.

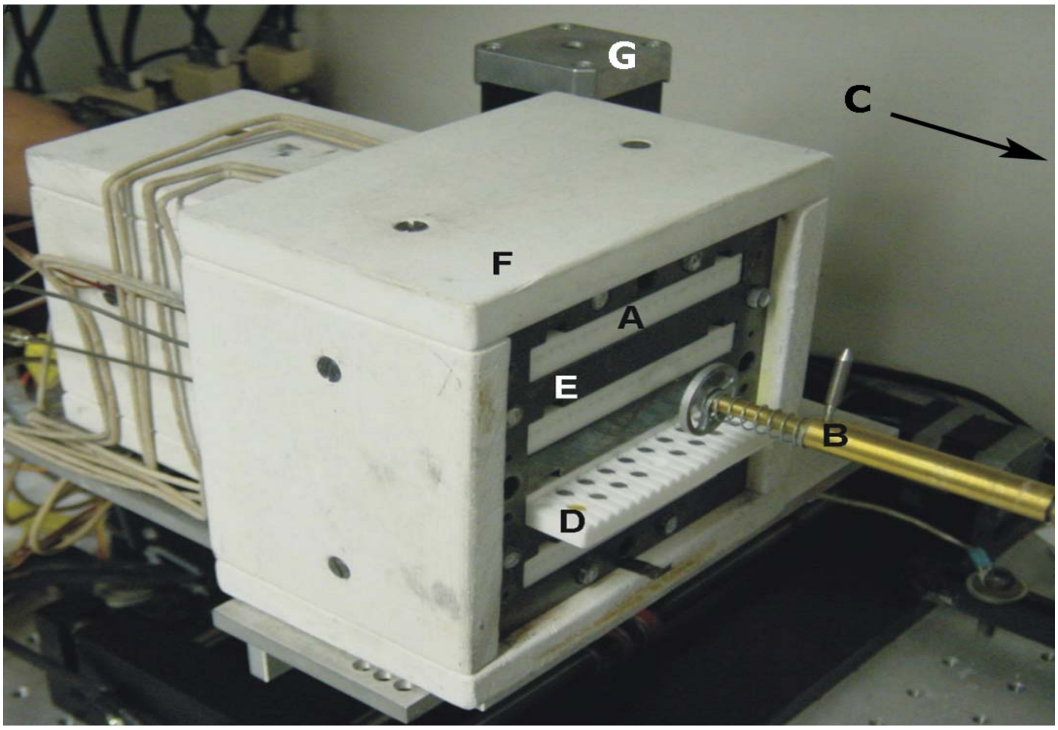
3.6. Synthesis Procedure of Incipent Wetness Method

Beside the direct sol-gel method, some catalysts were prepared with incepent wetness method. The support materials calcined at different temperatures and commercial α-alumina were prepared by this method. According to the method, the water pore volume of calcined silica, titanium silica and alpha alumina powder were measured by adding water drops to known amount of support materials. The volume was determined as the quantity of added water just before excess water appeared on the surface of the sample. Then wet sample was dried at 120 °C in the oven for 12 h. The desired amount of metal nitrate was dissolved in the pore volume of each sample and added to the dried sample by dropwise while stirring. Finally the prepared sample was dried again in an oven for 12 h and calcined at different temperatures.

3.7. Catalytic Activity Tests

The prepared catalysts were tested for the direct gas phase oxidation of propylene with molecular oxygen to PO by using the following reaction conditions. The catalyst screening test was performed in a computer controlled array channel microreactor system in University of California Los Angeles (UCLA). In the system, up to 80 catalysts could be screened simultaneously as displayed in Figure 3.2. The schematic representation of the system was given in Appendix C. However in the experiments, 20 catalyst candidates were tested in one screening experiment and one data point was obtained for one catalyst approximately in 3 min. In the array microreactors, reactant gases flow over the flat surfaces of catalyst powder which are individually isolated within reactor channels. All experiments were performed using 5 or 10 mg of catalyst under atmospheric pressure and at a gas hourly space velocity (GHSV) of 20,000 h^{-1}, representing a differential reactor condition. The gas flow rate over each plate was 100 cc min^{-1} and over each channel in one array was 5 cc min^{-1}.

a



A.Array Reactor (20 channels) B.Capillary Sampling Probe C.Gas Chromatograph D. Catalysts in Array Channels E. Heat Controlled Reactor Block F.Thermal Insulation G.Automated Motion Control System

b

Figure 3.2 a) Arroy channel micro-reactor b) Catalytic activity test unit

The initial screening experiments were performed at a temperature of 300 °C using feed gas composition of 14% C_3H_6, 28% O_2 (C_3H_6/O_2=0.5) and balance helium (He). The second screening tests were performed at a reaction temperature of 300 °C and 20% C_3H_6, 20% O_2 (C_3H_6/O_2=1.0) and 60% He. However the third and last screening experiments were performed at different reaction temperatures (225, 275, 300 and 350 °C) and volumetric ratio of C_3H_6/O_2 (0.1, 0.3, 0.5, 1.0 and 1.3).

Reactor effluent streams were analyzed by withdrawing the products using a heated capillary sampling probe followed by on-line gas chromatography (Varian CP-4900 Micro GC with thermal conductivity detector (TCD), Porapak Q (10m) and Molecular sieve 13X (10m) columns).

The selectivity of PO is defined as the percent of amount of carbon in PO in all the products. The selectivity of the other C_3 products, such as propionaldehyde plus acrolein (PaL+AC), acetone (AT) and acetaldehyde (AD) were calculated in the same way. The reaction pathway for each products formed in the oxidation of propylene and sample calculation for consumption and PO production rate for 3%Cu-2.25%K-m-SiO_2 catalyst were given in Appendix D.

3.8. Characterization

3.8.1. Thermo gravimetric and differential thermal analysis

By using thermo gravimetric and differential thermal analysis (TGA-DTA) technique, calcination temperature of catalyst samples was determined. The measurement of thermal analyses was done using Shimadzu DTG-60H apparatus in air flow.

3.8.2. X-ray powder diffraction

The structure and morphology of some of the catalysts that showed the high and low catalytic performance were examined with powder X-ray diffraction (XRD) technique as a function of metal composition and synthesis condition. The XRD technique was performed using Philips X'pert Pro XRD operated at 40 kV and 45 mA by using K α radiation. The scans were run at 2θ of 10 to 90° at a rate of 0.1°.

3.8.3. BET surface area and pore size measurements

Micromeritics Gemini V and Micromeritics ASAP 2010 apparatus was used to determine the BET surface area and average pore size of the catalysts. The samples were first degassed at 300 °C until reach constant weight to remove impurities and water then the nitrogen was introduced into the sample quartz tube to perform the adsorption of nitrogen under the liquid nitrogen temperature (-196 °C). The surface area of sample was calculated from the amount adsorbed nitrogene molecules on the surface between 0.05-0.35 relative pressure and pore size distribution of catalysts were calculated using Barrett-Joyner-Halenda (BJH) method.

3.8.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was performed to determine the oxidation states of the selected metals into the catalysts that gave different catalytic performance and to determine the effect of the promoter. The X-ray photoelectron spectra were obtained using Mg K α (hv=1253.6 eV) radiation with SPECS spectrometer in METU Central Laboratory.

3.8.5. Transmission electron microscopy

Transmission electron microscopy (TEM) was used to determine the shape and size of supported and modified particles. TEM micrographs were obtained using JEOL JEM-2000FX TEM in UCLA.

3.8.6. Scanning electron microscopy and energy dispersive X-ray

Scanning electron microscopy (SEM) was used to observe the topography of a catalyst surface. Experiments were conducted using a FEI Quanta 400F scanning electron microscope equipped with a cold field emission source operated at 30 kV with a limit of resolution of ~1.2 nm. The working distance (objective lens to specimen) was 8.7 mm. After coating the sample with gold (Au)-palladium (Pd) in sputter coating system, energy dispersive X-ray analyzer (EDX) system attached to SEM was used to carry out compositional analysis at the same time. EDX analysis does not give the exact chemical composition of sample, but it shows the composition approximately in 1% error.

3.8.7. Inductively coupled plasma-mass spectrometer

Perkin Elmer DRC II model inductively coupled plasma-mass spectrometer (ICP-MS) was used to determine the actual amount of metal loaded into the catalyst samples.

CHAPTER 4

RESULTS and DISCUSSION

4.1 Characterization Results

The catalysts synthesized in this study were investigated by spectroscopic techniques such as XRD, XPS, SEM-EDX and TEM to obtain information on the physico-chemical properties affected by different synthesized parameters and metal-metal and metal-support interaction.

The silica and alumina supports were synthesized at different solvent/alkoxide ratio at the beginning of the study. Silica was synthesized at solvent (EtOH)/TEOS molar ratio of 10, 20 and 30. Alumina was synthesized at water/AIP ratio of 5, 10 and 15. After synthesizing of the supports, they were X-rayed to determine the effect of solvent ratio on the crystalline phases. After that Ag and Cu metals were loaded into these support materials at 0-20% weight ratios by direct sol-gel method. In addition to the silica and alumina supports, metal containing supports and silica synthesized with template were tested by XRD technique.

Figure 4.1 shows the XRD patterns of the calcined powder of alumina. In the XRD analysis, there are three peaks for γ-alumina at 40, 46, 66°. The patterns for the powders were indicative of γ-alumina structure and this structure did not change with solvent ratio. Only the intensity of the peak assigned to γ-alumina increased with first two water ratios than decreased. There was a small enlargement in the peaks for support synthesized at a water ratio of 15. Broadening of the peaks indicates that the crystallite size has decreased with the increase of water ratio.

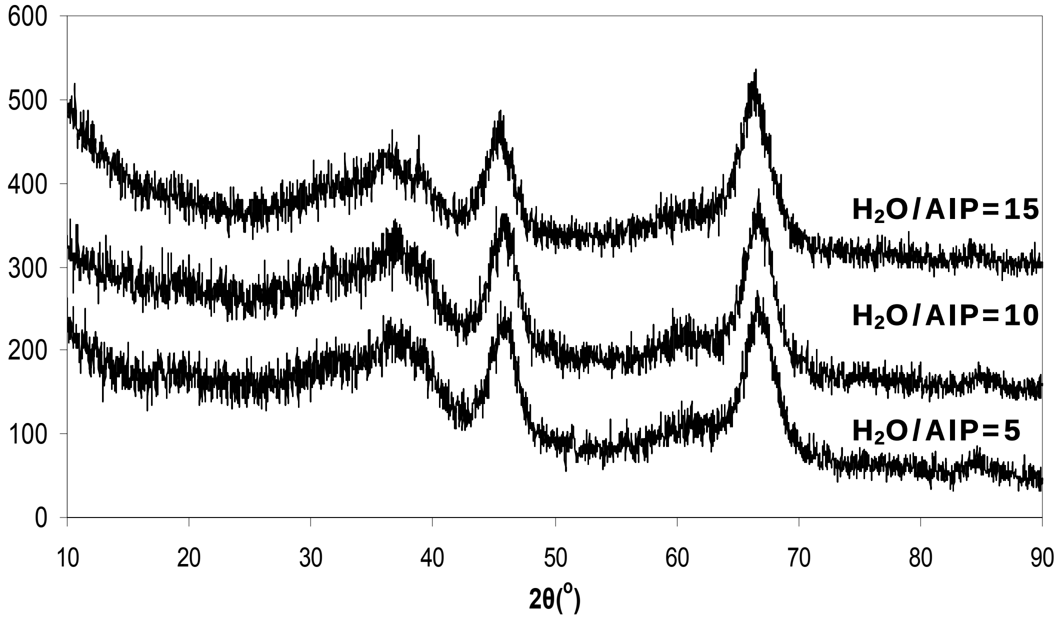


Figure 4.1 XRD patterns of calcined alumina powder synthesized at different H_2O/AIP ratios

Dumeignil and coworkers studied on the acidic properties of sol-gel prepared alumina powders by changing the hydrolysis ratio (R). They observed that when R=9 or 10, alumina powders have ink bottle type pores but with large necks i.e. pseudo-cylindrical pores and composed of alumina planes with stronger acidity than that of closely packed particles. For R<9 and R>10, the alumina were composed of closely packed particles that induced ink-bottle type pores (Dumeignil et al. 2003).

In the present study, the catalytic performance of the pure support material changed with R value. The results obtained for empty support showed that the propylene conversion of the catalyst synthesized at R=5 was 0.09% and the selectivity to PO, PaL+AC, AT and CO_2 were 3.94, 17.02, 4.82 and 74.02% respectively at a reaction temperature of 300 °C and C_3H_6/O_2 of 0.5. The conversion values increased to 0.12% at R=10, and the selectivities of oxygenated products were 3.74, 5.78, 4.05% respectively while CO_2 selectivity reached to 86.71%. According to Dumeignil and co-workers (Dumeignil et al., 2003), the acidic strength of the support material synthesized when R equals to 9-10 is stronger than that of R less than 9 and greater than 10. The catalytic activity results showed that propylene conversion was slightly higher for R=10 than that of R=5. Besides, the selectivity to CO_2 was higher for R=10 because of different acidic properties. The activity of the supports in oxidation reaction was found to be proportional to their surface acidity. It is generally stated that the selectivity towards epoxidate or CO_2 is strongly affected by the acidic properties of the support.

XRD analysis was also performed for pure silica synthesized with or without template. The diffraction pattern of silica is only seen at around at 22.5° with a broad peak which attributed to amorphous silica for both silicas as reported in the literature (Souza et al., 2000). Since silica supported catalysts had better catalytic performance than alumina, XRD analysis was performed for silica containing high and low amount of metal to determine the change in the metal crystallographic phase. XRD pattern for Cu and Ag/SiO_2 catalysts were shown in Figure 4.2. An addition of Cu in the range of 0.5 to 9wt% did not change the XRD pattern of amorphous silica. So it can be concluded that Cu was well-dispersed on the silica support. However an addition of 1wt%

Ag metal caused a very small peak at 38^o which belongs to Ag(111) and peak intensity increased with the Ag loading. At the same time, second small peak appeared at 44.4^o belonging to Ag(200) surface at 10 wt% Ag loading. The result showed that an increase in Ag loading caused particle agglomeration in the structure during sol stage. An evidence of this agglomeration and particle size growing can be easily seen in Ag peak.

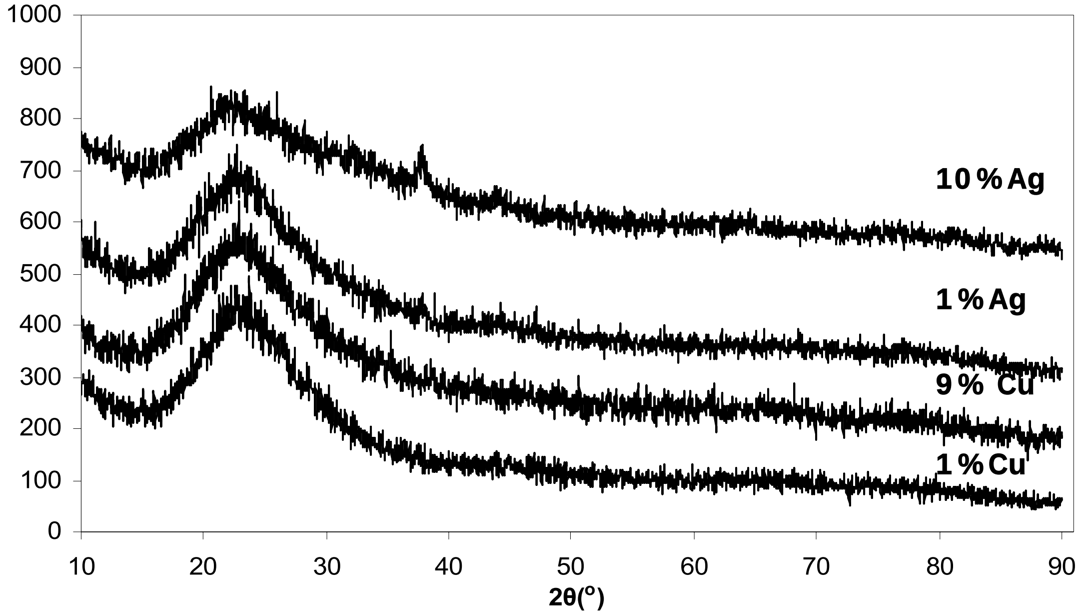


Figure 4.2 XRD patterns of silica supported Ag and Cu catalysts after calcination

The surface area and pore size distribution of alumina and silica with high and low surface area were obtained from BET plot and BJH analysis. For alumina support, the solvent ratio had not great effect on the surface area and pore diameter of material as shown in Table 4.1. However for silica support, the increase in the amount of solvent caused first increase than decrease in the surface area but there was no change in pore diameter. The calcination period so the surface area will decrease for silica. After addition of metals, the surface area of the both supports increased approximately three and four times but pore diameter decreased because of plugging of pore with metal. The increase in the surface area is the result of sol-gel method applied, because the metal loading occurs during sol stage and then obtained gel is dried and calcined. When silica synthesized with template its surface area increased to 1184 m^2/g but pore diameter decreased to 25 Å.

Table 4.1. Textural properties of empty and metal loaded Al_2O_3 and SiO_2 materials

Sample	**S_{BET} (m^2/g)**	**APD (Å)**
Al_2O_3(H_2O/AIP=5)	225	39.0
Al_2O_3(H_2O/AIP=10)	213	39.5
Al_2O_3(H_2O/AIP=15)	225	37.0
1% Ag/ Al_2O_3 (H_2O/AIP=10)	582	24.3
10% Ag/ Al_2O_3 (H_2O/AIP=10	662	23.3
SiO_2(EtOH/Si=10)	178	30
SiO_2(EtOH/Si=20)	207	39
SiO_2(EtOH/Si=30)	145	38
0.5% Cu/SiO_2 (EtOH/Si=20)	810	30
m-SiO_2	1184	25

APD: Average Pore Diameter

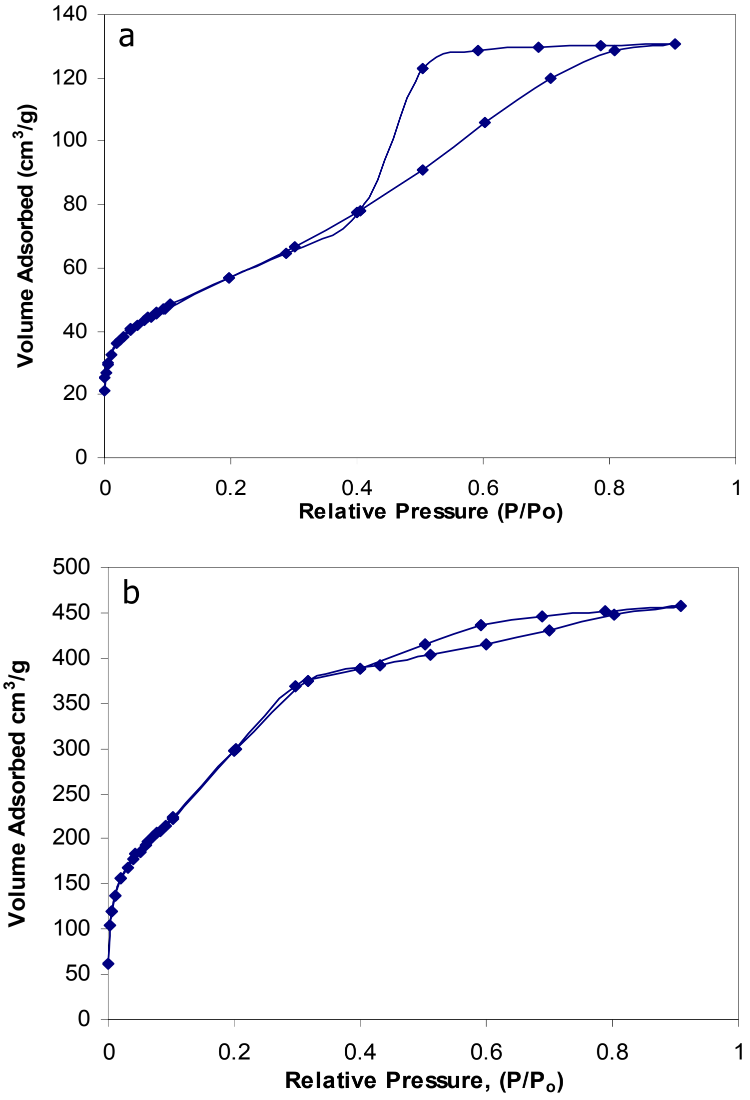


Figure 4.3 N_2 adsorption-desorption isotherm of a) SiO_2 synthesized at EtOH/Si=20 and b) m-SiO_2 support material

The N_2 adsorption-desorption isotherms of un-doped SiO_2 and m-SiO_2 materials were performed to find out the difference between the pore properties. As shown in Figure 4.3 both silicas showed type IV isotherm according to BDDT classification. The broad hysteresis loop belongs to SiO_2 indicates the filling and emptying of the mesopores by capillary condensation because of much steeper desorption branch than the adsorption branch. The nearly reversible isotherm of m-SiO_2 showed type IVc isotherm which forms due to reversible pore filling and emptying of a narrow range of uniform near-cylindrical pores of critical size (Rouquerol et al., 1999).

Table 4.2. ICP analysis results of some catalysts

Catalyst	**Actual metal loading**		
	Cu (%)	**K (%)**	**Ca (mg/kg)**
1% Cu/SiO_2	0.75	-	30.53
2% Cu/SiO_2	1.24	-	-
2%Cu-0.25%K/SiO_2	1.40	0.20	43.40
3% Cu/m-SiO_2	2.91	-	24.46
4%Cu-1%K/m-SiO_2	3.06	0.21	35.09

The actual metal loading into silica with the high and low surface area was measured by ICP analysis. The results were shown in Table 4.2. When Cu was loaded into silica with the low surface area, the measured amount was approximately 75% of the desired Cu amount at low loading (1%). However it was 60% at higher loading (2%) and addition of K at the same time into the structure again increased Cu amount. For high surface area silica, the actual Cu loading measured by ICP was consistent with the target Cu amount without promoter but it was again 75% of the target amount with promoter. The actual K loading was far away from the designed promoter amount for high surface area silica. There was also small amount of calcium (Ca) that might be coming from precursor used during synthesis.

4.2. Catalytic Activity Test Results

The first investigated catalysts group included alumina and silica supported Ag and Cu metals synthesized at different solvent/alkoxide ratios to determine appropriate amount of solvent by single step sol-gel method. For this purpose silica was synthesized at ethanol/Si ratio of 10, 20 and 30 and alumina was synthesized at water/Al ratio of 5, 10 and 15. The metals were added during solution stage. The catalytic performance of alumina silicate (Al-Si) was also investigated in this group. Besides, the incipient wetness method was used to observe the effect of preparation method on activity of catalysts. 160 catalysts were screened at a reaction temperature of 300 °C and C_3H_6/O_2 of 0.5 molar gas ratio in this group.

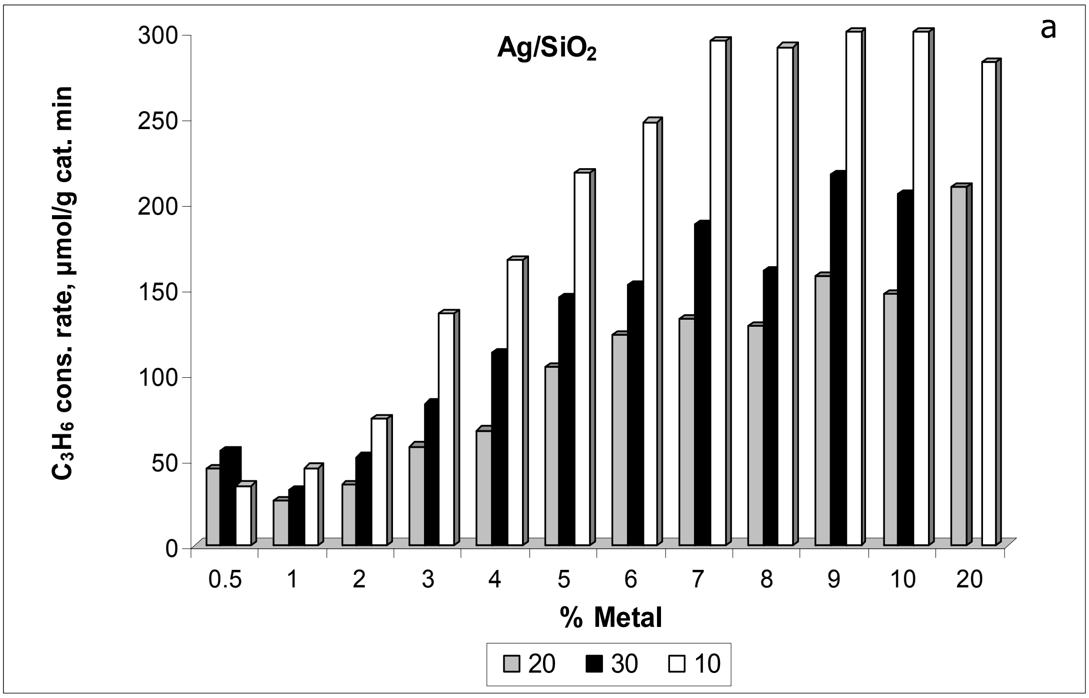
The catalysts prepared in the second group were determined based on the first screening activity test results. In this group, low and high surface area silica (SiO_2 and m-SiO_2), gamma and alpha alumina (γ-Al_2O_3 and α-Al_2O_3), titania (TiO_2) and high surface area silica (m-SiO_2) containing 2% and 4% Ti (Ti-SiO_2) supported mono metallic (Ag, Cu, Mn) and bi-metallic (Ag-Cu, Mn-Cu) systems were tested. The high surface area silica was synthesized with dodecylamine as a template. 231 catalysts were tested in this group at a reaction temperature of 300 °C and C_3H_6/O_2 ratio of 1.0. In this part, the first catalysts group (160 catalysts) was also screened at the same reaction conditions. 391 catalytic activity tests were performed.

After determining the catalysts that gave the highest PO activity, promoter such as K, Li, Y and Ce were used to increase the catalytic performance. Furthermore K-promoted Al-Si, bimetallic Ag and promoted Ag catalysts supported over SiO_2 and commercial α-Al_2O_3, and K-promoted Cu/TiO_2 catalysts were also screened in the third group. In this group 171 catalysts and some catalysts in previous groups that gave high catalytic performance were tested at the different reaction temperatures (225, 275, 300 and 350 °C) and C_3H_6/O_2 ratios of 0.1, 0.3, 0.5, 1.0 and 1.5. Approximately 800 catalytic activity tests were performed in this group.

The obtained results according to each metal were presented in the subsections below:

4.2.1. Supported mono-metallic Ag catalysts

Mono and bimetallic Ag catalytic systems with and without promoter over different supports were prepared. First the efficiency of silica and alumina supported catalysts synthesized at different solvent/alkoxide ratio were examined. For silica supported catalyst, propylene consumption rate and PO production rate showed the same trend with respect to solvent ratio at a reaction temperature of 300 °C and C_3H_6/O_2 gas ratio of 0.5 as shown in Figure 4.4.



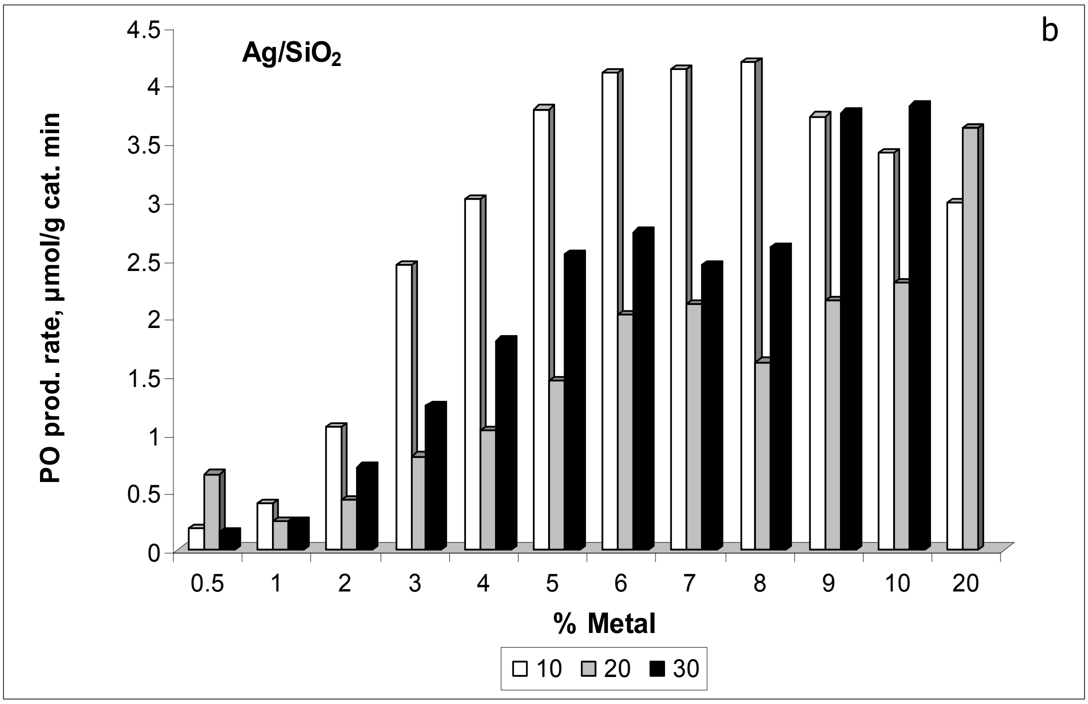


Figure 4.4. a) C_3H_6 consumption and b) PO production rate obtained for Ag/SiO_2 catalysts at 300 °C and $C_3H_6/O_2=0.5$

The consumption rate increased with metal loadings and reached the maximum value as 352.13 μmol/g cat. min. for 10%Ag catalyst synthesized at an ethanol (EtOH)/Si ratio of 10. However PO selectivity stayed very low (max.~1.88%) at all EtOH/Si ratios because of excessive CO_2 formation. The main product for Ag/SiO_2 catalysts was obtained as CO_2 (85-97%), and PaL+AC was observed as a second oxygenated products (1-12%) at low metal content. Because of high consumption rate, PO production reached to 4.19 μmol/g cat. min. for 8% Ag synthesized at again EtOH to Si ratio of 10. It can be inferred that the most appropriate solvent ratio for Ag/SiO_2 catalysts is 10. Silica synthesized at this solvent ratio showed low surface area (178 m^2 g^{-1}) and minimum average pore diameter (30 Å) when compared silica synthesized at solvent ratio of 20 and 30. This low surface area probably caused an increase in Ag particle diameter over support surface because of agglomeration and less Ag particle was captured in the small pore. Thus contact surface between silver particle and reactant gases increased and more propylene was converted into the products.

When γ-Al_2O_3 was used as a support material, the propylene conversion reached to 775.92 μmol/g cat min. for 20%Ag catalyst prepared at H_2O/Al of 10 while PO production rate decreased with metal loading because of complete combustion reaction. As illustrated in Figure 4.5, PO production obtained for Ag/γ-Al_2O_3 catalyst was very low and the results obtained at all metal loadings (0.5 to 20%) were close to each other regardless of the solvent ratio. The catalysts synthesized at a solvent ratio of 15 gave higher PO productivity than that of other ratios but it was again very low when compared with Ag/SiO_2 catalysts. Besides, PaL+AC selectivity (21.65%) was partially higher than Ag/SiO_2 catalysts at low Ag content.

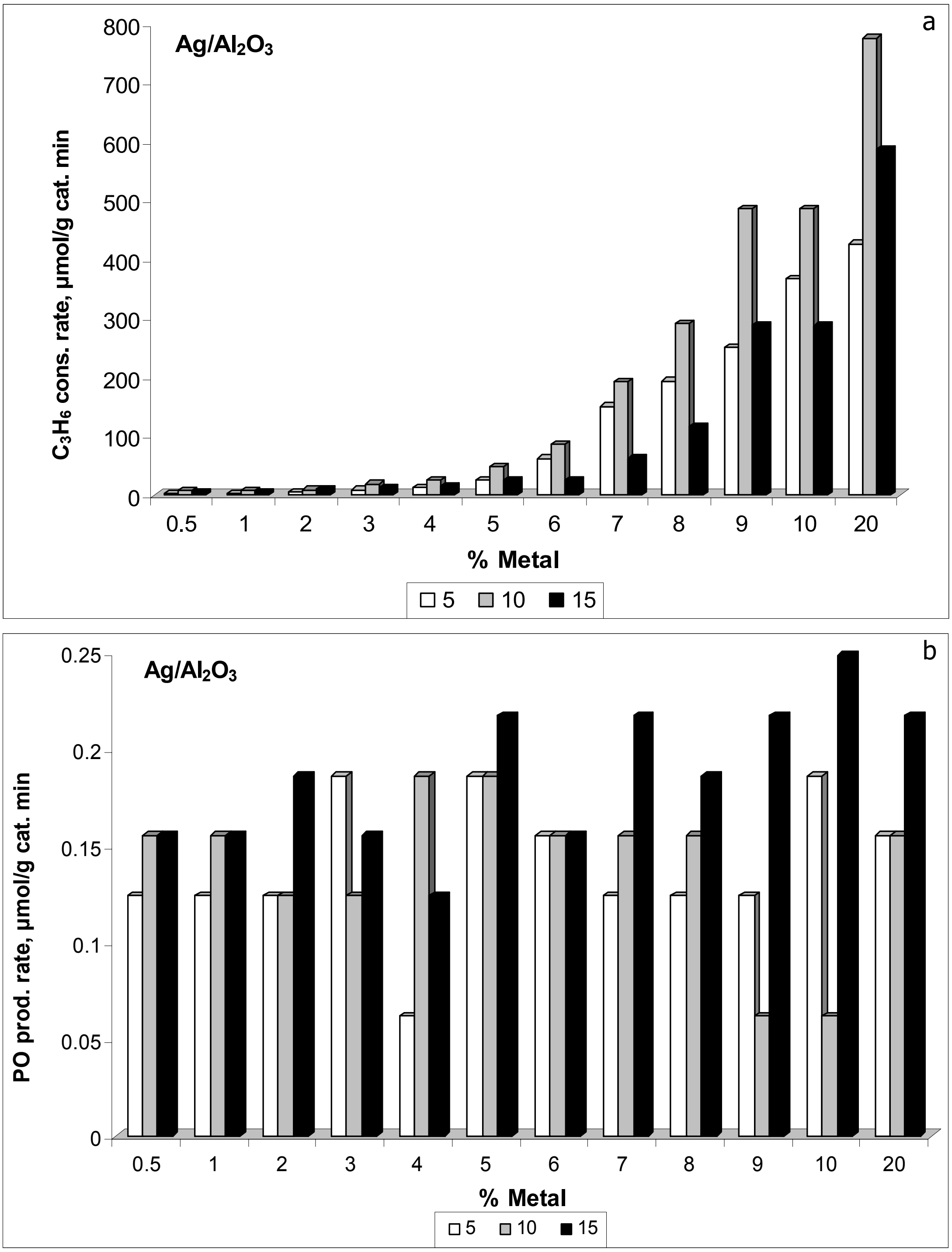


Figure 4.5 a) C_3H_6 consumption and b) PO production rate obtained for Ag/γ-Al_2O_3 catalysts at 300 °C and C_3H_6/O_2=0.5

In order to determine the state of the Ag metal on the catalyst surface at high and low metal loading, XPS analysis was performed for 1% and 10%Ag/SiO_2 catalysts. The results were shown in Figure 4.6. SiO_2 supported Ag catalysts were examined with XPS technique because they gave relatively higher PO productivity instead of lower propylene consumption rate when compared with Ag/γ-Al_2O_3. The selectivity to PO was significantly higher over SiO_2 support than γ-Al_2O_3 support because of lower acidic sites. As it is known stronger acidic sites cause catalytic cracking and polymerization of propylene and finally produced CO_2 and H_2O.

For Ag/SiO_2 catalysts, binding energy at 368.9 and 374.9 eV indicated that Ag is in metallic form regardless of silver loading and the intensity of Ag $3d_{5/2}$ peak increased with the metal loading. The increase in Ag metal particle size caused high propylene conversion because of high CO_2 production rate but the selectivity to PO decreased with the particle size. The big Ag particle is not desired for epoxidation reaction. The growing particle size with metal loadings was also confirmed by XRD analysis. XRD pattern for Ag/SiO_2 catalysts was shown in Figure 4.2. As stated before an addition of Ag metal into the amorphous silica caused a very small peak at 38^o which belongs to Ag (111) phase and peak intensity increased with the loading. At the same time, second small peak appeared at 44.4^o belong to Ag (200) surface. There is still no agreement on which particle size is proper for high PO production. Lu and coworkers reported that PO selectivity increases with particle size and small particle suppresses product selectivities. On the other hand, Lei and coworkers stated that small silver particle and Ag_3 cluster are favorable for high PO selectivity (Lu et al., 2006; Lei et al., 2010).

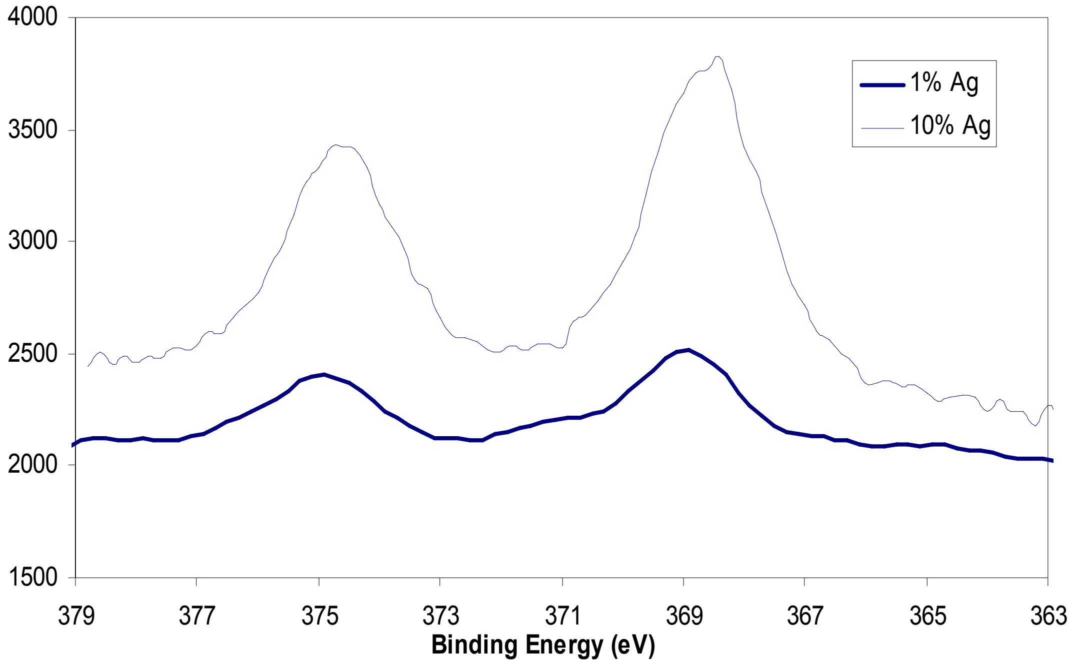
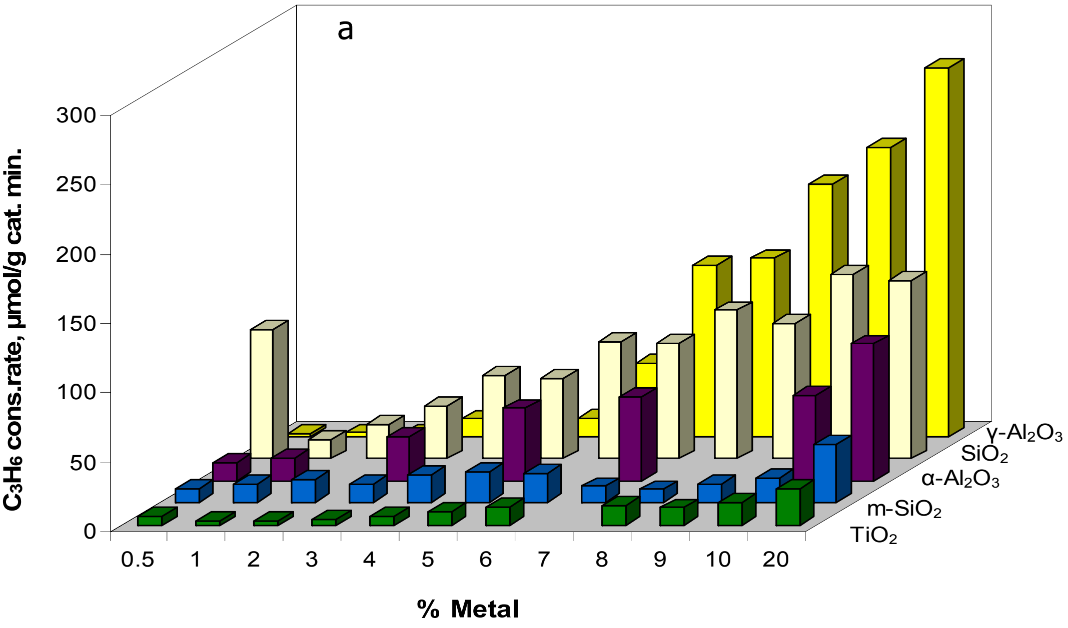


Figure 4.6. Silver 3d5/2 XPS spectra of 1% and 10% Ag/SiO_2 catalysts

The effect of support material over catalytic performance of Ag catalyst was investigated with other oxides such as α-Al_2O_3, m-SiO_2 and TiO_2 in the second part. The results for Ag catalysts loaded on the five different supports (γ-Al_2O_3, α-Al_2O_3, SiO_2, m-SiO_2 ve TiO_2) were given in Figure 4.7 a and b. Propylene consumption and PO production rate were shown in the figures with respect to metal loading at 300 °C and C_3H_6/O_2 of 1.0.

Generally propylene consumption rate increased with the metal loadings for all support materials. The maximum propylene consumption was obtained as 266.23 μmol/g cat. min. with very low PO production rate (0.06 μmol/g cat. min.) over 20%Ag-γ-Al_2O_3 catalyst as in the first group. The lowest conversion was obtained for TiO_2 and m-SiO_2 supported catalysts. Although the low propylene conversion was obtained over m-SiO_2 and α-Al_2O_3, PO selectivity reached the maximum value for these two supported catalysts. 5%Ag/m-SiO_2 catalyst had 22.27 µmol/g cat. min. consumption rate and 0.67 µmol/g cat. min. of PO production rate. If two types of silica materials were compared with each other according to activity results, the silica with high surface area had better PO selectivity at lower conversion. m-SiO_2 supported catalyst gave approximately 3 times larger PO selectivity than that of SiO_2 catalyst at the same propylene conversion value. The Ag particle size over m-SiO_2 support was probably lower than that of over SiO_2 support. Thus Ag/m-SiO_2 catalyst gave lower propylene conversion with relatively higher PO selectivity.

Among the five support materials considered, α-Al_2O_3 held the most promise for PO formation. The maximum PO production rate was obtained as 4.14 µmol/g cat. min. at 98.57 µmol/g cat. min. consumption rate over 20% Ag/α-Al_2O_3 catalyst prepared by incipient wetness method.



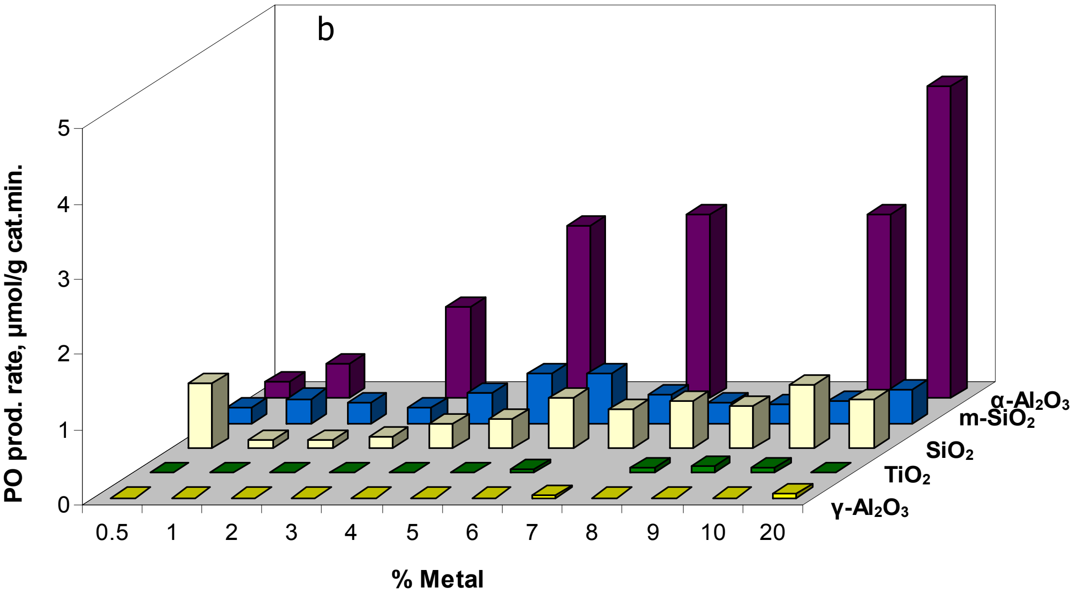


Figure 4.7 a) C_3H_6 consumption and b) PO production rate of supported Ag catalysts

Silver catalysts mostly caused combustion reaction and produced CO_2, especially for Ag/γ-Al_2O_3. However, the maximum PaL+AC selectivity as a major C_3 product reached to 30% over Ag/m-SiO_2 and the maximum AT selectivity as a second major C_3 product was 5% over Ag/γ-Al_2O_3. When reaction mechanisms taking place over Ag surface during gas reaction between propylene and oxygen was investigated, the reason behind the low PO efficiency can be well understood. Fellah investigated the energy barriers of each reaction paths given in the Appendix D over Ag_{13}(111) cluster by DFT calculation and reported that the energy barrier for formation of PO, PaL, π-allyl, and AC as 15.71 kcal/mol (when the first carbon of propylene reacts with adsorbed oxygen), 21.85 kcal/mol, 6.11 kcal/mol and 36.03 kcal/mol respectively. The energy barrier for π-allyl formation is very low when compared with other product barriers. So allylic hydrogen in propylene reacts with adsorbed oxygen over Ag and this leads mostly to combustion reaction.

However Al-Si supported Ag catalysts showed different tendency when compared with other supported Ag catalysts. Ag was also loaded into the aluminum silicate (Al-Si) support because high PO selectivity with low propylene conversion was obtained for pure Al-Si support in the initial screening experiment. For this purpose 1-5% Al containing SiO_2 was synthesized first and then 0.5wt% and 1wt% Ag were loaded in each supports. However when the results obtained at different reaction temperatures in the third screening test were examined carefully, it was seen that the peak belongs to PO in the gas chromatography combined with ethanol peak and did not separate clearly. So it can be said that Al-Si supported catalyst catalyzed ethanol formation mostly and its selectivity reached 80% but no PO. Potassium promoted Ag catalyst over Al-Si and K-promoted Al-Si catalyst were also prepared but they gave again high selectivity to ethanol.

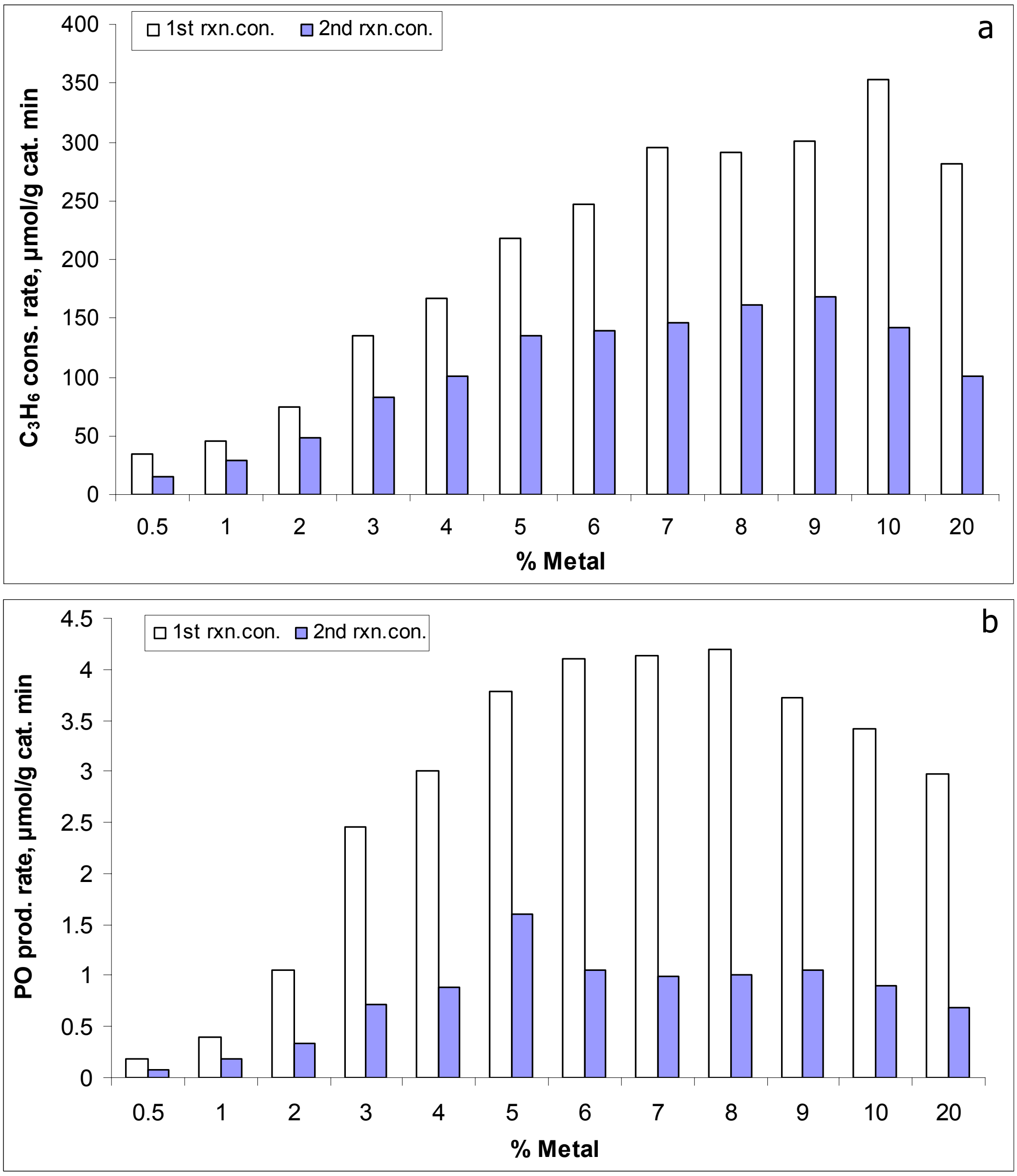


Figure 4.8. The effect of first ($C_3H_6/O_2=0.5$) and second ($C_3H_6/O_2=1.0$) reaction conditions over a) C_3H_6 consumption and b) PO production rate for Ag/SiO_2

Besides metal ratio, another reaction parameter investigated in the first group was reactant gas ratio in feed stream. When the ratio of propylene to oxygen was increased to 1.0, the consumption of propylene and the production rate of PO were 142.29 μmol/g cat. min and 0.90 μmol/g cat. min. respectively for 10%Ag/SiO_2. When the ratio was 0.5 (first reaction condition), the consumption of propylene was 353.31 μmol/g cat. min and the PO production reached 3.41 μmol/g cat. min. for 10% Ag/SiO_2 catalyst. The same trend was observed for alumina supported catalysts. So it can be concluded that the proper reactant gas ratio for supported Ag catalysts is 0.5 as displayed in Figure 4.8.

4.2.2. Supported mono-metallic Cu catalysts

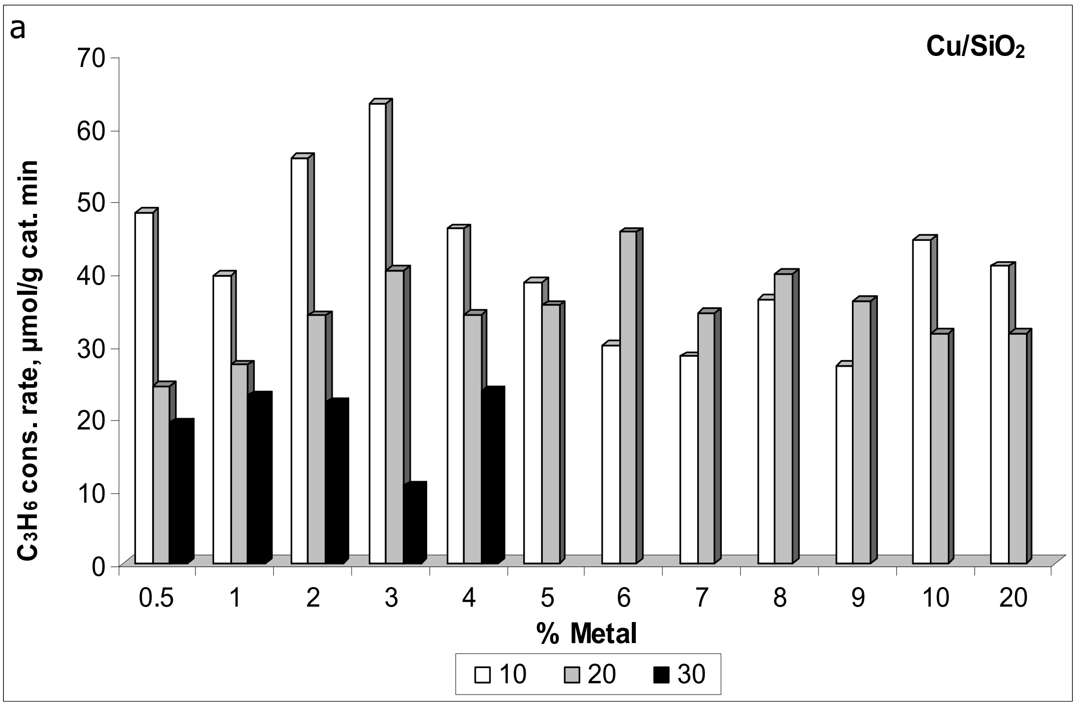
The effectiveness of Cu containing catalyst was investigated after determining that Cu is more selective than Ag catalysts for alkene epoxidation (Cowell et al., 2000). So Cu is the second widely investigated metal after Ag in this thesis.

At the beginning of the study, Cu metal was loaded into the γ-Al_2O_3 and SiO_2 support synthesized at different solvent/alkoxide ratio as in the case of Ag to determine the most appropriate solvent ratio and support type.

The propylene consumption rate showed a different trend for Cu/SiO_2 catalysts synthesized at different solvent/alkoxide ratios as illustrated in Figure 4.9. Among the three different solvent/alkoxide ratios, the maximum consumption rate was obtained at 3% Cu catalyst synthesized at 10 molar ratio. Generally at low metal content catalysts synthesized at 10 molar ratio showed better performance whereas the catalysts synthesized at 20 molar ratio were more effective at high Cu loadings. Also the lowest consumption rates were obtained for catalysts synthesized at a solvent ratio of 30. This support had the lowest surface area (145 m^2/g) with big pore size (38 Å) according to the BET results and it was not possible to synthesize catalyst above 5% Cu content at this solvent ratio. The gelling time of solution is directly related with the amount of ions in the solutions. So the solution containing 6% or further amount of Cu precursor at solvent rich medium did not get gel point and it was not possible to observe the performance of the catalyst above this point.

In the case of PO production, PO selectivity reached a maximum (8.65%) for 0.5% Cu catalyst at 20 solvent ratio. It was still high for 1% Cu catalyst (7.40%) instead of lower propylene consumption rate than that obtained at 10 solvent ratio. The highest PO production rate reached to 2.73 µmol/g cat. min. at 55.78 µmol/g cat. min. consumption rate for 2% Cu/SiO_2 catalyst synthesized at EtOH/Si=10. However PO production rate was 2.11 µmol/g cat. min. at 24.40 µmol/g cat. min. consumption rate for 0.5% Cu catalyst synthesized when the ratio equals to 20. So the research was focused on silica support containing low amount of Cu in the latter of study.

Generally the PO yield decreased with an increase in metal loadings at all solvent ratios. If the results are investigated according to the reaction by-product, the selectivity to PaL+AC and AT for Cu catalysts (60-70%) is greater than those of Ag catalysts. The amount of CO_2 produced (20-30%) in the reaction decreased because of an increase in PaL+AC production.



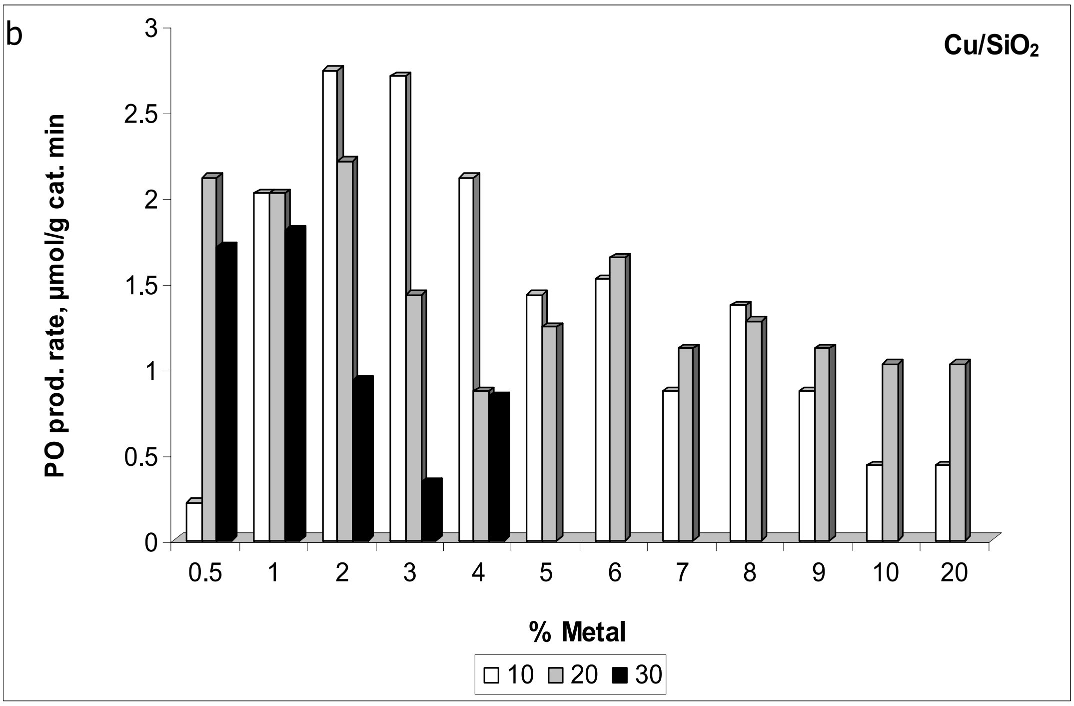


Figure 4.9 a) C_3H_6 consumption and b) PO production rate obtained for Cu/SiO_2 catalysts

For $Cu/\gamma\text{-}Al_2O_3$ catalysts, propylene consumption rate was relatively high but the selectivity to PO was less than that obtained for Cu/SiO_2 catalysts. The consumption of propylene was directly related with metal content but PO selectivity was generally very low (<2.0%) and decreased with loading. 0.22 µmol/g cat. min. was the maximum PO production rate at 33.05 µmol/g cat. min. consumption rate for 10%Cu catalyst synthesized at $H_2O/Al=5$. Instead of very low PO selectivity, PaL+AC formation reached 35% at high Cu content and CO_2 remained at ~65%.

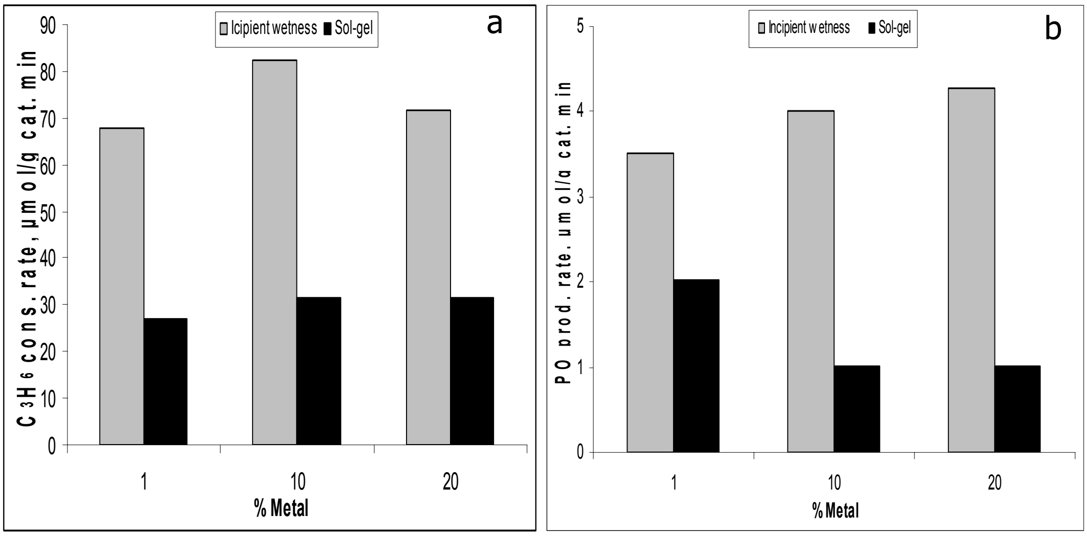


Figure 4.10 The comparison of a) propylene consumption and b) PO production rate obtained for Cu/SiO_2 catalyst prepared by incipient wetness and sol-gel methods as a function of metal loading

The effect of preparation technique on the performance of the catalyst was also investigated for Cu/SiO_2 catalyst. For this purpose silica support was synthesized at a solvent ratio of 20 first and then 1, 10 and 20 wt% Cu were loaded separately into this support by incipient wetness method. The comparison of the results obtained by different preparation techniques was illustrated in Figure 4.10. Cu/SiO_2 catalyst prepared by incipient wetness method showed higher performance when compared with direct one step sol-gel method. In the direct sol-gel method, the selectivity to PO decreased with the amount of Cu loaded (the maximum PO rate was 2.02 μmol/g cat. min. for 0.5% Cu/SiO_2), but in the incipient wetness method, the observation was controversial. An increase in the Cu amount improved the catalytic activity. But according to the selectivity to PO the best catalyst was 1%Cu prepared by sol-gel method. For this reason the catalysts were prepared with sol-gel method in the study.

Since Cu/SiO_2 catalysts gave remarkably higher catalytic performance by considering both PO selectivity and propylene consumption, some of the catalysts were investigated by XRD and XPS techniques to determine the crystalline phases and oxidation state of Cu as a function of metal content. 1% Cu and 9% Cu catalysts were chosen for analysis because high PO productivity was obtained at low Cu loading whereas it decreased with further amount of Cu. XRD pattern of 1% and 9%Cu/SiO_2 catalyst were shown in Figure 4.2. However absence of any diffraction peaks corresponding to copper or copper oxides indicated that copper/copper oxide crystallite size was less than 5 nm. So it could be concluded that Cu is highly dispersed over support regardless to the Cu amount.

In order to determine the oxidation state of Cu at high and low metal loadings and the difference between catalysts, XPS analysis was performed on the fresh 0.5 and 9% Cu/SiO_2 as shown in Fig 4.11. The binding energy at 937.6 and 935.8 eV indicates the presence of isolated ionic-like Cu^{2+} species for the catalyst with low metal loading. However, for 9% Cu/SiO_2 catalyst, the binding energy at 933.7 eV is attributed to the existence of Cu^{2+}

species in CuO form and the binding energy at 934.3 and 936.5 eV indicates Cu existing in the isolated ionic-like form.

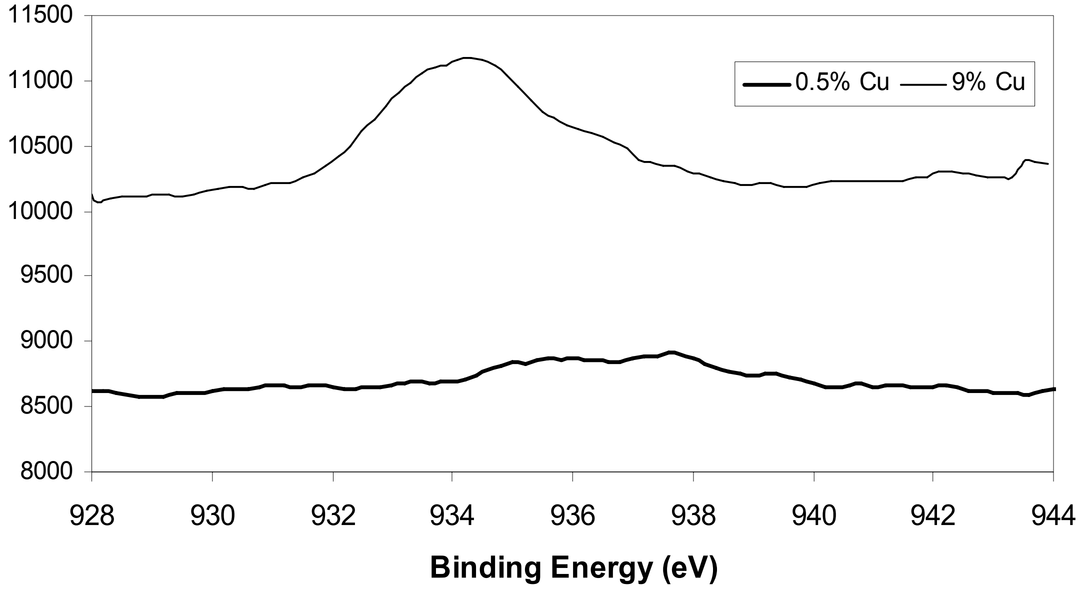


Figure 4.11. Copper 2p XPS spectra of 0.5% and 9% Cu/SiO_2 catalysts

This point seems to be controversial in the literature. For example, Lu et al. stated that metallic copper is an active state for propene epoxidation and Cu with high valence causes combustion reaction and acrolein production. In other studies, Vaughan et al. stated that the active form of copper is Cu^0 species in highly dispersed atomic like form while Zhu et al. stated that of Cu^I is active form. In addition to these, Su et al. concluded that both forms of Cu (Cu^0 and Cu^I) especially Cu^0 form in the small oxide cluster are necessary for propene epoxidation (Lu et al., 2002a; Vaughan et al. 2005; Zhu et al., 2008; Su et al., 2009).

Since Cu containing catalysts was found to be the more effective than Ag, it was tried to enhance its performance with other support materials. In addition to the five supports tested for Ag catalyst, 2 and 4 mol% titanium containing silica that synthesized with surfactant were prepared to investigate the catalytic activity of supported Cu catalyst. The propylene consumption and PO production rate obtained at a reaction temperature of 300 °C and $C_3H_6/O_2=1.0$ ratio in the second group was summarized in Figures 4.12 and Figure 4.13 a and b. The results were presented in two groups. First group included low surface area supports (SiO_2, TiO_2, γ-Al_2O_3 and α-Al_2O_3) and second group included high surface area supports (m-SiO_2, 2%Ti-m-SiO_2, 4%Ti-m-SiO_2).

The maximum propylene consumption rate was obtained on 10% Cu/TiO_2 as 250.46 μmol/g cat. min. in the first group. A further addition of Cu caused an increase in propylene consumption to 418.90 μmol/g cat. min. for 20% Cu/TiO_2 catalyst but these catalysts produced the lowest C_3 epoxidation products (max. PaL+AC selectivity as 11.85% and AT selectivity as 2.17% respectively). The second highest consumption rate was obtained for SiO_2 supported catalysts. Although γ-Al_2O_3 is the least effective support material in terms of PO selectivity, the selectivities to C_3 products reached to 35.77% for PaL+AC and 8.40% for AT over 2% Cu/γ-Al_2O_3 catalyst. Among the 7 support materials showed in figures, high and low surface area silicas were the most promising supports for PO synthesis.

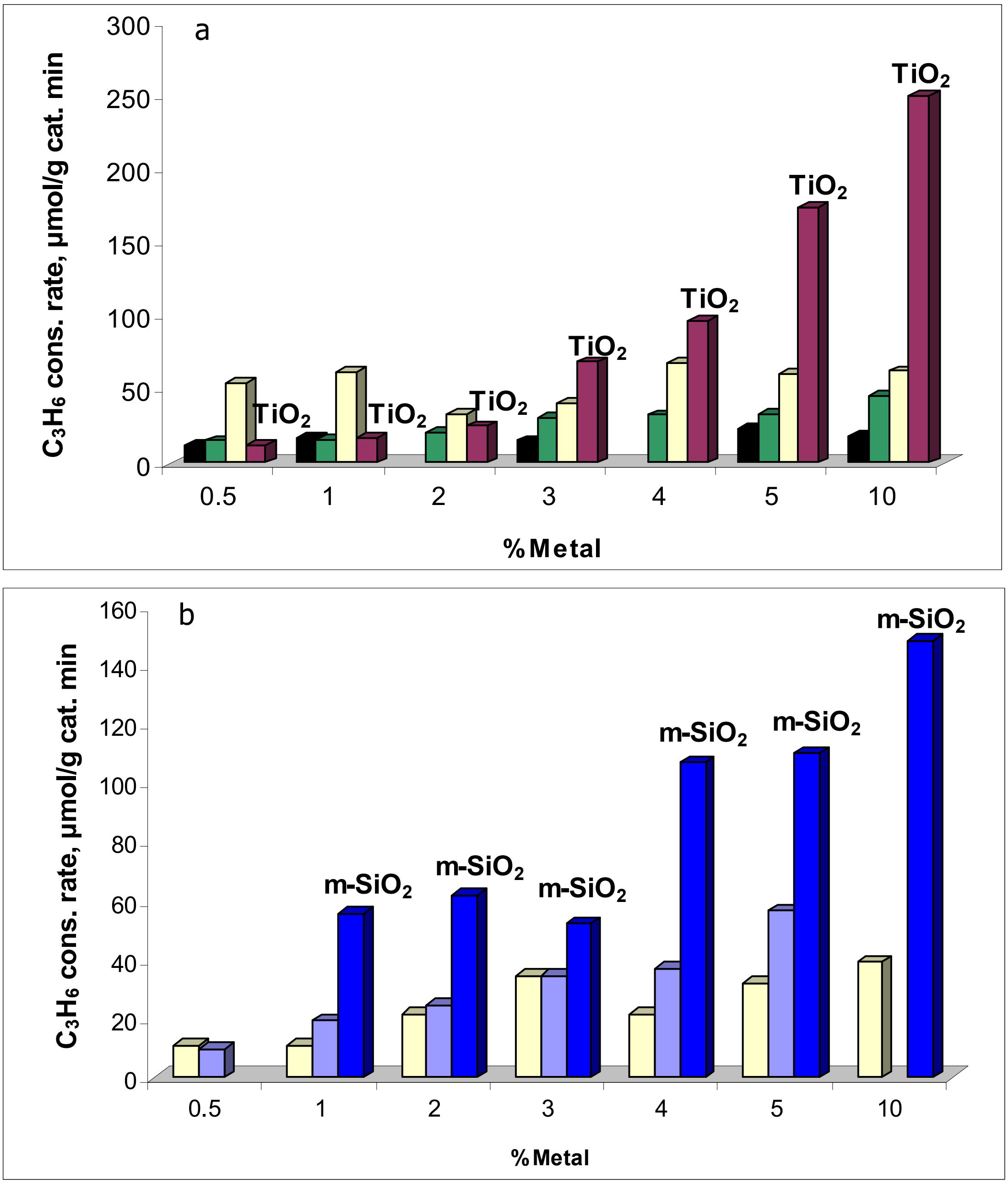


Figure 4.12 C_3H_6 consumption rate of Cu catalysts supported on a) low surface area (SiO_2, TiO_2, γ-Al_2O_3 and α-Al_2O_3) b) high surface area (m-SiO_2, 2%Ti-m-SiO_2, 4%Ti-m-SiO_2) supports

The maximum selectivity toward PO reached to 10.71% for 2%Cu/m-SiO_2 catalyst at 62.0 µmol/g cat.min. (2% propylene conversion). At the same conversion value, the PO selectivity obtained over SiO_2 was five times lower than m-SiO_2. For m-SiO_2, an increase in Cu loading from 1 to 3% resulted in a slightly decrease in PO production and then it increased because of high propylene consumption rate. However, a further increase caused a significant decrease in PO selectivity (3.4% PO selectivity for 10 wt% Cu). For SiO_2 and m-SiO_2 supported Cu catalysts, the major product was PaL+AC (60–70%) almost at all metal loadings. AT selectivity was 9.5% for SiO_2 but it was 1.8% for m-SiO_2 at low metal content and it decreased with an increase of loading. Both silicas showed different trend in consumption rate at this reaction condition. There was no significant change in propylene consumption for SiO_2 supported catalysts as a function of metal loadings. But there is a meaningful increase in consumption of propylene over m-SiO_2 supported catalysts. Moreover the increase in loading remarkably decreased PO selectivity for both supports as illustrated in Figures 4.13. Other oxygenated products were also decreased with loadings for m-SiO_2 catalysts.

To improve the activity of m-SiO_2 support material, 2 and 4 mol% titanium were added into the structure separately in accordance with literature studies (Liu et al., 2006). However no significant increase in the performance was observed both in propylene consumption and in PO production rate for titanium silicate supports. An addition of Ti only increased CO_2 production with Ti amount. The acidic amount of catalyst probably increased by introducing Ti into the m-SiO_2 framework and this caused the more combustion reaction.

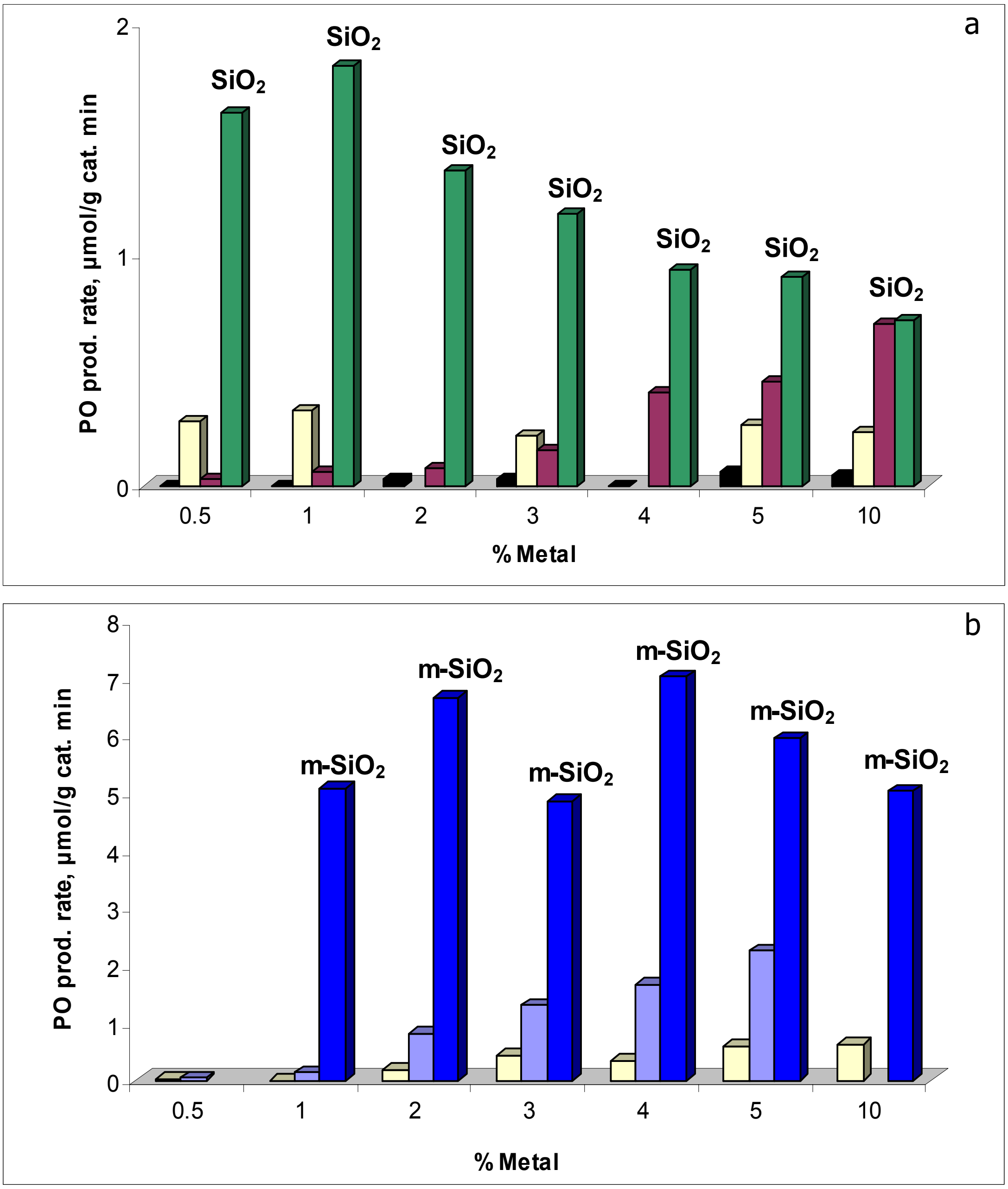


Figure 4.13 PO production rate of Cu catalyst supported on a) low surface area (SiO_2, TiO_2, γ-Al_2O_3 and α-Al_2O_3) b) high surface area (m-SiO_2, 2%Ti-m-SiO_2, 4%Ti-m-SiO_2) supports

In this group the effect of different preparation techniques for m-SiO_2 catalyst was also investigated. The effect of calcination temperature was also investigated for catalysts prepared by incipient wetness method. For this purpose, the empty m-SiO_2 support was calcined at 650 (IW, 650C) and 800 °C (IW, 800C) and then the desired amount of Cu was loaded into the structure. Contrary to the Cu/SiO_2 catalysts, the most effective method for high surface area silica was direct sol-gel method as illustrated in Figure 4.14 a and b. Besides there was no significant change in the catalytic performance with respect to calcination temperature.

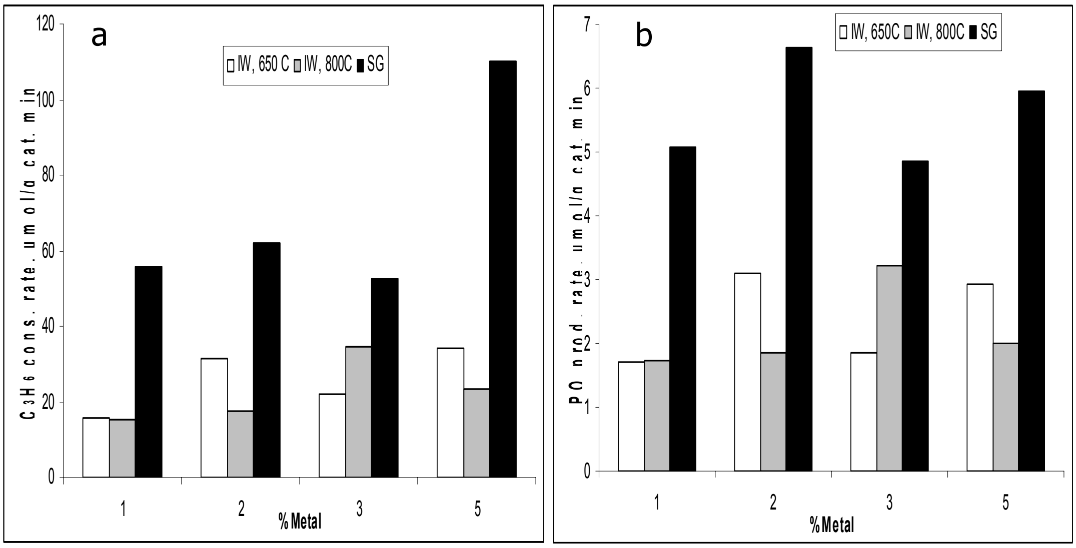


Figure 4.14 The comparison of a) propylene consumption and b) PO production rate obtained for Cu/m-SiO_2 catalyst prepared by incipient wetness and sol-gel methods

When the reaction conditions applied in the initial and second screening tests were compared, the reactant gas ratio in the feed stream of 0.5 was found to be more favorable than the ratio used in the second screening experiment at 300 °C. Because PO production rate was higher at C_3H_6/O_2 of 0.5 despite lower propylene consumption rate as summarized in Figure 4.15 a and b.

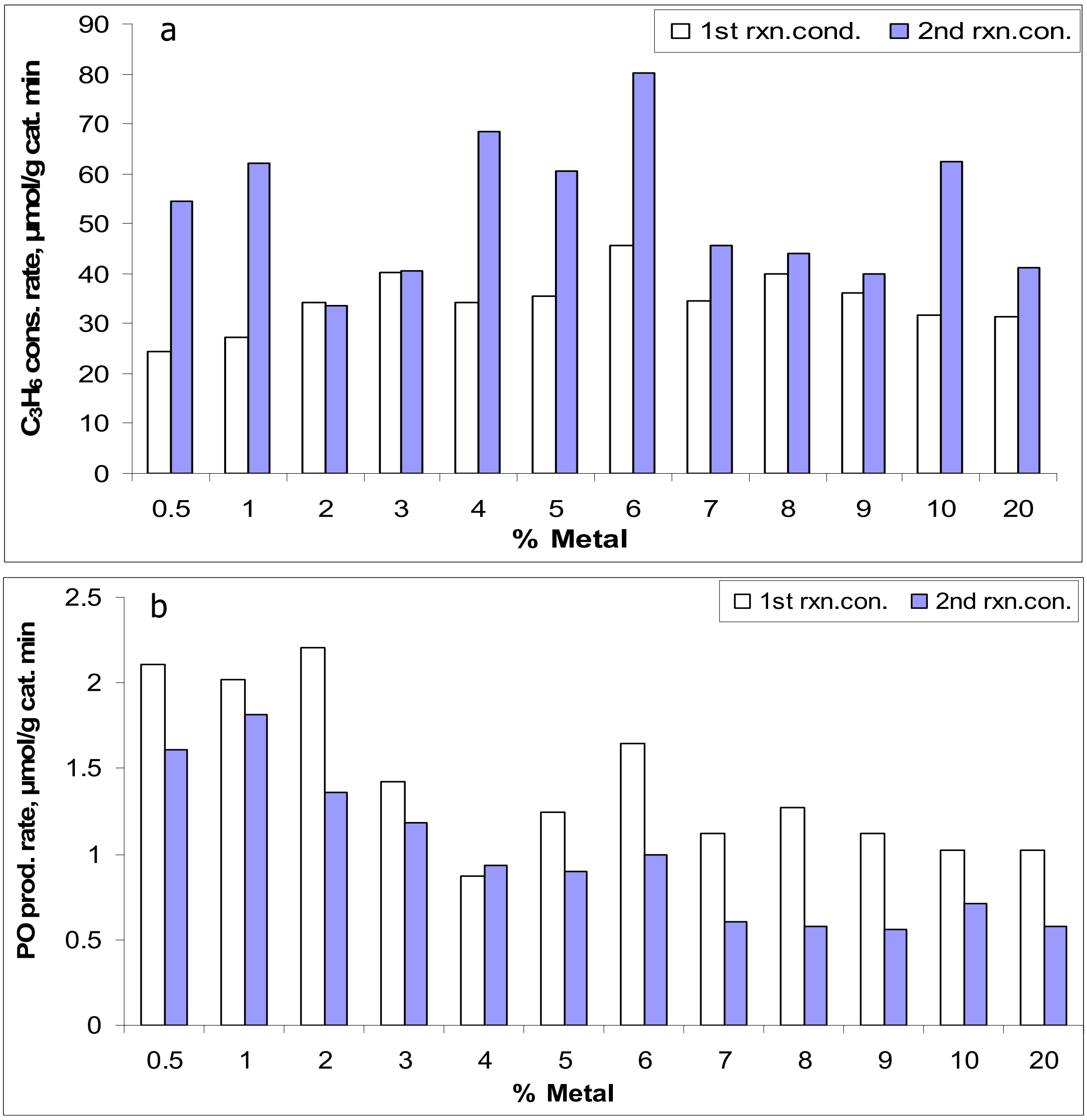


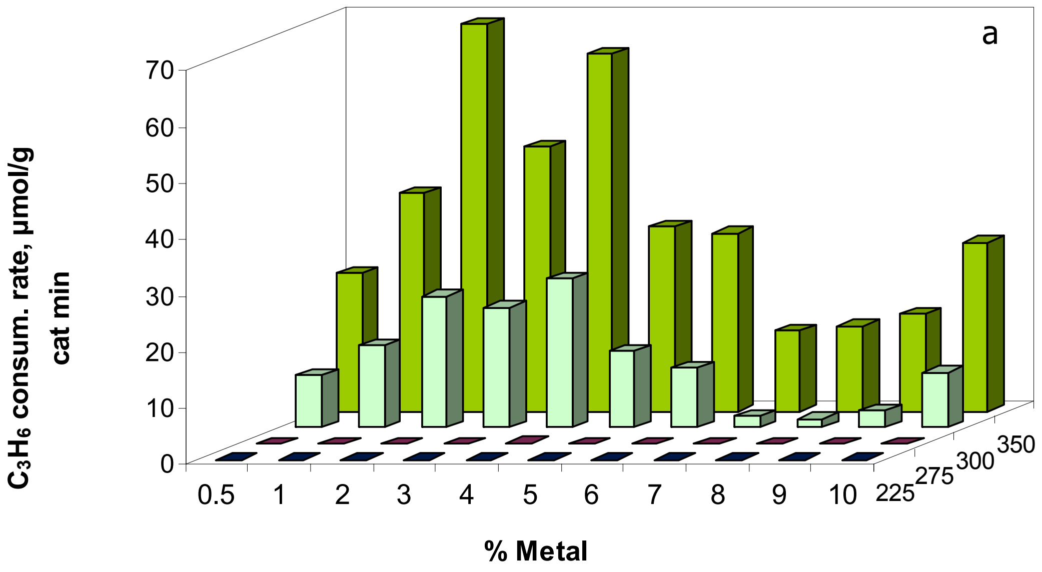
Figure 4.15 The effect of first ($C_3H_6/O_2=0.5$) and second ($C_3H_6/O_2=1.0$) reaction conditions over a) C_3H_6 consumption and b) PO production rate for Cu/SiO_2

For this reason, at the beginning of third catalytic screening test was performed at a C_3H_6/O_2 molar ratio of 0.5 on modified and un-modified Cu containing low surface area silica (SiO_2) at 225, 275, 300 and 350 °C reaction temperatures. And then the catalytic screening test was continued at the other reactant gas ratios.

After first and second catalyst screening tests, the most promising catalyst for epoxidation reaction was determined as silica supported Cu catalyst. For this reason, Cu/SiO$_2$ and Cu/m-SiO$_2$ catalysts were modified with different promoters (K, Li, Ce and Y) to enhance their catalytic performance in the third group. The promoted and un-promoted catalysts were tested at different reaction temperatures (225, 275, 300 and 350 °C) and reactant gas ratios (C_3H_6/O_2=0.3, 0.5, 1.0 and 1.5).

For un-modified catalysts, the highest PO production rate was obtained as 3.51 μmol/g cat. min. for 2%Cu containing silica at 350 °C due to high propene conversion (68.76 μmol/g cat. min.). Above 2%Cu loading, PO production rate decreased with metal loading. The highest consumption rates were obtained in 2-4%Cu loading range and further increases in the metal loading decreased the catalytic activity.

The effect of reaction temperatures on the propylene consumption and PO production rates were shown in Figure 4.16 a and b. As seen in figures both consumption and production rates increased with reaction temperature. Although there was a slightly decrease in PO selectivity above 300 °C, conversions continued to increase with temperature. Hence PO production rates stayed at high level.



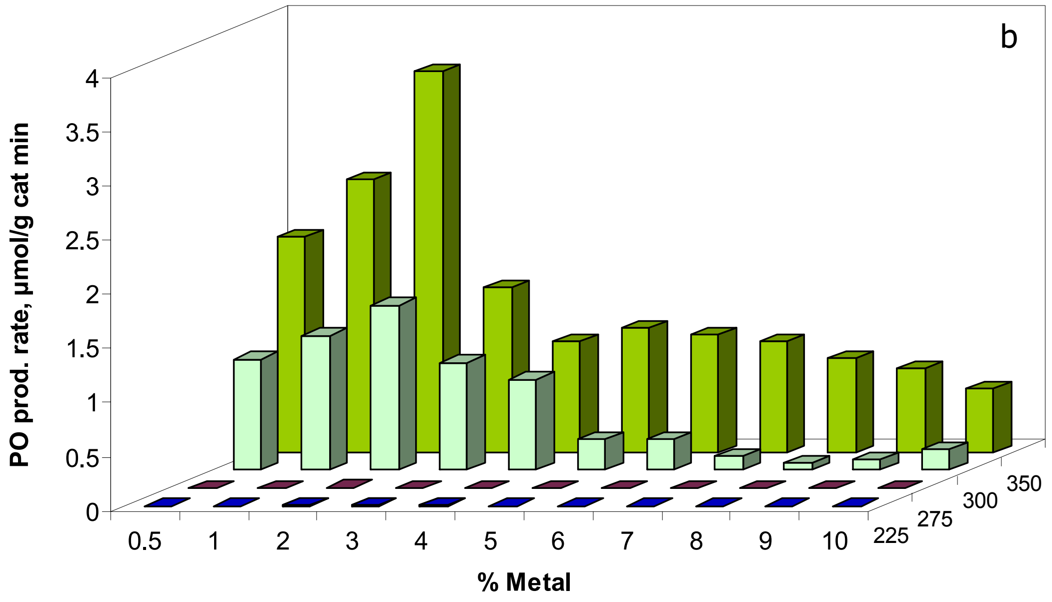
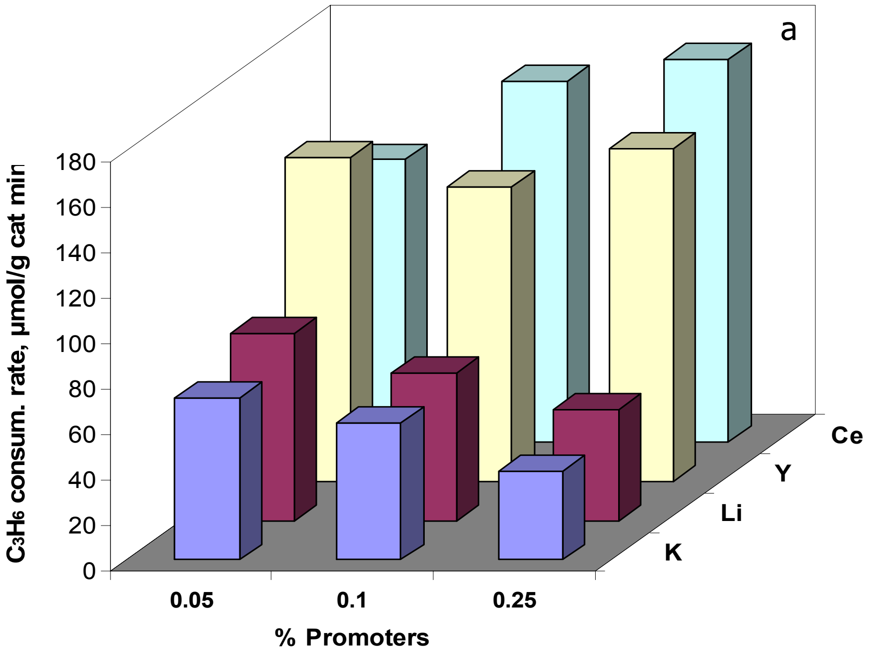


Figure 4.16 a) C_3H_6 consumption and b) PO production rate of Cu/SiO_2 catalysts at different reaction temperatures

Since the low PO yield was observed, Cu/SiO_2 catalysts were promoted with metals, such as K, Li, Ce and Y. The amount of promoter added into the structure was changed from 0.05 wt% to 0.25 wt%. Although in the literature, the promoter effect of K or Li over Cu containing catalysts has been investigated by several research groups (Yang et al., 2008; Chu et al., 2006; Su et al., 2009), the promoter effect of Ce or Y for Cu based catalysts has not been studied. The activity test results in this study showed that Ce and Y enhanced the overall propene consumption rate sharply while decreasing PO selectivity but increasing PaL+AC selectivity. As shown in Figure 4.17 a and b, the propylene conversion was very high for Ce and Y, especially for Ce. CeO_2 material has ability to store and release oxygen and this property promoted PaL+AC selectivity for catalysts prepared in this study. The product distribution with propylene conversion was listed in Table 4.3. Yao and coworkers used Y_2O_3 as a second promoter for $K_2O/\alpha\text{-}Al_2O_3$ catalysts and reported that an addition of Y_2O_3 to K_2O modified catalysts caused a decrease in the strong basic sites of catalysts and it increased the selectivity to PO (Yao et al., 2007). However for Cu/SiO_2 catalyst, Y promoter had negatively effect on PO selectivity. Like Ce, Y again promoted the formation of PaL+AC.



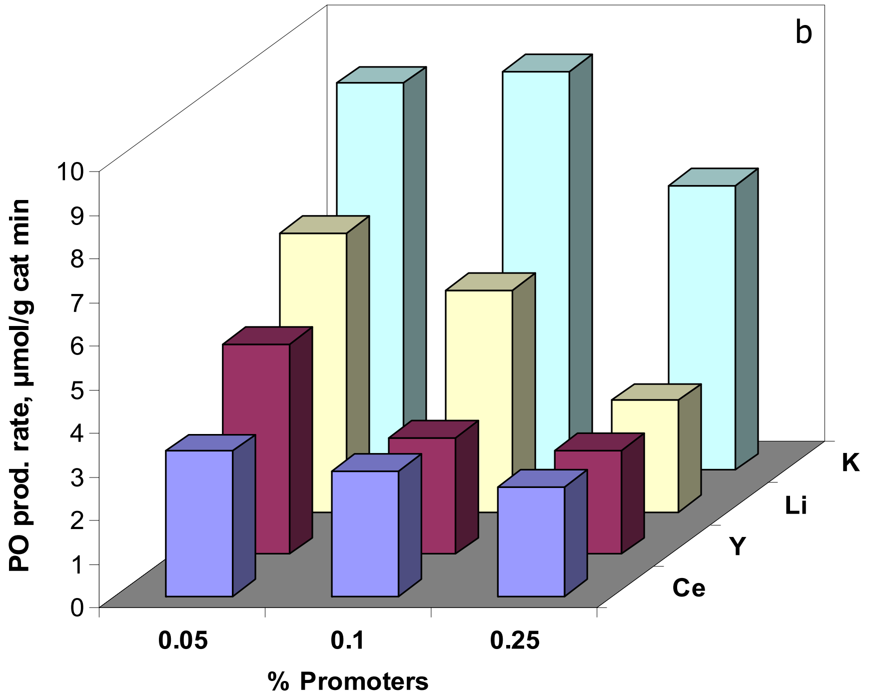


Figure 4.17 The effect of different promoters on a) consumption and b) PO production rate for 0.5%Cu/SiO_2 catalyst at 350 °C and 0.5 reactant gas ratio

Table 4.3 Catalytic properties of promoted 0.5%Cu/SiO2 catalyst at 350 °C and 0.5 reactant gas ratio

Promoters (0.1wt%.)	Conv. (%)	Selectivity (%)				
		PO	PaL+AC	AT	CO_X	AD
Cu	0.56	8.08	65.18	3.66	22.15	1.39
Li	1.5	7.82	45.57	1.22	44.64	0.75
Ce	3.65	1.80	66.36	1.74	29.40	0.69
K	1.41	15.21	52.53	1.32	30.47	0.47
Y	2.92	2.06	66.58	2.33	28.26	0.78

However, K and Li enhanced both the overall propene consumption and PO production rate when compared with un-promoted Cu/SiO_2 catalysts. The effect of addition of K or Li over 0.5%Cu catalyst was summarized in Figure 4.18 a and b at 300 and 350 °C, respectively. As seen in the figures, the addition of 0.05 wt% of K and Li sharply increased overall propylene consumption rate and this was significant especially for Li promoted catalyst. In fact, at 350 °C, the consumption rate increased from 24.57 to 82.21 µmol/g cat. min. on 0.05 wt% Li promoted catalyst whereas to 71.12 µmol/g cat. min. on 0.05 wt% K promoted catalyst. In contrast to this activity trend, K was more effective promoter for PO production rate than Li because of relatively higher PO selectivity. It increased from 1.99 to 8.87 µmol/g cat. min on K-promoted catalyst whereas it was 6.39 µmol/g cat. min. over Li-promoted catalyst at 350°C. PO productivity reached to 9.13 µmol/g cat. min. at 60.00 µmol/g cat. min. consumption ratio for 0.1 wt%K-0.5%Cu/SiO_2 catalyst. Further increase in the promoter amount diminished both consumption and production rates. However the highest PO selectivity was determined at 0.25 wt% K (K/Cu=0.5) modification as 19.80% at 300 °C and 16.69% at 350 °C.

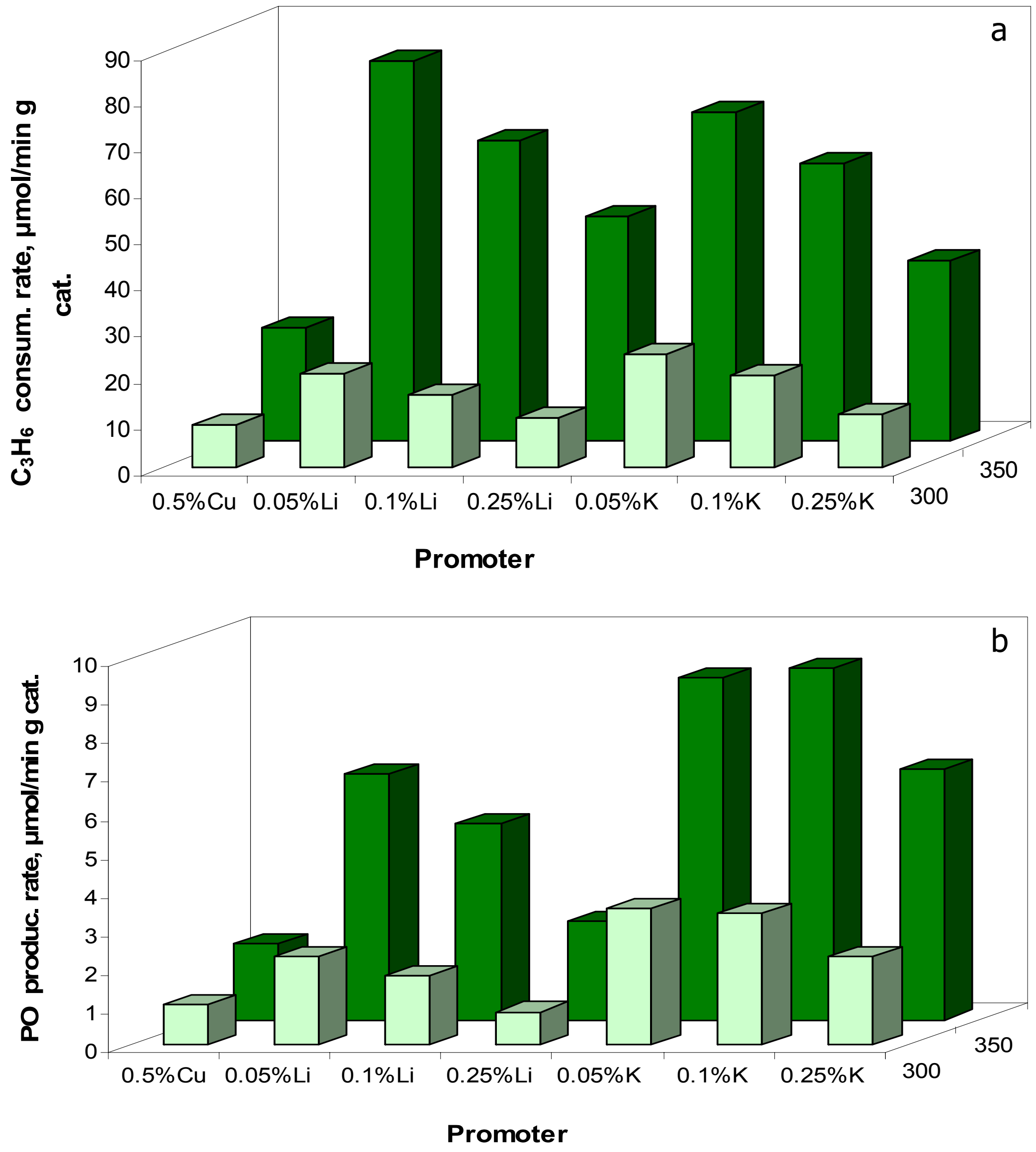


Figure 4.18 a) Overall consumption and b) PO production rate of K and Li-promoted 0.5%Cu/SiO_2 catalyst at 300 and 350 °C

The influence of K-promoter on the other oxygenated product was depicted in Table 4.4 with respect to promoter amount. The main product for unpromoted catalyst was PaL+AC and then CO_2 and PO. The amount of AD and AT could be negligible. The increase in the PO selectivity with the addition of K between 0.05%-0.25wt% correlated with a decrease in the selectivity to PaL+AC and other oxygenated products. Besides K promoted not only PO selectivity but also CO_2 selectivity however an enhancement in PO selectivity was partially more significant than CO_2. With an increase in K amount, propylene conversion quenched from 0.55% to 0.26% at a reaction temperature of 300 °C.

Table 4.4. Promoter effect of K on selectivity of reaction products for 0.5%Cu/SiO_2 catalyst at 300 °C

Promoters	Conv.	Selectivity (%)				
(%)	(%)	PO	PaL+AC	AT	CO2	AD
0	0.21	11.04	66.22	4.01	18.00	1.00
0.05	0.55	14.49	63.52	1.94	19.53	0.52
0.10	0.47	17.04	60.24	1.37	20.94	0.41
0.25	0.26	19.80	55.55	1.10	23.19	0.37

The same amount of K and Li were also loaded into the 1 wt% and 2 wt% Cu/SiO_2 catalysts. Despite the selectivity to PO diminished with the further amount of Cu, the effect of promoter was investigated for these catalysts. The maximum PO productivity was reached for 0.25 wt%K-2%Cu/SiO_2 catalyst as 10.99 µmol/g cat. min. at 139.12 µmol/g cat. min. consumption rate at 350 °C.

In the third screening experiment, the effect of feed gas composition was investigated at all temperatures between 0.1-1.3. It was observed that when the ratio of propylene to oxygen was 0.1, the consumption rate showed maximum (21.00 µmol/g cat. min.) and diminished to 9.28 µmol/g cat. min. with further increase of propylene content in the feedstock and approximately remained constant above that point. In spite of the lower propylene consumption, PO production reached maximum at propylene rich atmosphere (0.78 to 1.18. µmol/g cat. min.). It can be concluded from these results that the proper feed gas ratio for Cu/SiO_2 catalysts is 1.0-1.3 as illustrated in Figure 4.19. However when 0.5 and 1.0 gas ratios were compared, it was observed that 0.5 gas ratio is the best for high PO formation in the second screening experiment.

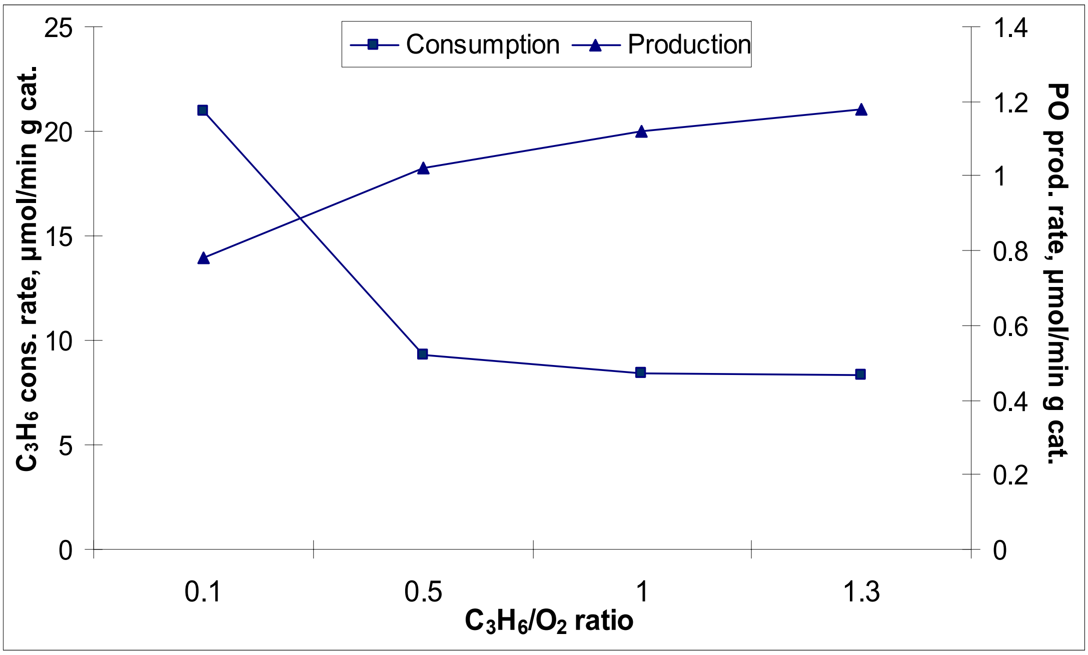


Figure 4.19 The effect of feed gas ratio over catalytic performance for 0.5%Cu-SiO_2 catalyst

The appropriate feed gas ratio for un-promoted catalyst was determined as 1.0-1.3. However after modification of catalyst with K, propylene consumption decreased continuously with an increase in C_3H_6/O_2 ratio as displayed in Figure 4.20. Besides PO production increased sharply (5.79 to 9.42 μmol/g cat. min.) when the ratio of propylene to oxygen increased to 0.5 while propylene consumption rate fell from 90.29 to 79.65 μmol/g cat. min. Further increase in propylene ratio decreased both conversion and the selectivity to PO. When the ratio was increased from 0.5 to 1.0, the consumption decreased from 79.65 to 58.35 with a slightly decrease in selectivity.

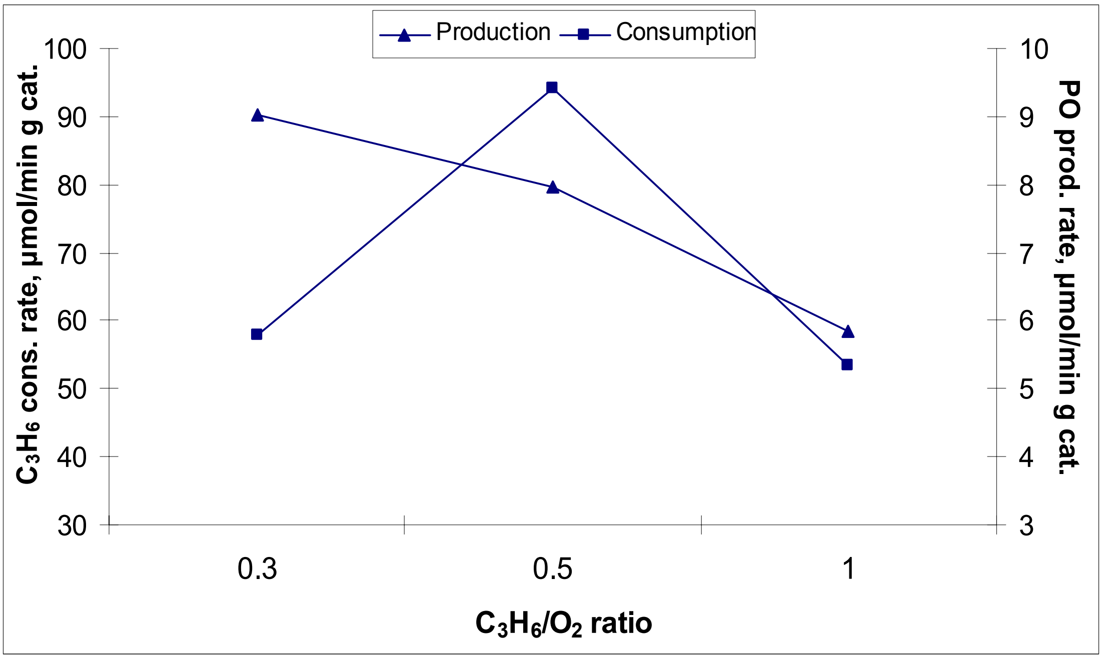


Figure 4.20 The effect of feed gas ratio over catalytic performance for 1%Cu-0.1%K-SiO_2 catalyst

After screening the low surface area silica based catalysts, the catalytic activity tests were performed for high surface area silica (m-SiO_2) based catalysts. First, the screening test was performed over un-modified catalysts. On contrary to the SiO_2 supported catalysts, propylene consumption rate increased with Cu loading and reached to 653.39 μmol/g cat. min. for 10% Cu/m-SiO_2 catalyst at 350 °C with low PO selectivity (2.49%). It was 79.65 μmol/g cat. min. for 2%Cu/SiO_2 catalyst at the same reaction temperature and relatively higher PO selectivity (5.10%). However, PO selectivity reached maximum value for the 2%Cu loading at all reaction temperatures and a further increase in the loading decreased PO selectivity for low silica with surface area.

After seeing the effect of promoter for the low surface area silica based catalysts, the same promoters were loaded into the Cu/m-SiO_2 catalysts in the same amount (0.05-0.25%). The first screening test showed that all the promoter had very closed enhancement effect on PO yield at all ratios, but it was more on K and Li-promoted catalysts as depicted in Figure 4.21 a and b. Lithium promoted catalysts gave better PO yield because of partially higher PO selectivities. The effect of Li should be investigated more detail in the further study. However in this group more attention was given to K promoted Cu/m-SiO_2 catalysts to find out the optimum K/Cu ratio. For this purpose K/Cu ratio was changed in the interval of 0.1-1.0 for 1-10wt% Cu containing catalysts.

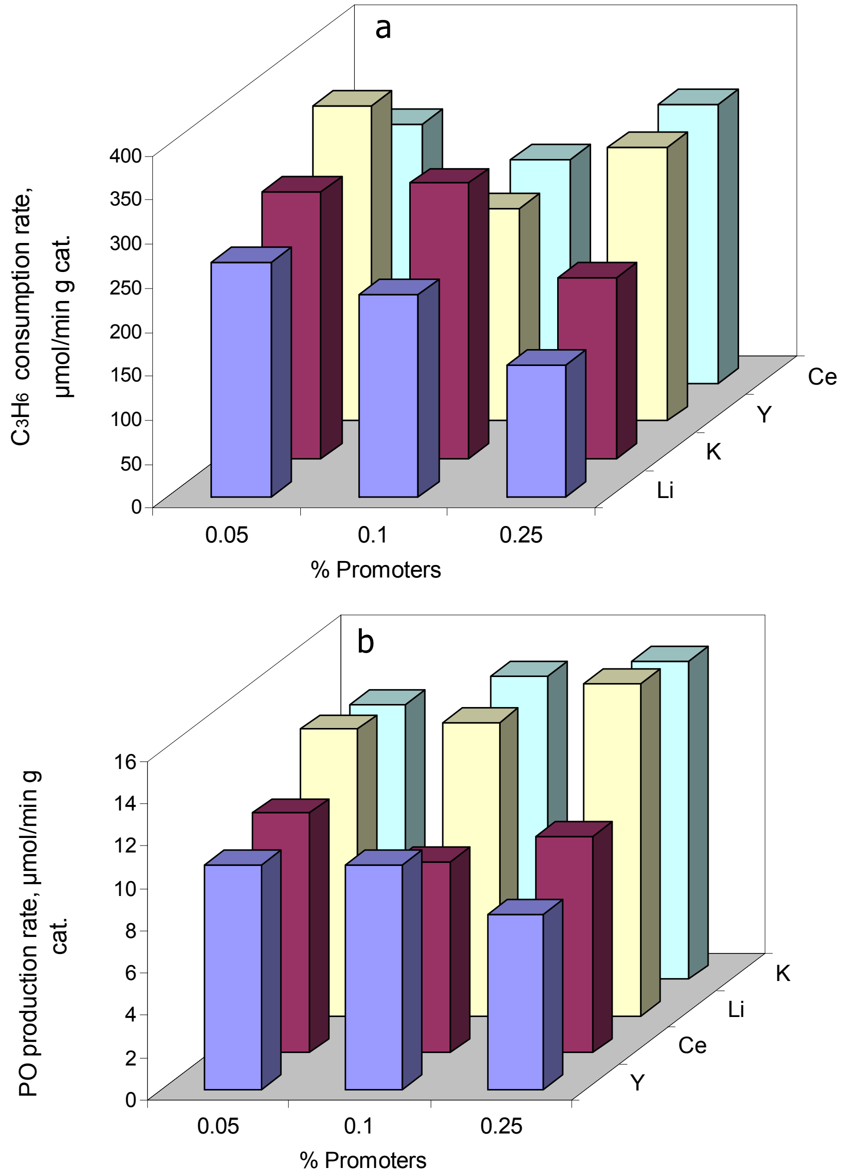
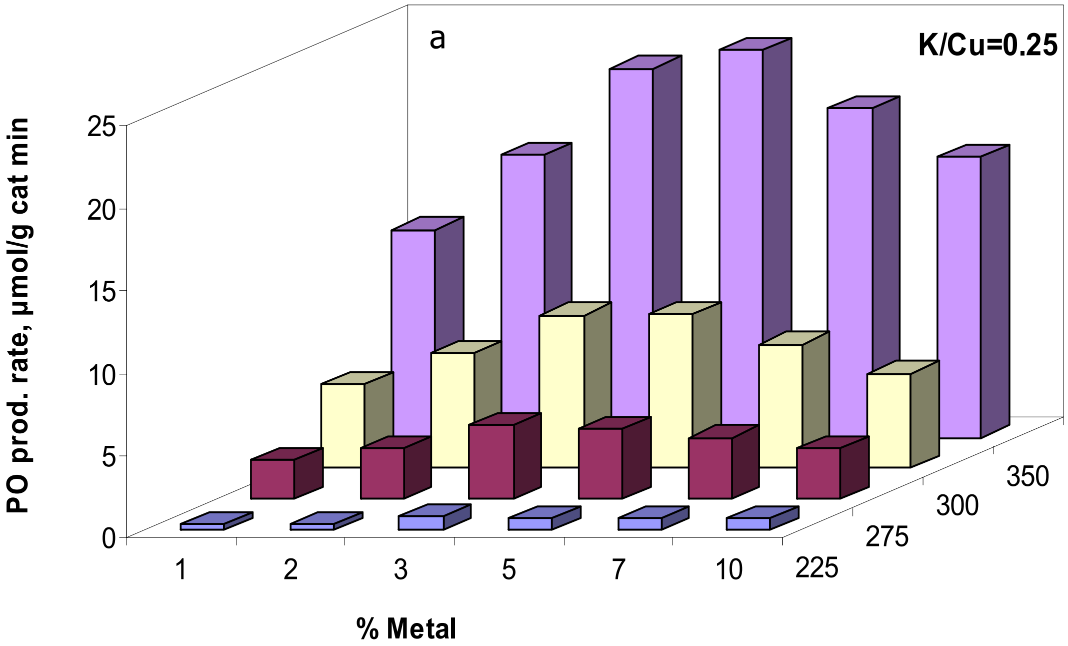


Figure 4.21 a) Overall consumption and b) PO production rate 1.0 %Cu/m-SiO_2 catalyst at 350 °C

The addition of K for all Cu ratio lowered catalytic performance but PO selectivity was significantly improved with modification. The improvement in PO production was significant at the K/Cu ratio of 0.5 and 0.75. The effect of

K loading was given in Figure 4.22 a-d. The PO rate showed a dome shape of activity versus metal loading at each temperature and this was easily seen at 350 ^{o}C and K/Cu ratio of 0.25 and 0.5. When K/Cu ratio was 0.25, the highest PO production rate was obtained for 5% Cu catalyst as 23.52 μmol/g cat. min. and then 22.40 μmol/g cat. min. for 3%Cu catalyst.

When K/Cu=0.5, the maximum PO productivity was reached at 5 and 7% metal loadings and then PO production dropped due to noticeable decrease in propylene conversion for 10%Cu-m-SiO_2 catalyst as seen in Fig. 22 b. The PO production rate of 5%Cu catalyst increased from 14.39 μmol/g cat. min (13.77% conversion with 2.45% selectivity) to 23.61 μmol/g cat. min (5.92% with 9.18% respectively) with 0.5 K/Cu modification at 350°C. However, it changed from 16.26 μmol/g cat. min. (15.04% conversion with 2.49% selectivity) to 16.90 μmol/g cat. min. (3.46% with 11.47% respectively) for 10%Cu catalysts at the same modification. The effect of further amount of K at 0.75 and 1.0 ratios showed different tendency with respect to Cu content. 2% Cu catalyst had the lowest PO production rate for both ratios because it reached the maximum value (19.70 μmol/g cat. min.) at K/Cu=0.25.



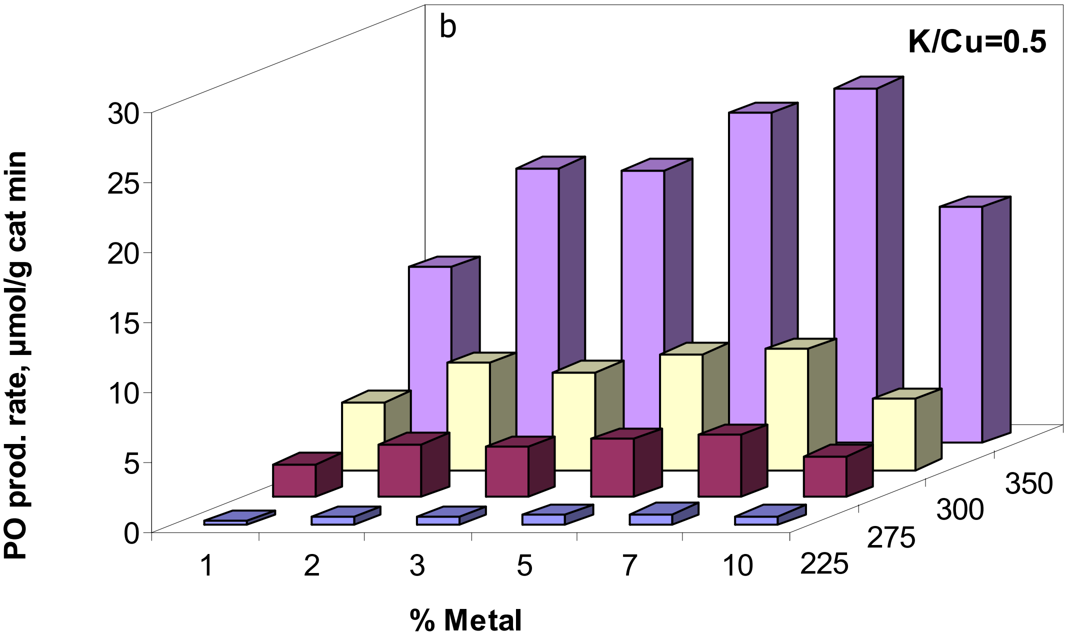
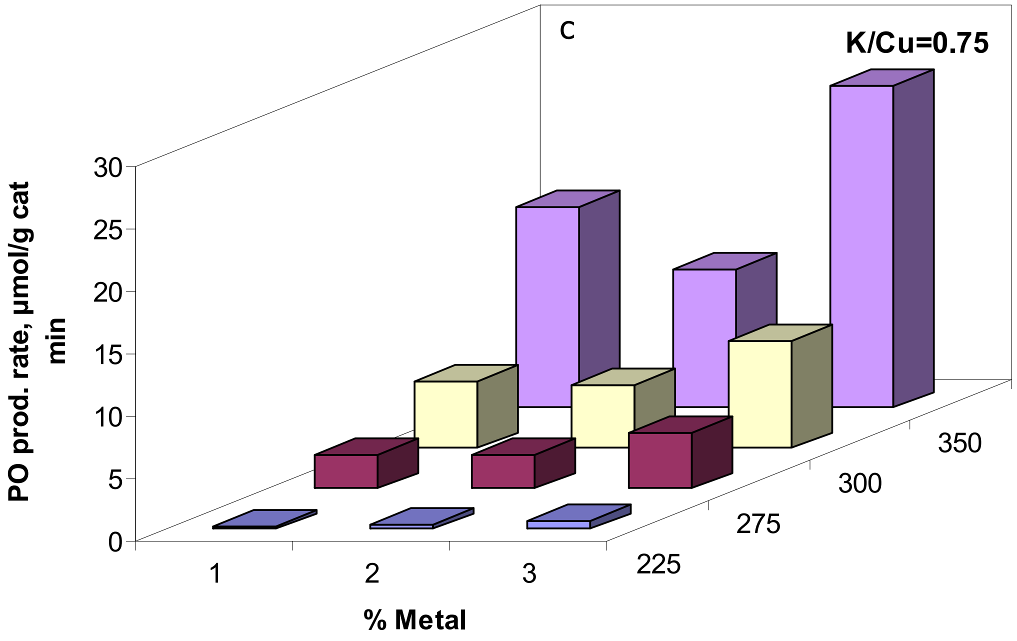


Figure 4.22 PO production rate for modified Cu-m-SiO_2 catalysts at a K/Cu ratio of a) 0.25, b) 0.5, c) 0.75 and d)1.0



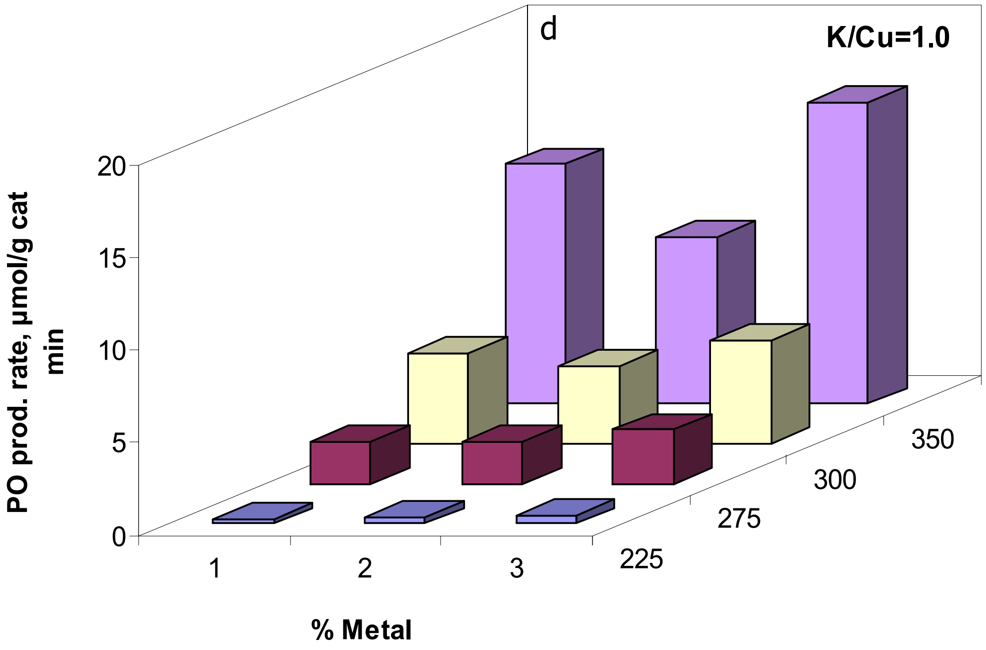


Figure 4.22 PO production rate for modified Cu-m-SiO_2 catalysts at a K/Cu ratio of a) 0.25, b) 0.5, c) 0.75 and d)1.0 (continue)

Among all the catalysts, the maximum PO production rate was reached for 3%Cu catalyst at a reaction temperature of 350 °C and by 0.75 K/Cu modification. The promoter effect of K over PO production and overall consumption rate together with all oxygenated products were summarized in Figure 4.23 and Table 4.5 for 3%Cu-m-SiO_2 catalyst.

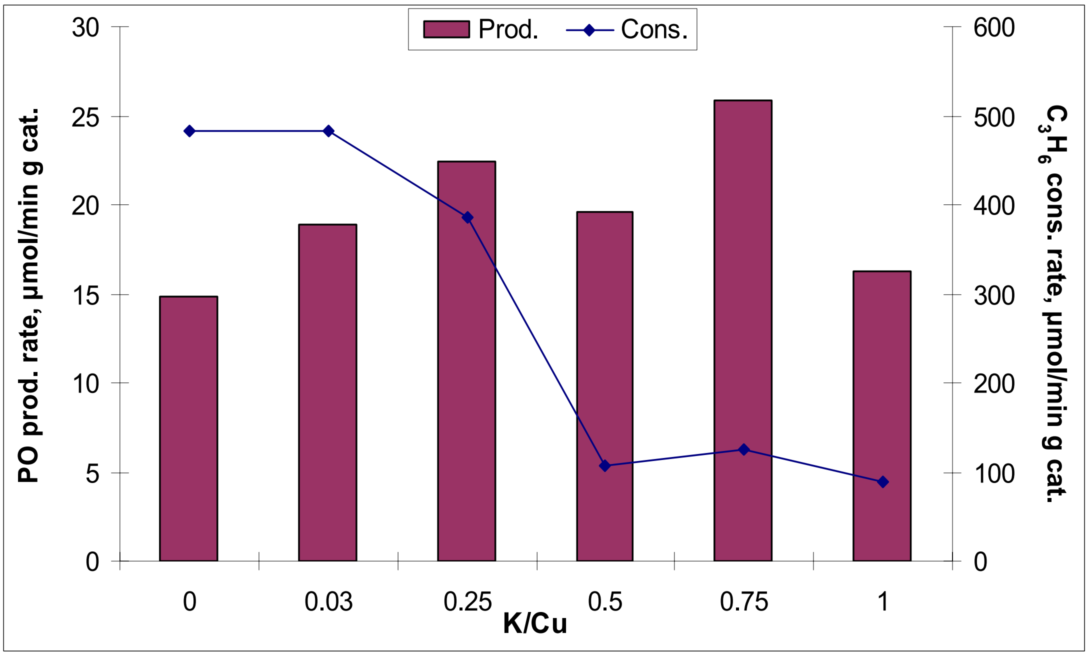


Figure 4.23 PO production and propylene consumption rate for promoted 3.0%Cu/m-SiO_2 catalyst at 350°C

As seen in Figure 4.23, there was a sharp decrease in consumption rate especially above 0.25 K/Cu ratio. Potassium is known as a basic metal and addition of it into the Cu catalysts probably neutralize the acidic sites of catalyst. Above that point the consumption rate approximately stayed constant. Despite this noticeable decrease in propylene consumption, PO production rate showed two maxima; one at 0.25 and the other one at 0.75

K/Cu ratio. The maximum value at 0.75 was due to high PO selectivity while the maximum at 0.25 was due to high propylene consumption. The PO production rate was 22.40 μmol/g cat. min. (5.80% selec. at 8.89% conv.) at 0.25 modification and 25.82 μmol/g cat. min. (20.49% selec. at 2.89% conv.) at 0.75 modification.

The epoxidation of propylene to PO with Cu-based catalysts reported until now is very limited. The first results reported by Lu as 0.17 mmol $g^{-1}h^{-1}$ over a NaCl-modified $VCe_{1-x}Cu_x$ oxide catalyst. Vaughen reported that Cu/SiO_2 without NaCl catalyst gave 0.014 mmol $g^{-1}h^{-1}$ while Chu obtained 2.1 mmol $g^{-1}h^{-1}$ PO formation rate over halogen-free K^+-modified CuO_x/SBA-15. PO formation rate reached to 2.50 mmol $g^{-1}h^{-1}$ finally in Su study (Lu et al., 2002; Vaughan et al., 2005; Chu et al., 2006; Su et al., 2009). In this study the maximum PO formation rate was obtained as 1.55 mmol $g^{-1}h^{-1}$ (25.82 μmol/g cat. min.) over 3%Cu/m-SiO_2 catalyst modified at a K/Cu ratio of 0.75.

Table 4.5 lists the product distributions as a function of K/Cu ratio for 3%Cu/m-SiO_2. Unpromoted Cu catalyst generally gave PaL+AC and CO_2 as the main oxygenated products. However, the addition of K caused inhibition of PaL+AC production while increasing the PO selectivity and also small change was observed for other reaction products.

In addition to the testing at different reaction temperatures, C_3H_6/O_2 molar gas ratio was also changed from 0.3 to 1.3 to determine an appropriate reactant gas ratio leading to a high PO production rate. The obtained results showed that like promoted Cu/SiO_2 catalysts an optimum gas ratio was to be 0.5 for Cu/m-SiO_2 catalysts at all temperatures.

Table 4.5 Promoter effect of K on selectivity of reaction products for 3%Cu/m-SiO_2 catalyst at 350 °C

K/Cu	Conv. (%)	Selectivity (%)				
		PO	PaL+AC	AT	CO_2	AD
0	11.12	3.1	55.7	1.0	39.9	0.4
0.03	11.34	3.9	52.7	0.9	42.1	0.3
0.25	8.89	5.8	53.6	0.7	39.5	0.4
0.5	2.48	18.2	42.2	0.5	38.9	0.3
0.75	2.90	20.5	40.8	0.6	37.7	0.3
1.0	2.10	18.2	43.2	0.5	37.8	0.3

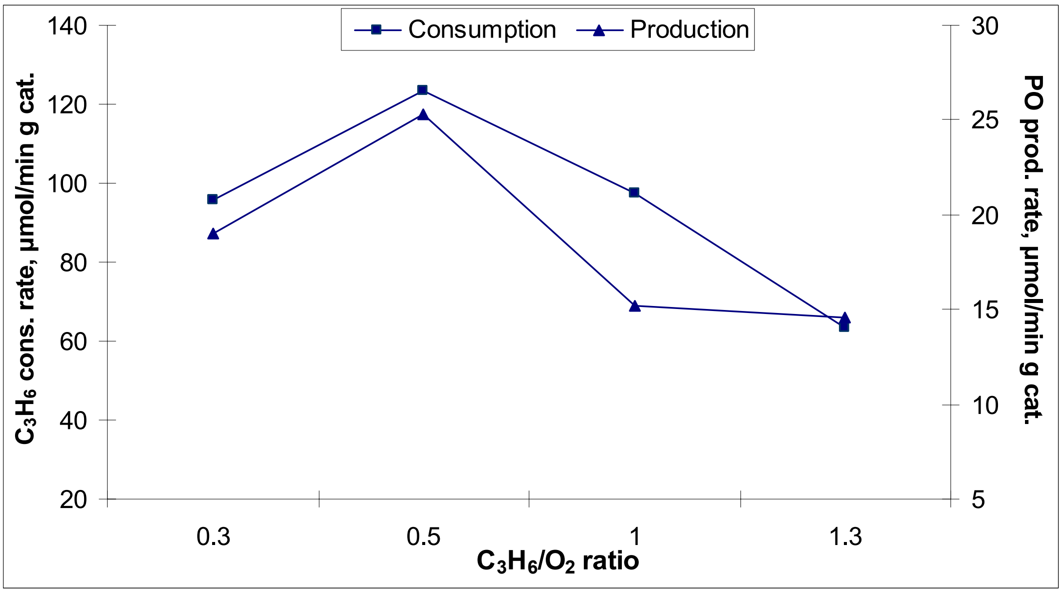


Figure 4.24 The effect of feed gas ratio over catalytic performance for 3%Cu-2.25%K-m-SiO_2 catalyst

The influence of the presence of K was investigated by UV-vis, NH_3-TPD and IR analysis techniques as reported in the literature. Wang et al. observed that CuO_x clusters became smaller with modification of K and it decreased both strength and amount of acid sites over the catalysts (Wang et al., 2008). Similarly, Su et al. concluded that addition of K or other modifier has no effect on activation of the double bond of propylene while suppressing the reactivity of lattice oxygen species by changing acidity of catalyst (Su et al., 2009).

In this study, the promoted and un-promoted catalysts were first examined by XRD technique to determine the crystalline phases of the metal. The results showed that both high and low surface area silicas were amorphous and also any diffraction peaks corresponding to copper or copper oxides was observed when these silicas were loaded at different copper amounts as shown previously in Figure 4.2. This indicates that copper/copper oxide crystallite size is less than 5 nm. In fact, these findings were confirmed with SEM and TEM measurements as shown in Figures 4.25 and 4.26 a and b. Instead of lower resolution compared to TEM analysis, SEM technique was performed to image the surface of 3%Cu/m-SiO_2, 3%Cu-2.25%K/m-SiO_2 catalysts.

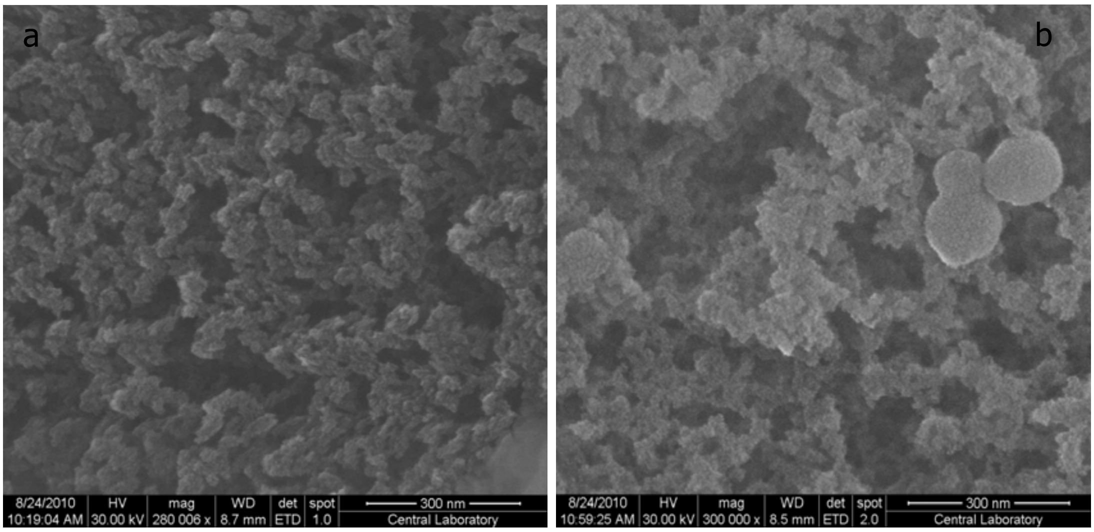


Figure 4.25. SEM images for a) 3%Cu/m-SiO_2, b) 3%Cu-2.25%K/m-SiO_2 catalysts

As seen in the images there was no evidence in the microscopy of the formation of any particles on the surface. In SEM microscopy only seen was porous structure of supports. However there was some big powder group over surface for promoted catalyst and it might be the more sensitive structure of catalyst against the humidity in air. Any trace of copper oxide particle in SEM was observed but they were detected by EDX analysis. The EDX analysis results were given in Appendix E.

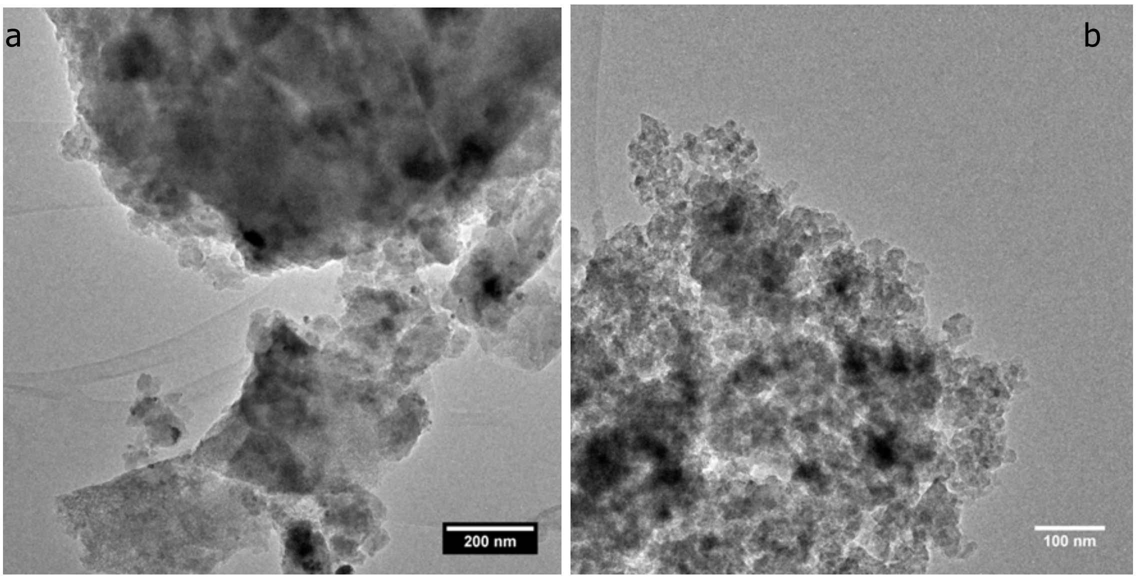


Figure 4.26 TEM image of a)1%Cu-SiO_2 and b)3%Cu-m-SiO_2 catalysts

In addition to the XRD and SEM results, there was no sufficient contrast between metal/metal oxide particles and silica supports in TEM image which may be due to well-dispersed particles. When the TEM image of 1%Cu-SiO_2 was investigated closely again there is no fringe belongings to any crystalline phase. Especially 3%Cu-m-SiO_2 catalyst consist of uniform fine powder with sponge-like structure and containing highly dispersed Cu in SiO_2 matrix. It can be proposed that the structure is amorphous SiO_2 or Cu-silicate. The particle size of loaded Cu is smaller than the XRD and TEM detection limits. An addition of KNO_3 did not result in the agglomeration of Cu particles as seen in Figure 4.27 a and b.

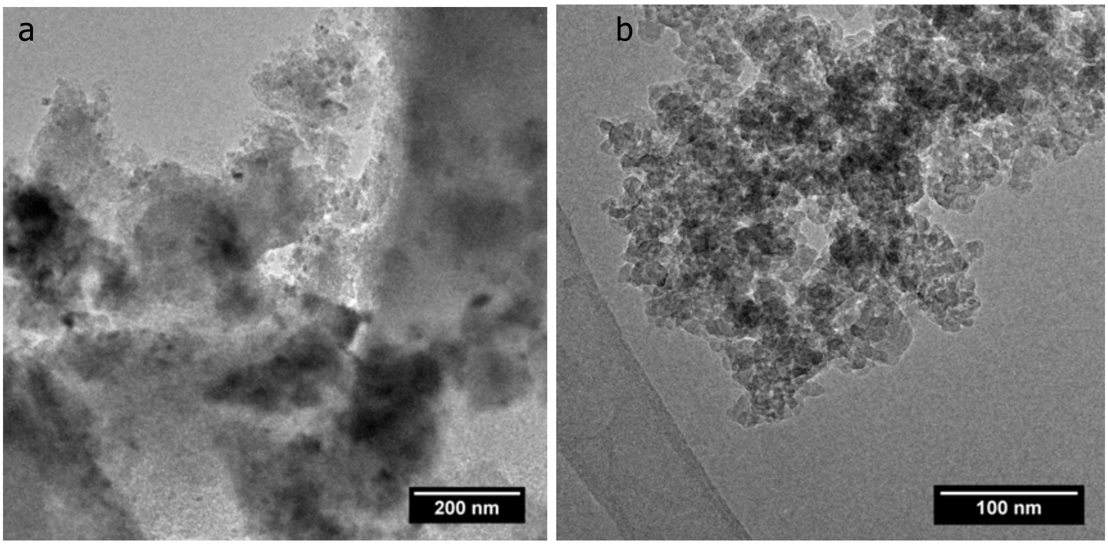


Figure 4.27 TEM image of a)1%Cu-0.1%K-SiO_2 and b) 3%Cu-2.25%K m-SiO_2 catalysts

To observe the difference between promoted and un-promoted catalyst, a XPS analysis was again performed on the fresh catalysts. The oxidation state of un-promoted Cu and K-promoted Cu catalysts (fresh 1%Cu/SiO_2, 1%Cu-0.1%K/SiO_2 and 3%Cu/m-SiO_2, 3%Cu-2.25%K/m-SiO_2) were analyzed and shown in Figure 4.28. The spectra of catalysts were calibrated by taking Si2p peak at 103.4 eV. The measured binding energies of un-promoted and 0.1wt%K promoted 1%Cu catalyst are the same as 935.6 eV. For 3%Cu/m-SiO_2 and 2.25%K promoted 3%Cu/m-SiO_2 catalysts, they are 935.9 and 935.8 eV, respectively. These binding energies indicate that Cu stays as isolated-ionic Cu^+ or Cu^o species over both silicas with and without the addition of K. Unfortunately, there were no peaks or Auger photoelectrons to distinguish the copper oxidation states due to low photoelectron counts for low loadings, 1% and 3% Cu.

Similarly, Takezawa et al. reported that for Cu/SiO_2 catalysts, monovalent copper was present on the catalysts with low copper loadings, such as 1%

(Takezawa and Kobayashi, 1982). Also, it is known that XPS is sensitive to depth of 2-10 nm. The reason why only high degeneracy $3p_{3/2}$ peak is barely visible in Figure 4.28 could be explained by the well dispersed Cu species. In fact, XRD and TEM results also indicated that copper crystallite size must be less than 5 nm. Besides, it could be concluded that the oxidation state and charge density of Cu did not change with K modification at low or high amounts. Therefore, the contribution of K over the structure and electronic properties of catalysts must be investigated by other characterization techniques such as NH_3-TPD, IR vs.

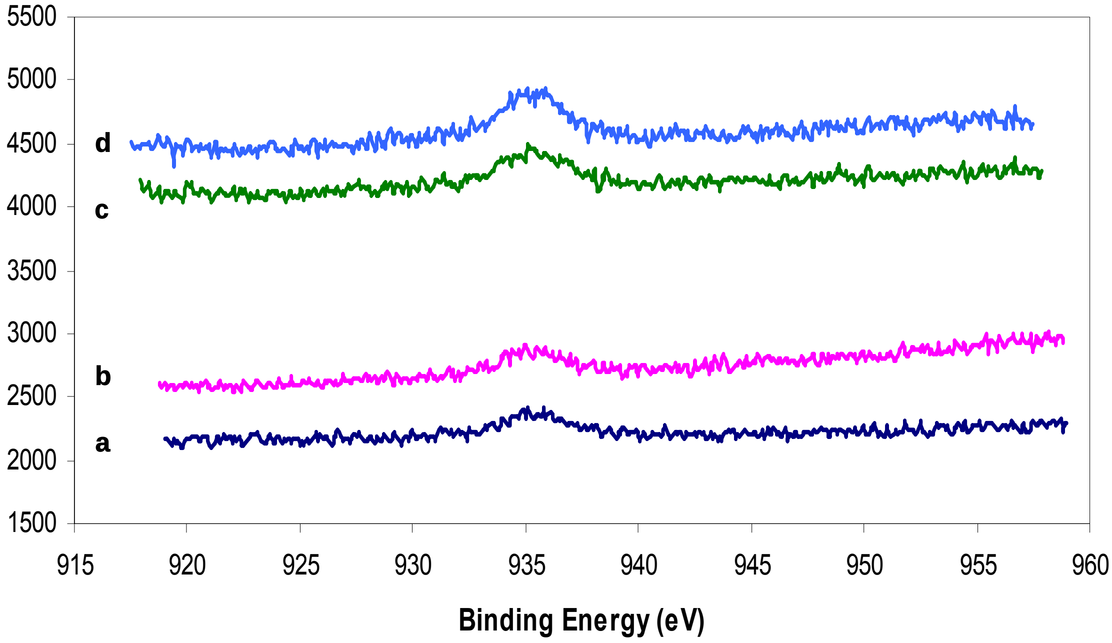


Figure 4.28 Copper 2p XPS spectra of (a) 1%Cu-SiO_2 (b) 1%Cu-0.1%K-SiO_2 (c) 3%Cu-m-SiO_2 and (d) 3%Cu-2.25%K-m-SiO_2 catalysts

To explain the effect of addition of K over the temperature dependence of propylene consumption and PO production, Arrhenius plots were given in Figure 4.29. The activation energy of un-promoted 3% Cu catalyst (92 kJ mol^{-1}) was higher than 2.25 wt% K promoted catalyst (71 kJ mol^{-1}). The obtained activation energies for overall consumption rate of modified and un-modified catalysts are the same as that obtained for CuO_x/SBA-15 catalyst by Wang et al. (Wang et al., 2008). However, the addition of K promoted PO production rate and an activation energy of two catalysts were approximately the same (~75 kJ mol^{-1}).

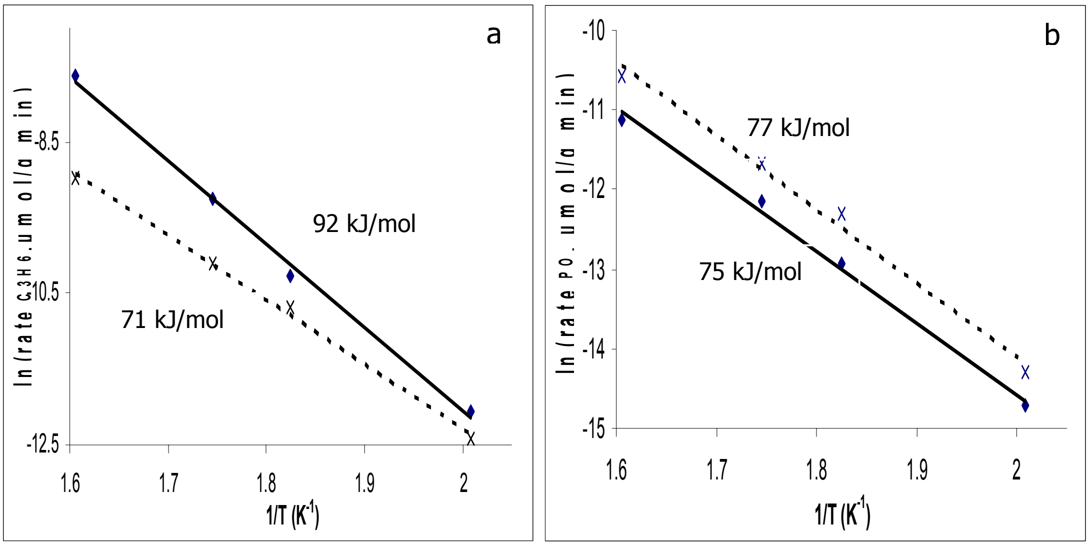


Figure 4.29 Arrhenius plots for a) oxidation of propylene and b) PO production over 3%Cu-m-SiO_2 (solid line) and 2.25%K-3%Cu-m-SiO_2 (dashed line) catalysts

After seeing the effect of promoter on silica supported Cu catalysts, K was added into the TiO_2 supported Cu catalysts. Among all the catalysts tested in the second group the maximum propylene consumption rate (418.90 μmol/g cat. min.) was obtained for 20%Cu catalyst. K ratio was changed from 0.1 to 1.0 at 0.2wt% interval. An addition of K decreased propylene consumption rate sharply while PO selectivity reached 17.41% at 2.31 μmol/g cat.min.

consumption rate and a reaction temperature of 225 °C. A further increase in the reaction temperature improved combustion reaction while decreased C_3 epoxidation products especially in PaL+AC selectivity (from 48.98% to 1.43%). Besides there was a slightly decrease in selectivity to PO. The maximum PO production was obtained as 12.26 μmol/g cat.min. at 350 °C (4.35% PO selectivity at 6.76% conversion) as seen in Figure 4.30. However the expected improvement in PO productivity was not observed for Cu/TiO_2 catalyst. It was seen that lowering the acidic strength of TiO_2 with K promoted propylene epoxidation at low temperature and low amount of K (0.1 wt%) but when temperature was increased, the complete combustion reaction again took place but PO was the second reaction product with low selectivity. The promotion of the catalysts with K did not show any improvement for the catalyst which contains less than 20% Cu content.

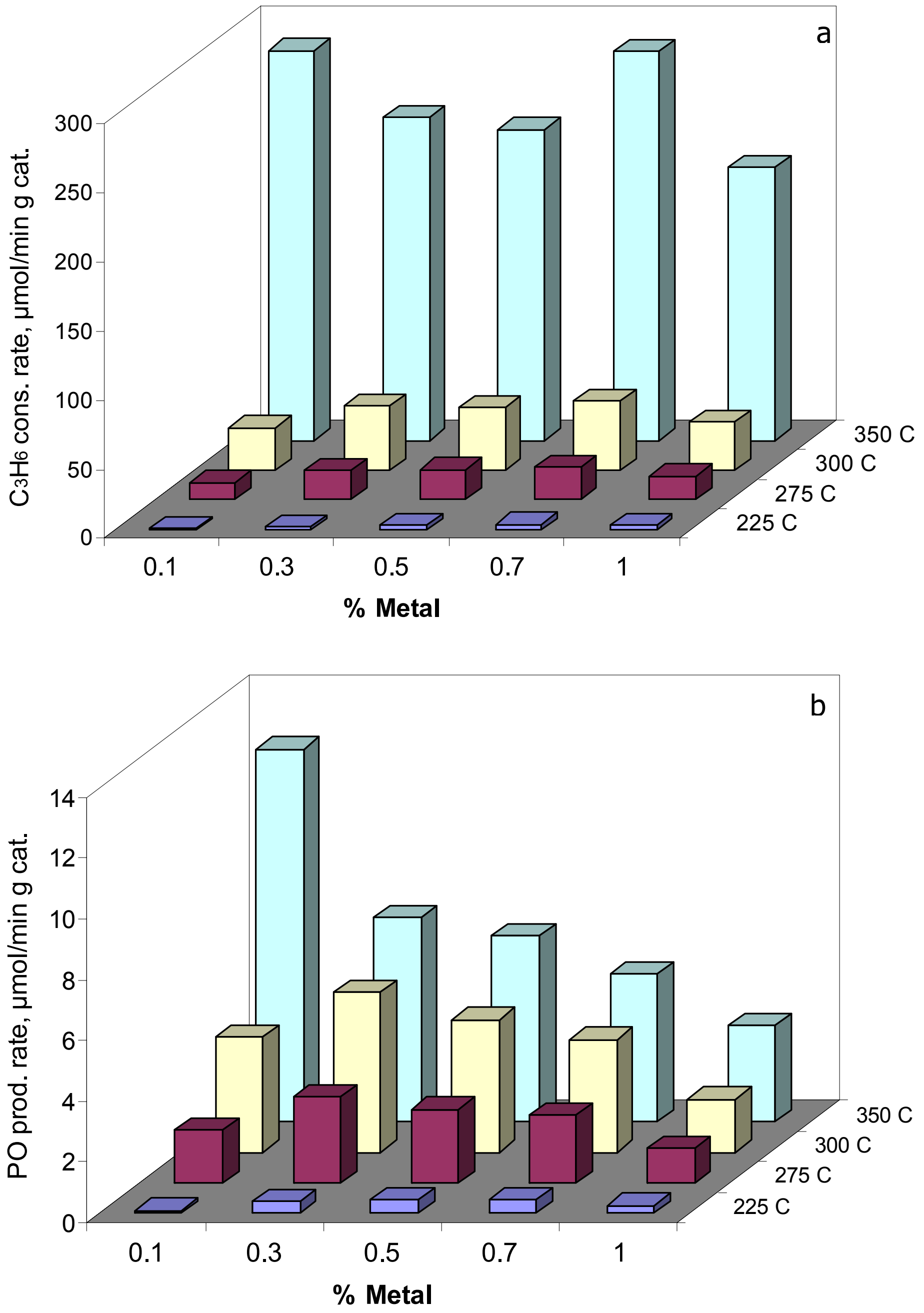
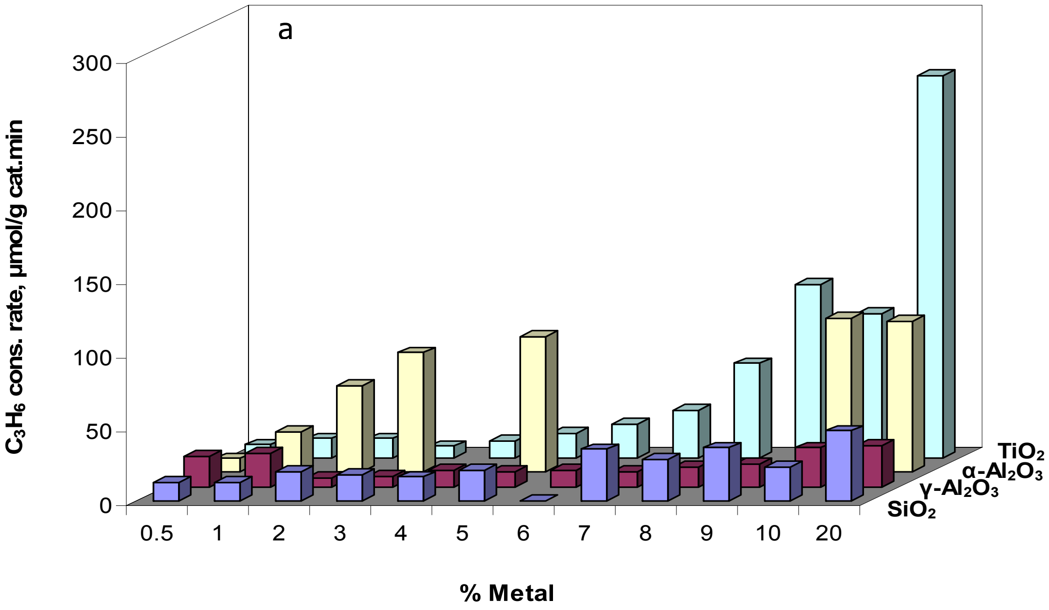


Figure 4.30 a) C_3H_6 consumption and b) PO production rate of K-promoted 20%Cu/TiO_2 catalysts

4.2.3. Supported mono-metallic Mn catalysts

In this study, the catalytic performance of the Mn over different supports synthesized by sol-gel method was tested at 300 °C and 1.0 gas ratio. The test results given in Figures 4.31 and 4.32 a and b showed that Mn catalysts generally gave low catalytic activity for propene oxidation. Only TiO_2 gave high propylene consumption because of complete oxidation reaction. 95% CO_2 formed at propylene conversion rate of 259.15 μmol/g cat.min for 20 %Mn/TiO_2. Despite of low PO selectivity, PaL+AC and AT selectivities were high at low Mn content. 53% PaL+AC and 19% AT selectivities were obtained at low consumption rate (7.94 μmol/g cat. min) for 2% Mn/TiO_2. The highest PO selectivity (4.46%) was reached over 1%Mn/m-SiO_2 at low propylene conversion (0.16%). At low Mn content generally PaL+AC formed during reaction and it decreased with loading for all support materials except for TiO_2 and γ-Al_2O_3. They catalyzed combustion reaction because of acidic sites on the surface.



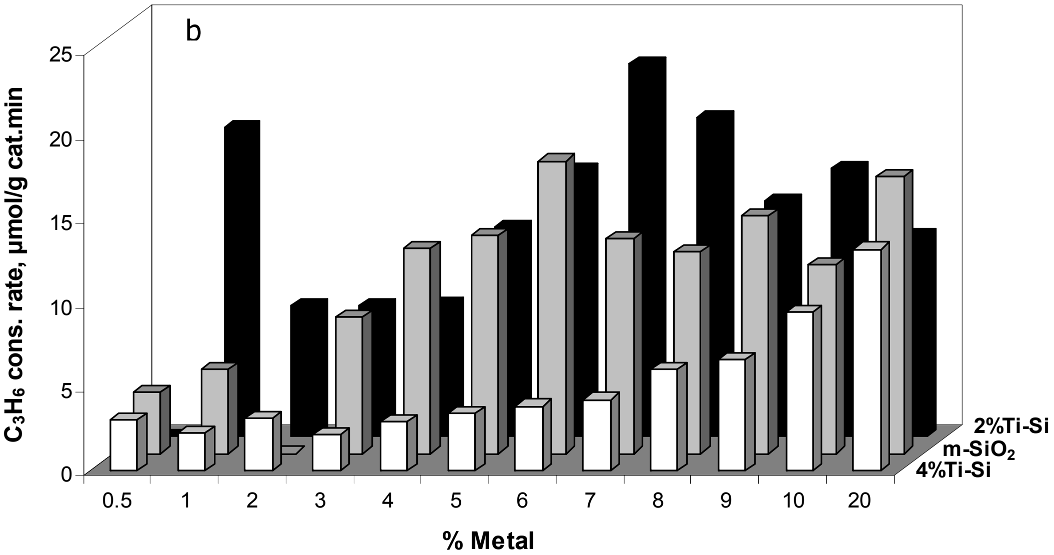
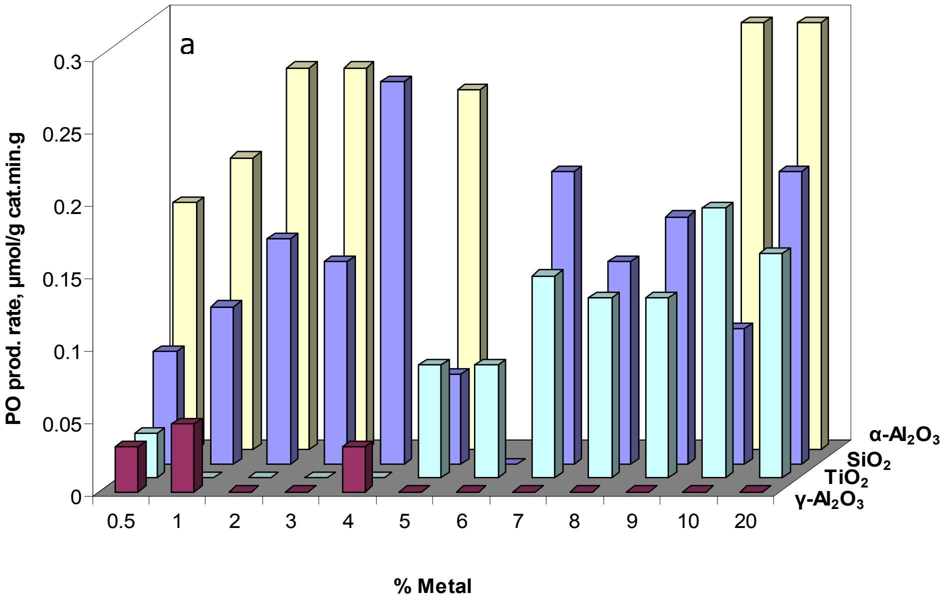


Figure 4.31 C_3H_6 consumption rate of Mn catalyst supported on a) low surface area and b) high surface area supports



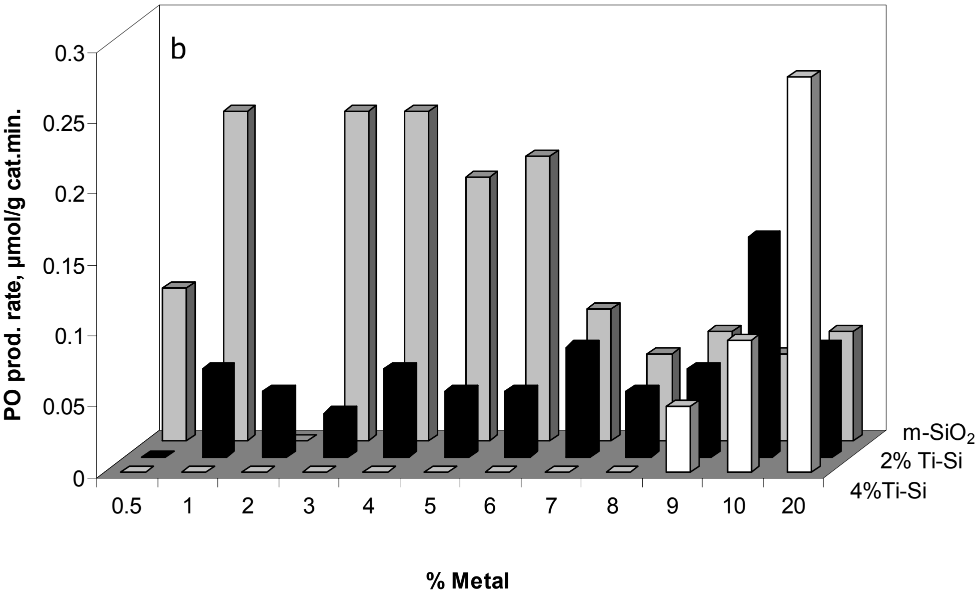


Figure 4.32 PO production rate of Mn catalyst supported on a) low surface area and b) high surface area supports

4.2.4 Bimetallic systems

4.2.4.1. Bimetallic Ag catalysts

The evaluation of the initial group of catalyst showed that PO selectivity increased with an increase in the Ag amount on the support. On contrary, an increase in the Cu amount caused a depression in both propylene conversion and selectivity. For these reason, in the second part of the study SiO_2 supported 10 wt% and 20 wt% Ag catalysts were promoted with low amount of Cu and Mn (0.5 and 1wt%) to improve the PO yield at 300 °C and 1.0 reactant gas ratio. The results were shown in Figure 4.33 a and b.

As evident from Figure 4.33, propylene conversion and PO production rate reached optimum value for Cu-promoted Ag catalysts. In the absence of Cu and Mn, the propylene consumption and PO production rate were 133.12 µmol/g cat-min. and 0.84 µmol/g cat-min. for 10% Ag/SiO_2 and 128.87 µmol/g-cat min and 0.65 µmol/g cat-min. for 20%Ag/SiO_2 respectively. It was of interest that, after addition of Cu at 0.5 and 1wt % levels, both rates increased significantly for 10%Ag/SiO_2 catalyst. When 0.5%Cu was added to the 10%Ag, C_3H_6 consumption rate and PO production increased to 212.85 µmol/g cat-min and 6.07 µmol/g cat-min. Further addition of Cu (1wt%) increased consumption rate to 149.14 µmol/g cat-min and PO production to 6.64 µmol/g cat-min. The consumption rate of propylene over 20%Ag catalyst was promoted with 0.5 and 1 wt%Cu and decreased from 128.87 to 109.14 and 56.72 µmol/g cat.min. respectively but it led to an improvement toward the PO selectivity by a factor of 4 to 7 as compared with an unpromoted Ag catalyst and by a factor of ~2 as compared to single Cu catalyst at almost the same conversion level.

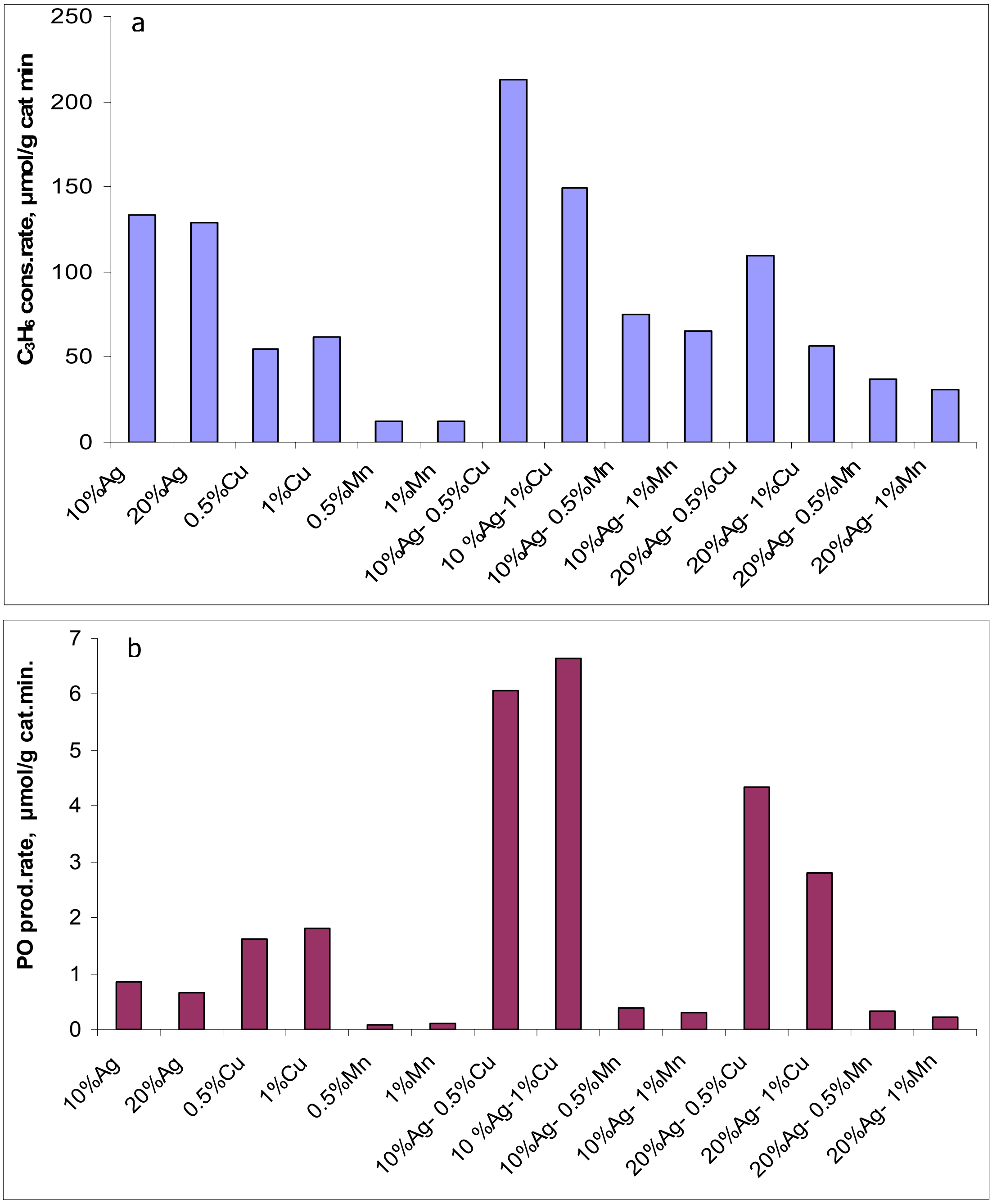


Figure 4.33. a) Propylene conversion and b) PO selectivity for Ag-Cu&Mn/SiO_2 catalysts

10%Ag/SiO_2 catalyst promoted with 0.5 and 1wt% Mn did not show neither better PO production nor propylene consumption rate. Although slightly better PO selectivities were observed over the 0.5%Mn-20%Ag/SiO_2 and 1%Mn-20%Ag/SiO_2 catalysts, these catalysts showed remarkably low propylene consumption (~45 µmol/g cat. min).

A synergetic effect of bimetallic Ag catalysts was clearly illustrated on low and high consumption–production graphs as seen in Figure 4.34 a and b. When propylene consumption rate was between 10-100 µmol/g cat. min (Fig. 4.34a) and 130-220 µmol/g cat-min (Fig. 4.34b), the highest selectivity toward PO was obtained for 20%Ag-0.5%Cu as 4.33 µmol/g cat-min and as 6.64 µmol/g cat. min. for 10%Ag-1%Cu catalyst.

The performance of monolith-supported Ag and Cu-Ag bimetallic catalysts at different ratio were investigated by Jankowiak et al. in epoxidation of ethylene to ethylene oxide. The results they obtained showed that Cu-Ag bimetallic catalysts decrease activation energy by 1-2 kcal/mol relative to pure Ag catalysts (Jankowiak and Barteau 2005 a and b).

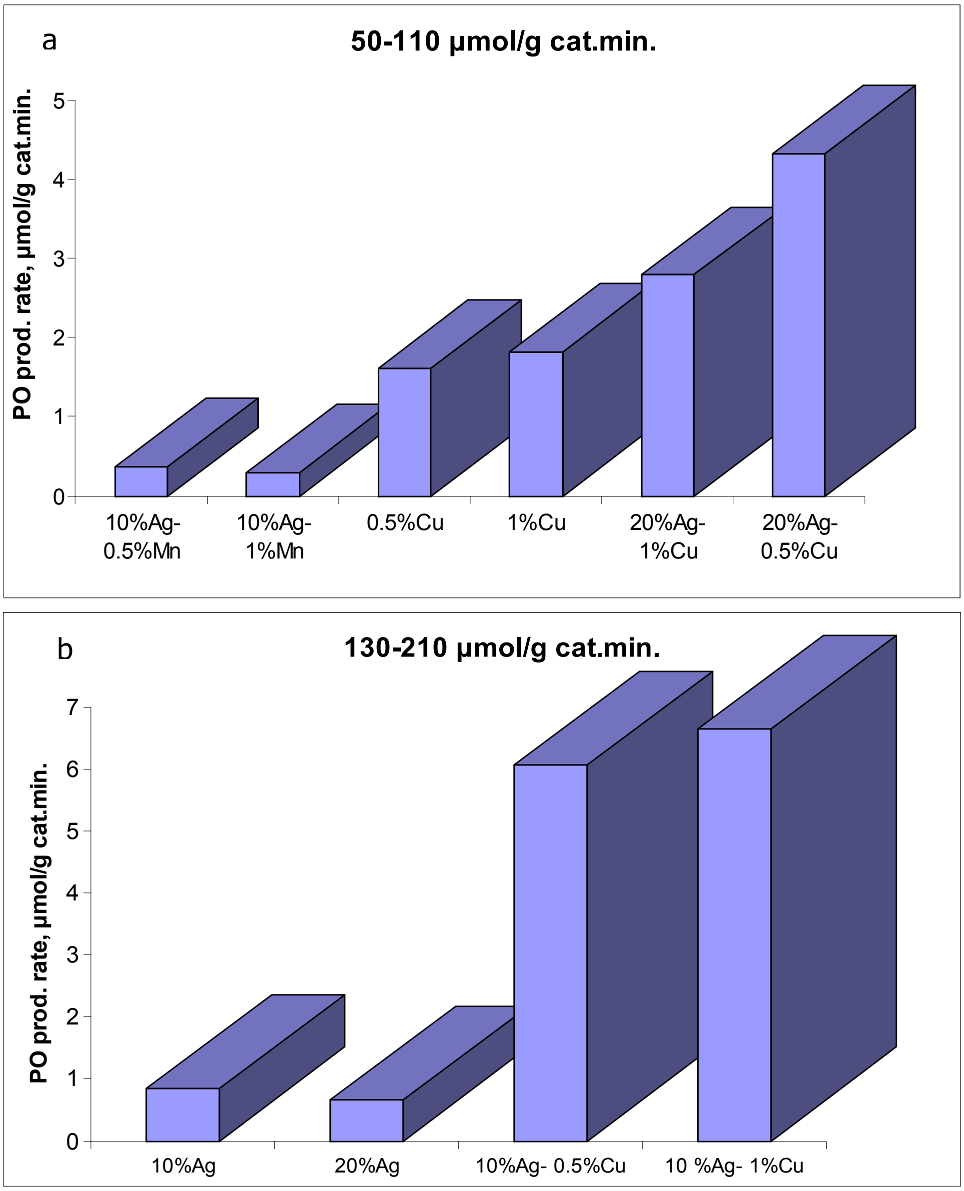


Figure 4.34. PO production of Ag&Cu and Ag&Mn/SiO_2 catalysts at the same consumption rate a) 50-110 and b) 130-210 µmol/g cat. min.

After an increase was observed in catalytic activity over Ag-based catalyst by modification with low amount of Cu, it was continued to modified Ag catalyst with different promoters such as Li, Ce, Mo and also Cu to investigated the effect of different gas ratio and metal amounts in the later part of the study.

In third screening test Cu-Ag and other catalysts were screened at 300 °C and C_3H_6/O_2=0.5 gas ratio but they were tested at a reactant gas ratio of 1.0 in the second group at the same reaction temperature. According to the obtained results, 20% Ag catalyst gave slightly better PO productivity at the low propylene consumption rate when C_3H_6/O_2 equal to 0.5. Therefore the catalytic screening tests were performed at 0.5 gas ratio. The obtained results were summarized in Figure 4.35 a and b at 300 °C. The consumption rate obtained for 6-9% Ag catalysts were much closed to each other (230-310 μmol/g cat. min.). Besides PO productivity was again high for the catalysts containg Ag less than 10wt%. However the maximum PO rate (15.71 μmol/g cat. min.) was obtained for 9%Ag-1%Cu catalyst. Further increase in the metal loading caused a decrease in the consumption rate accordingly in PO production. Despite this ratio, Ag-based catalysts with the presence of the Cu generally gave high CO_2 as a main product.

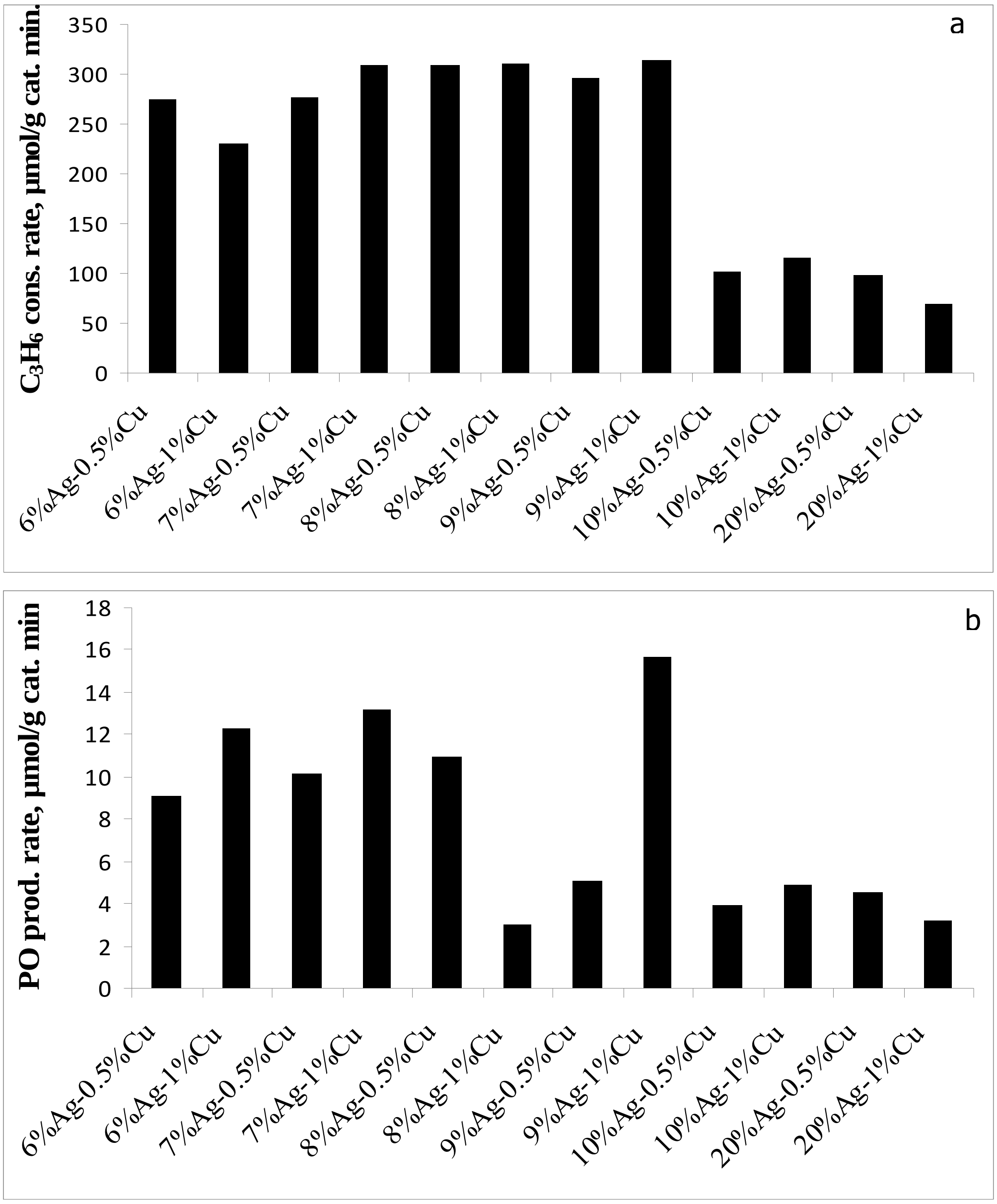


Figure 4.35 a) C_3H_6 consumption and b) PO production rate for Cu-Ag/SiO_2 bimetallic system

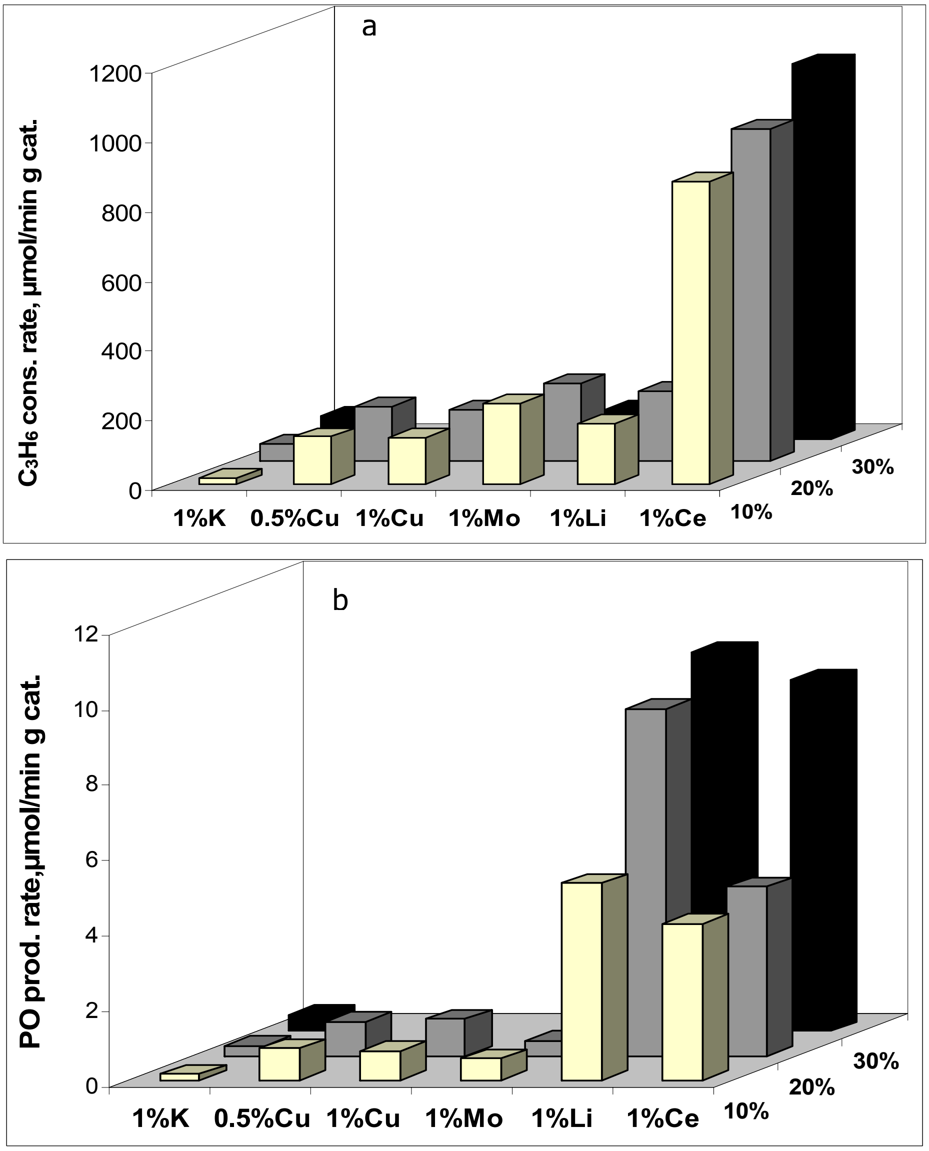


Figure 4.36. a) C_3H_6 consumption and b) PO production rate for promoted Ag/α-Al_2O_3 catalysts at 350°C

Ag metal was also loaded on commercial α-Al_2O_3 support and modified with Cu, Li, Ce and Mo metals to enhance catalytic activity. For this purpose 10, 20 and 30% Ag catalysts were prepared and modified with 1wt% of Ce, Li Cu and Mo metals. Among all metals, Li gave the better PO productivity at all temperatures and Ag amounts. PO production rate reached 10.04 µmol/g cat. min. for 30%Ag-1%Li/α-Al_2O_3 catalyst at 243.64 µmol/g cat. min. consumption rate and at a reaction temperature of 350 °C as seen in Figure 4.36 a and b. The complete oxidation reaction occurred over Ce-modified catalyst while Cu and Mo improve neither consumption nor selectivity to PO.

4.2.4.2. Bimetallic Cu-Mn systems

Cu and Mn supported on m-SiO_2, α-Al_2O_3 and TiO_2 were also studied to investigate the catalytic performance of the bimetallic system according to the literature report. Among the three supports, α-Al_2O_3 and TiO_2 supported Cu-Mn bimetallic system showed better catalytic performance than their corresponding single metal catalysts. The synergy between Cu and Mn on these support materials improves PO yields by several folds. For α-Al_2O_3 supported bimetallic and unimetalic catalysts, Cu-Mn combination gave a better PO selectivity and propylene consumption rate than their unimetallic counterparts as shown in Figure 4.37 a and b. At the similar low consumption levels (20-30 µmol/g cat. min.), PO productivity was approximately 5 times higher as compared to single metal catalysts. The PO production rate was 1.16 µmol/g cat. min. for Cu-Mn catalyst and 0.26 and 0.20 µmol/g cat. min. for Cu and Mn catalysts respectively.

TiO_2 supported catalysts again showed a better activity and PO selectivity for the bimetallic systems (Figure 4.38 a and b). At 10-25 µmol/g cat. min. consumption rate, uni and bimetallic systems showed approximately the same catalytic performance. However, at high conversions (70-180 µmol/g cat. min.), PO production rate of Mn-Cu/TiO_2 catalyst was higher than the unimetallic system. But the desired improvement was not observed for these catalysts.

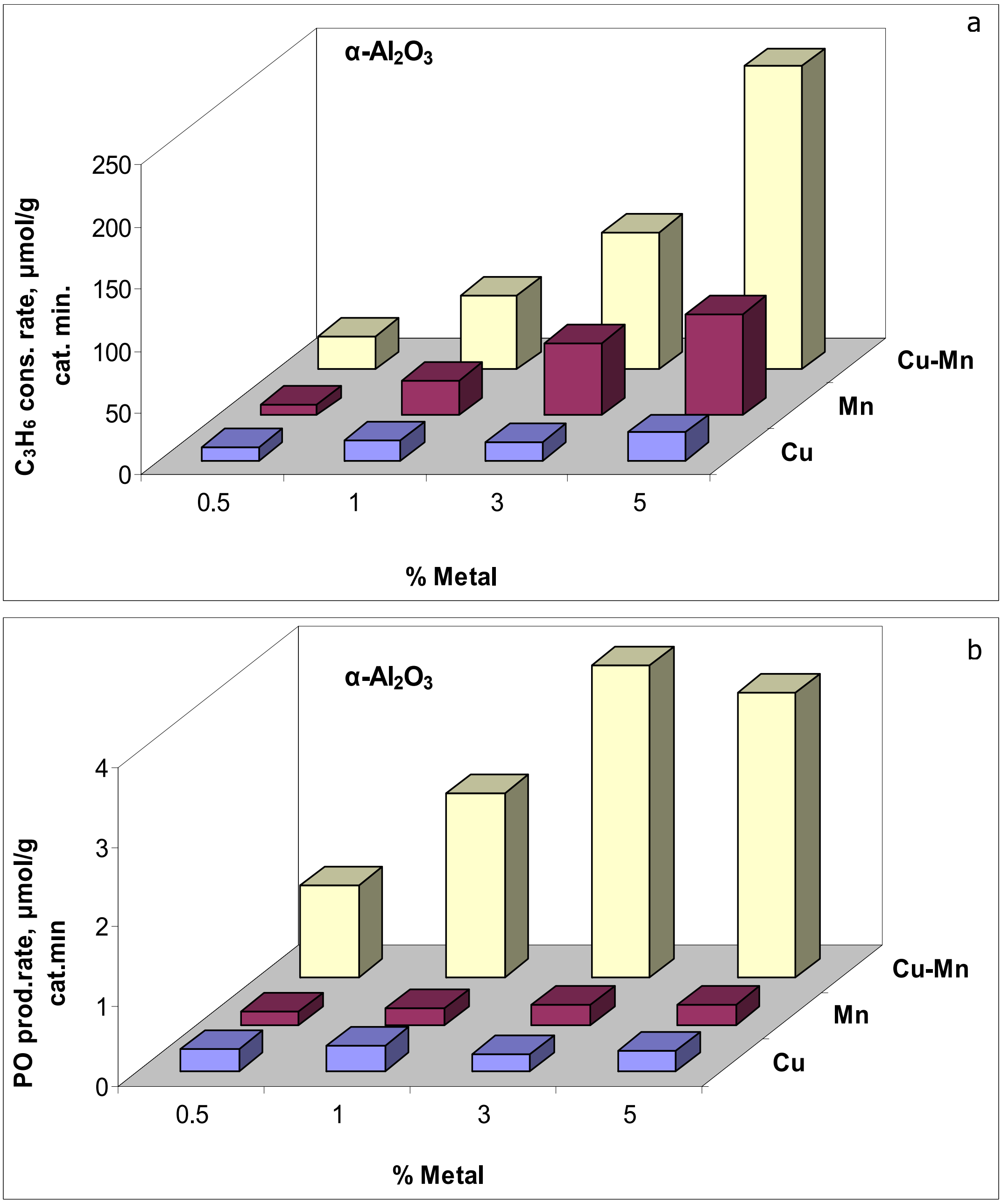


Figure 4.37. a) C_3H_6 consumption and b) PO production rate of bimetallic Cu-Mn/α-Al_2O_3 catalysts at 300°C and $C_3H_6/O_2=0.5$ with respect to metal ratio

Cu-Mn/m-SiO_2 catalysts did not enhance the catalytic activity and the PO productivity as compared with single Cu and Mn/m-SiO_2 catalyst at high consumption rate.

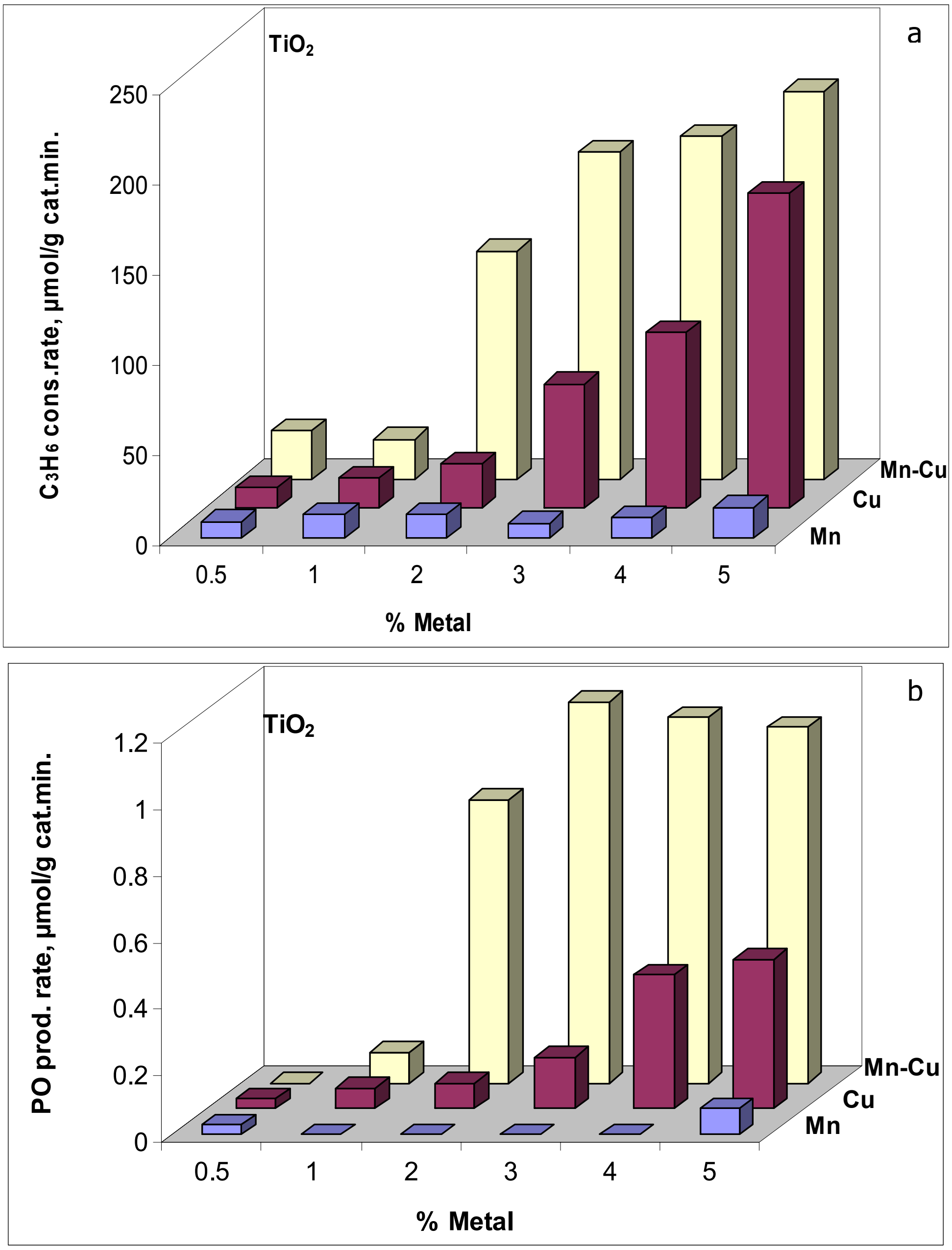


Figure 4.38 a) C_3H_6 consumption and b) PO production rate of bimetallic Cu-Mn/TiO_2 catalysts at 300°C and $C_3H_6/O_2=0.5$ with respect to metal ratio

4.3. Deactivation of Catalyst

Many of catalyst poisons act by blocking active surface sites. In addition, poisons may change the atomic surface structure in a way that reduces the catalytic activity.

Figure 4.39 shows the deactivation of catalyst observed for 3%Cu-2.25%K-m-SiO_2 catalyst in 223 minutes reaction time. The initial propylene consumption rate was 17.85 µmol/g cat. min. after 3 min on stream but consumption slowly decreased to 12.00 µmol/g cat. min. after 223 minutes at 300 °C. However PO productivity decreased slightly when compared with consumption rate. At first, PO production was 0.69 µmol/g cat. min. and it fell to 0.62 µmol/g cat. min. after 223 minutes. The decreased in PO productivity was approximately 10% while it was 33% for consumption rate. The deactivation of the high surface area silica supported copper catalyst is lower than any other catalysts reported in the literature (Liu et al., 2007).

The overall propylene conversion decreased with time while PO selectivity increased during reaction. It may be concluded that carbonaceous deposits formed on the catalyst surface cover the acidic or basic sites and it prevents the reaction between allylic H of propylene and adsorbed oxygen and then production of CO_2 and H_2O. The results showed that not only PO selectivity increased during reaction but also selectivity to the other oxygenated products increased while CO_2 production decreased with time. Beside of coking, water forming during reaction may result in decrease in the catalytic performance. The catalyst should be characterized after reaction to better understand the real reason for deactivation.

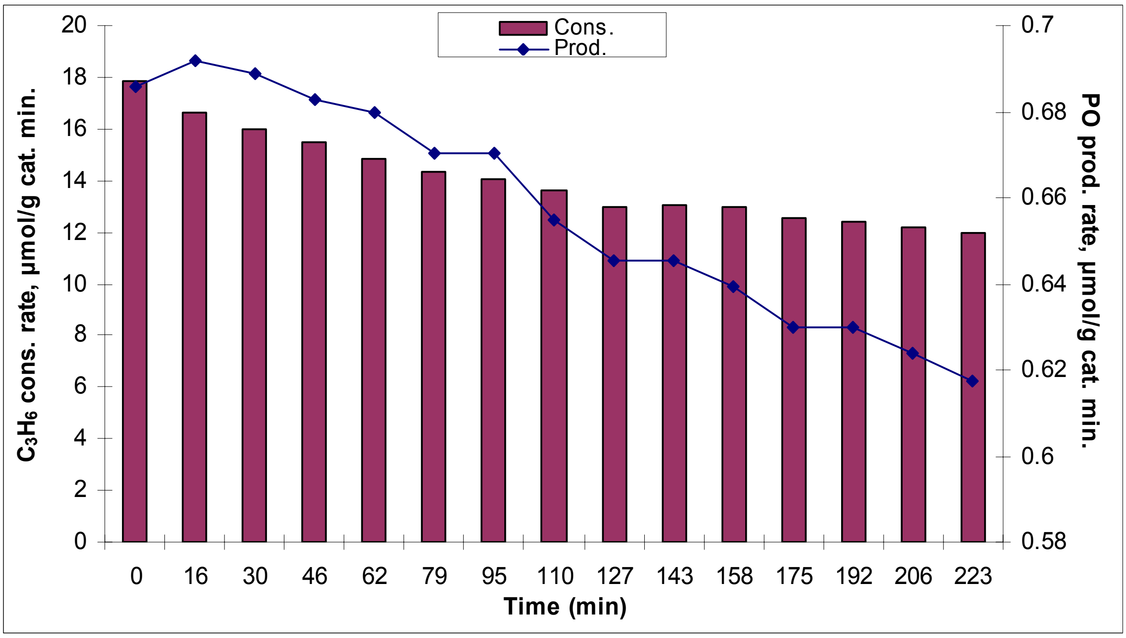


Figure 4.39 Time dependency of the propylene epoxidation over 3%Cu-2.25%K/m-SiO_2 catalyst

The reproducible result is important for catalytic science. So the most effective catalyst was tested two times after the first screening test. As summarized in Figure 4.40 a and b, the catalyst was so sensitive to humidity in air so its catalytic performance went down sharply with a decrease in the selectivity to PO. However when the catalyst was calcined again at 650 °C for 3 h, it showed again the same PO productivity with a small decrease in consumption and small increase in PO selectivity.

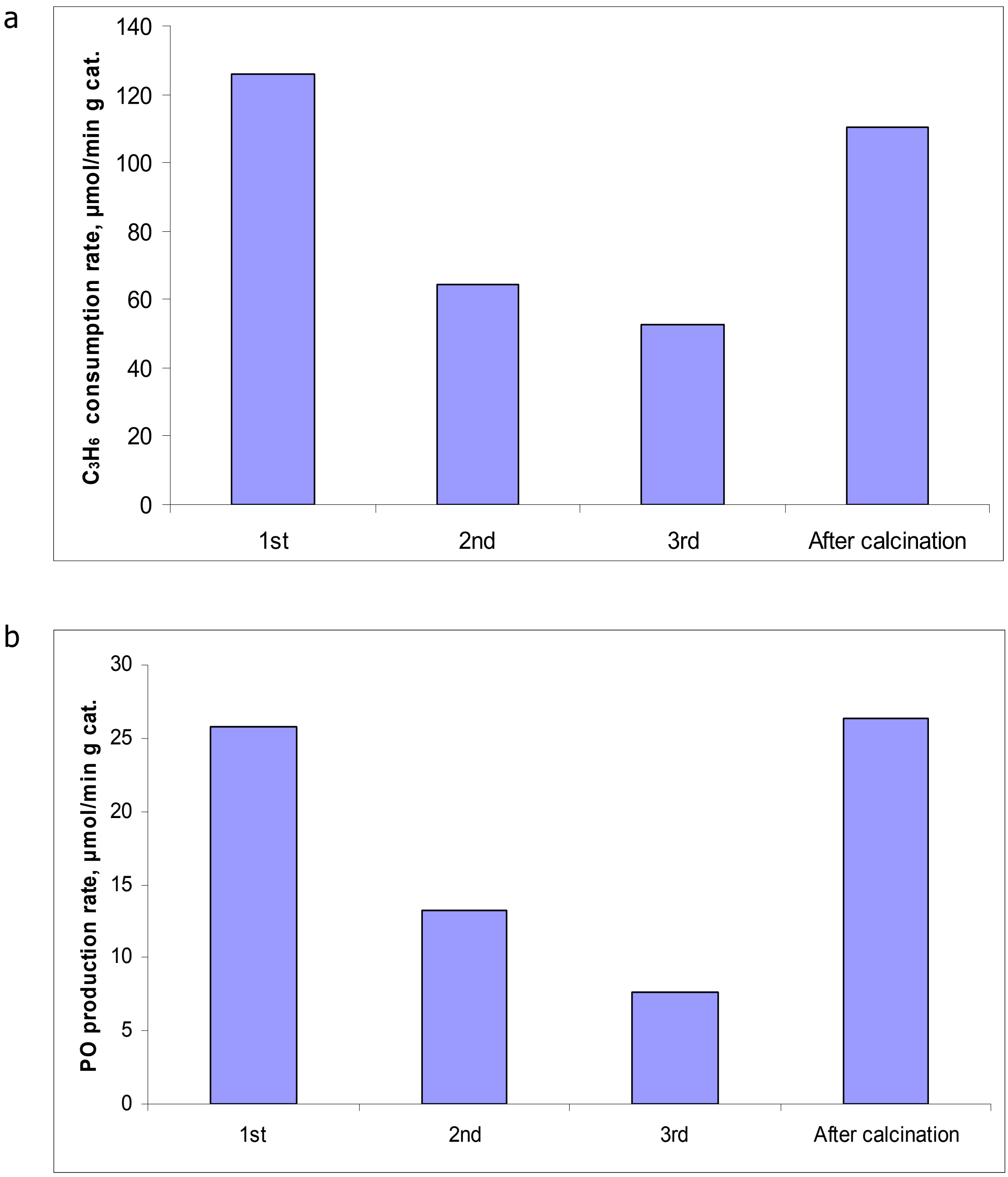


Figure 4.40 The reproducibility of 3%Cu-2.25%K/m-SiO_2 catalyst

CHAPTER 5

CONCLUSIONS

High-throughput sol-gel catalyst synthesis and also high-throughput screening methods were used to investigate the effects of metal loading, metal-metal interaction, support type, reactant gases ratio, reaction temperature and promoter effect for the direct synthesis of PO from propene and oxygen at atmospheric pressure. It has been taken into account the results obtained in previous experiments in order to prepare the new catalysts candidates during the study.

The first catalyst group including alumina and silica supported Ag and Cu catalysts were prepared at different solvent ratios and examined to determine the most effective metal and support that give the high catalytic activity and selectivity to PO. The results showed that the solvent ratio during the preparation of supports was not greatly effective over the catalytic performance. However the support-metal interaction showed different tendency. Among the Ag catalysts, silica supported catalysts gave lower propylene conversion with higher PO production rate when compared with alumina supported catalysts because of more acidic property of alumina support. An increase in metal particle size with loading effected propylene consumption positively but there was no significant effect over PO selectivity. However other oxygenated product such as PaL+AC selectivity decreased with Ag amount because big Ag particle over both support catalyzed only combustion reaction. These results are consistent with the last reported study (Lei et al., 2010) and contrary with the previous study (Zemichael et al., 2002; Jin et al., 2004).

When alumina and silica supported Cu catalysts were examined according to the PO formation rate, the most effective support was again silica. For Cu/SiO_2 catalysts, both consumption and the rate of PO formation were suppressed with deposit of further amount of Cu. The reason behind the difference in the performance of catalysts containing high and low Cu amount was detected by XPS analysis. For catalyst with low Cu content, isolated ionic-like Cu^{+2} species is detected. However the existence of Cu^{+2} species in CuO form is available beside isolated ionic-like form for catalyst with high Cu content. The existence of CuO suppresses the formation of oxygenated reaction products. This observation is supported by the other experimental study (Lambert et al., 2005; Su et al., 2009). Besides, there was no detected XRD peak for both catalysts because the particle size of Cu was smaller than XRD detection limit regardless of the Cu loading because of highly dispersed Cu particle.

The first investigated bimetallic system, Cu-Ag system, contains low amount of Cu because of highest PO selectivity and high amount of Ag because of highest propylene consumption rate. An addition of Cu into the Ag/SiO_2 catalyst increased the PO productivity by a factor of 4 to 7 as compared with an unpromoted Ag catalyst and by a factor of at least 2 than the corresponding unimetallic Cu catalyst at almost the same conversion level. Barteu et al. stated that an addition of Cu improve ethylene oxide (EO) production by several factor. The synergetic effect of Ag-Cu bimetallic system is again efficient in PO production but not as expected as in EO.

In the second part of the study, different supports were used to increase PO productivity over Ag and Cu catalyst. Ag metal supported on five different oxides gave mostly CO_2 for all supports. Only α-Al_2O_3 and m-SiO_2, especially α-Al_2O_3, supported catalysts gave PO as an oxygenated product. For this reason, commercial α-Al_2O_3 support was used to prepare promoted Ag catalysts by incipient wetness method with a low amount (1wt.%) of different metals such as Mo, Ce, Li and Cu in addition to the sol-gel synthesized SiO_2 support. Among these metals, Ce is the most effective modifier to increase propylene consumption but Li enhanced PO productivity significantly despite of low consumption rate when compared with other metals. However desired improvement cannot be obtained for Ag-based catalysts. The allylic hydrogen abstraction from propylene leads to combustion reaction which overcomes epoxidation reaction over Ag catalyst.

Copper metal was deposited into the seven different supports including silica containing different amount of titanium due to it is the most promising metal for PO production. Among the seven oxides, high surface area (m-SiO_2) and low surface area silica (SiO_2) gave the maximum PO productivity with low consumption rate compared with other supports. However (m-SiO_2) is the most effective support because of high propylene consumption and selectivity to PO. The main difference between these supports is the tendency in propylene consumption with respect to metal deposit. It increased with metal content over m-SiO_2 while that decreased over SiO_2 above 3%Cu loading. However PO production decreased with metal for both silicas. According to Su et al. study big Cu particle are not desired for PO formation (Su et al., 2009). Probably when Cu is loaded into silica with high surface area, small Cu cluster forms and it gives higher PO production as observed in their study.

The role of promoters on the activity and selectivity of the catalysts was investigated with metals such as Li, K, Ce and Y to enhance PO formation for silica supported Cu. Among the promoters Ce gave the highest propylene consumption rate due to its ability to store and release of oxygen (Dibenedetto et al., 2006). Both Y and Ce generally increased the selectivity to PaL+AC. However K and Li especially K increased both consumption and PO formation rate when compared un-modified Cu/SiO_2 catalyst. Promotion of m-SiO_2 supported catalyst enhanced the selectivity to PO but suppressed the propylene consumption. The main product obtained for Cu catalysts is the propylene aldehyde and acrolein (PaL+AC) over silica supports. And the PO is the second epoxidation product at all C_3H_6/O_2 ratios. The promotion of the catalyst with K and Li increased PO selectivity while decreased PaL+AC selectivity. K is reported as an effective promoter for Cu catalyst before (Chu et al., 2006) but Li is stated as effective promoter like K in this study.

The obtained PO formation rate for promoted Cu/m-SiO_2 catalyst is closed to the maximum value reported in the literatures to date (Chu et al., 2006; Su et al., 2009). To understand the effect of K on the silica supported Cu, XRD, XPS, TEM and SEM analysis were performed. However there was no noticeable change in Cu XPS peak, XRD diffraction patterns and SEM and TEM images due to addition of K.

The only difference observed between promoted and un-promoted catalysts is the activation energy in propylene consumption. The obtained activation energy for overall consumption rate of modified catalyst is less than that obtained for unmodified catalyst (71 vs 92 kJ mol^{-1}). However, the addition of K promoted PO production rate and activation energy of two catalysts were approximately the same (77 vs. 75 kJ mol^{-1}). This indicates that K neutralizes the acid sites of silica and it can be proved by TPD and IR analysis.

Generally for all catalysts except unpromoted Cu/SiO_2 catalysts, the proper C_3H_6/O_2 ratio was determined as 0.5 and further increase of C_3H_6 in the feed gas caused a decrease in both consumption and PO selectivity.

REFERENCES

Ananieva, E., Reitzmann, A., *Direct gas-phase epoxidation of propene with nitrous oxide over modified silica supported FeO_x catalysts*, Chem. Eng. Sci. 59 (2004) 5509-5517

Baer, H. G.; Ralek, M. *Direct liquid-phase oxidation of propene to propene oxide*, Appl. Catal. 7 (1983) 11-20

Chorkendorff, I., Niemantsverdriet, J. W., *Concept of Modern Catalysis and Kinetics*, Wiley, Weinheim, 2003

Chowdhury, B., Bravo-Suarez, J. B., Date, M., Tsubota, S., Haruta, M., *Trimethylamine as a gas-phase promoter: highly efficient epoxidation of propylene over supported gold catalysts*, Angew. Chem. Int. Ed. 45 (2006) 412-415

Carter, E.A., Goddard, W.A., *The surface atomic oxyradical mechanism for Ag-catalyzed olefin epoxidation The surface atomic oxyradical mechanism for Ag-catalyzed olefin epoxidation,* J. Catal. 112 (1988) 80-92

Chretien, S., Gordon Mark, S., Metiu, H., *Binding of propene on small gold clusters and on Au(111): Simple rules for binding sites and relative binding energies,* J. Chem. Phys. 121 (2004a) 3756

Chretien, S., Gordon Mark, S., Metiu, H., *Density functional study of the adsorption of propene on mixed gold-silver clusters,* Au_nAg_m*: Propensity rules for binding*, J. Chem. Phys. 121 (2004b) 9931

Chretien, S., Gordon Mark, S., Metiu, H., *Density functional study of the adsorption of propene on silver clusters,* Ag_m^q *(m = 1–5; q= 0, +1)*, J. Chem. Phys. 121 (2004c) 9925

Cowell J. J., Santra A. K., Lambert R. M., *Ultraselective Epoxidation of Butadiene on Cu{111} and the Effects of Cs Promotion*, J. Am. Chem. Soc., 122 (2000) 2381-2382

Chu, H., Yang, L., Zhang, Q., Wang, Y., *Copper-catalyzed propylene epoxidation by molecular oxygen: Superior catalytic performance of halogen-free* K^+*-modified* CuO_x*/SBA-15*, J. Catal. 241 (2006) 225-228

Cowell J. J., Santra A. K., Lambert R. M., *Ultraselective Epoxidation of Butadiene on Cu{111} and the Effects of Cs Promotion*, J. Am. Chem. Soc. 122 (2000) 2381-2382

Cropley, R. L., Williams, F. J., Vaughan, O. P. H., Urquhart, A. J., Tikhov, M.S., Lambert, R. M., *Copper is highly effective for the epoxidation of a "difficult" alkene, whereas silver is not*, Surf. Sci. 578 (2005) L85–L88

Dibenedetto, A., Aresta, M., Nocito, F., Pastore, C., Venezia, A.M., Chirykalova, E., Kononenko, V. I., Shevchenko, V. G., Chupova, I. A., *Synthesis of cyclic carbonates from epoxide: Use of reticular oxygen of* Al_2O_3 *or* Al_2O_3 *-supported* CeO_x *for the selective epoxidation of propene,* Catal. Today 115 (2006) 117-123

Dibenedetto, A., Aresta, M., Fragale, C., Distaso, M., Pastore, C., Venezia, A. M., Liu, C., Zhang, M., *High throughput experiment approach to the oxidation of propene-to-propene oxide with transition-metal oxides as O-donors*, Catal. Today 137 (2008) 44-51

Duan, S., Kahn, M., Senkan, S., *High-throughput nanoparticle catalysis: Partial oxidation of propylene*, Com. Chem. High T. Scr. 10 (2007) 111-119

Duma, V., Dieter, H., *Gas phase epoxidation of propene by nitrous oxide over silica-supported iron oxide catalysts*, J. Catal. 191 (2000) 93-104

Dumeignil, F., Sato, K., Imamura, M., Matsubayashi, N., Payen, E., Shimada, H., *Modification of structural and acidic properties of sol-gel-prepared alumina powders by changing the hydrolysis ratio*, Appl. Catal. A-Gen. 241 (2003) 319-329

Fellah, M. F., *A Density Functional Theory Study of Catalytic Partial Epoxidation of Ethylene and Propylene*, PhD Thesis, METU (2009)

Guo, X, Wang, R., Wang, X., Hao, J., *Effects of preparation method and precipitator on the proplene epoxidation over Ag/TS-1 in the gas phase*, Catal. Today 93-95 (2004) 211-216

Hagemeyer, A., Jandeleit, B., Liu, Y., Poojary, D. M., Turner, H. W., Volpe Jr., A. F., Weinberg, W. H., *Applications of combinatorial methods in catalysis*, Appl. Catal. A- Gen. 221 (2001) 23-43

Hayashi, T., Tanaka, K., Haruta, M., *Selectivity vapor-phase epoxidation of propylene over Au/TiO2 catalysts in the presence of oxygen and hydrgen,* J. Catal. 178 (1998) 566-575

A. Jankowaik, J. T., Barteau, M. A., *Ethylene epoxidation over silver and copper-silver bimetallic catalysts: I. Kinetics and selectivity*, J. Catal. 236 (2005) 366-378

B. Jankowaik, J. T., Barteau, M. A., *Ethylene epoxidation over silver and copper-silver bimetallic catalysts: II. Cs and Cl promotion*, J. Catal. 236 (2005) 379-386

Jin, G., Lu, G., Guo, Y., Guo, Y., Wang, J., Liu, X., *Direct epoxidation of propylene with molecular oxygen over Ag-*MoO_3/ZrO_2 *catalyst*, Catal. Today 93-95 (2004) 173-182

Jin, G., Lu, G., Guo, Y., Guo, Y., Wang, J., Kong, W., Liu, X., *Effect of preparation condition on performance of Ag-*MoO_3/ZrO_2 *catalyst for direct epoxidation of propylene by molecular oxygen*, J. Mol. Catal. A-Chem. 232 (2005) 165-172

Jin, G., Guo, Y., Liu, X., Yao, W., Guo, Y., Wang, Y., Yuan, F., Lu, G., *In situ FT-IR study on the direct gas phase epoxidation of propylene over Ag-*MoO_3 *catalyst*, Acta Phy.-Chim. Sin. 22 (2006) 809-814

Joshi Ajay, M., Nicholas Delgass, W., and Thomson, K.T., *Partial oxidation of propylene to propylene oxide over a neutral gold trimer in the gas phase: A density functional theory study*, J. Phys. Chem. B 110 (2006) 2572-2581

Kahn, M., Seubsai, A., Onal, I., Senkan, S., *High Throughput Synthesis and Screening of New Catalytic Materials for the Direct Epoxidation of Propylene,* Com.l Chem. High T. Scr. 13 (2010) 67-74

Kırk-Othmer Encyclopedia of Chemical Engineering, John-Wiley&Sons, 1997

Kizilkaya, A. C., Fellah, M. F., Onal, I., *Direct gas-phase epoxidation of propylene to propylene oxide through radical reactions: A theoretical study* , Chem. Phys. Lett. 487 (2010) 183-189

Lambert, R. M. Willams, F. J., Rachael, L. C., Palermo, A., *Heterogeneous alkene epoxidation: past, present nad future*, J. Mol. Catal. A-Chem. 255 (2005) 27-33

Lei, Y., Mehmood, F., Lee, S., Greeley, J., Lee, B., Seifert, S., Winans, R.E., Elam, J.W., Meyer, R.J., Redfern, P.C., Teschner, D., Schlögl, R., Pellin, M.J., Curtiss, L.A., Vajda, S., *Increased Silver Activity for Direct Propylene Epoxidation via Subnanometer Size Effects*, Science 328 (2010) 224-228

Levenspiel, O., *Chemical Reaction Engineering*, 2nd Edition, John Willey, New York, 1972

Liu, Y., Murata, K., Inaba, M., Mimura, N., S*yntheses of Ti- and Al-containing hexagonal mesoporous silica for gas-phase epoxidation of propylene by molecular oxygen*, Appl. Catal. 309 (2006) 91-105

Lu, J., Luo, M., Lei, H., Li, C., *Epoxidation of propylene on NaCl-modified silver catalysts with air as the oxidant*, Appl. Catal. A: Gen. 237 (2002a) 11-19

Lu, J., Luo, M., Bao, X., Lei, H., Li, C., *Epoxidation of Propylene on NaCl-Modified* $VCe_{1-x}Cu_x$ *Oxide Catalysts with Direct Molecular Oxygen as the Oxidant*, J. Catal. 211 (2002b) 552–555

Lu, J., Bravo-Suarez, J. J., Takahashi, A., Haruta, M., Oyama, S. T., *In situ UV-vis studies of the effect of the particle size on the epoxidation of ethylene and propylene on supported silver catalysts with molecular oxygen*, J. Catal. 232 (2005) 85-95

Lu, J., Bravo-Suarez, J. J., Haruta, M., Oyama, S. T., *Direct propylene epoxidation over modified* $Ag/CaCO_3$ *catalysts*, Appl. Catal. A: Gen. 302 (2006) 283-295

Mimura, N., Tsubota, S., Murata, K., Bando, K. K., Bravo-Suarez, J. J., Haruta, M., Oyama, S. T., *Gas-phase radical generation by Ti oxide clusters supported on silica: application to the direct epoxidation of propylene to propylene oxide using molecular oxygen as an oxidant*, Catal. Lett. 110 (2006) 47-51

Miyazaki, T., Ozturk, S., Onal, I., Senkan, S., *Selective oxidation of propylene to propylene oxide using combinatorial methodologies*, Catal. Today 81 (2003) 473-484

Monnier, J. R., *The direct epoxidation of higher olefins using molecular oxygen*, Appl. Catal. A-Gen. 221 (2001) 73-91

Murata, K., Liu, Y., Mimura, N., Inaba, M., *Direct vapor phase oxidation of propylene by molecular oxygen over MCM-41 and MCM-22 based catalysts,* Catal. Commun. 4 (2003) 385-391

Murata, K., Liu, Y., Inaba, M., Mimura, N., *Effect of Ti-modified mesoporous materials on the direct epoxidation of propylene by molecular oxygen*, Catal. Today 91-92 (2004) 39-42

Niemantsverdriet, J. W., *Spectroscopy in Catalysis*, 3rd Edition, Wiley-ECH, Weinheim, 2007

Nijhuis, T. A., Huizinga, B. J., Makkee, M., Moulijn, J. A., *Direct Epoxidation of Propene Using Gold Dispersed on TS-1 and Other Titanium-Containing Supports*, Ind. Eng. Chem. Res. 38 (1999) 884-891

Nijhuis, T. A., Makkee, M., Moulijn, J. A., Weckhuysen, B. M., *The production of propene oxide: Catalytic processes and recent deveplopments*, Ind. Eng. Chem. Res. 45 (2006) 3447-4359

Palermo, A., Husain, A., Tikhov, M. S., Lambert, R. M.*, Ag-catalysed epoxidation of propene and ethene: An investigation using electrochemical promotion of the effects alkali,* NO_x*, and chlorine*, J. Catal. 207 (2002) 331-340

Rouquerol, F., Rouquerol, J., Sing, K., *Adsorption by powders and porous solids*, Academic Press, London, 1999

Qi, C., Akita, T., Okumura, M., Haruta, M., *Epoxidation of propylene over gold catalysts supported on non-porous silica*, Appl. Catal. A- Gen. 218 (2001) 81-89

Senkan, S. M., *High-throughput screening of solid-state catalyst libraries*, Nature 39 (1998) 350-353

Senkan, S. M., Ozturk, S., *Discovery and optimization of heterogeneous catalysts by using combinatorial chemistry*, Angew. Chem. Int. Ed. 38 (1999a) 791-795

Senkan, S. M., Krantz, K., Ozturk, S., Zengin, V., Onal, I., *High-throughput testing of heterogeneous catalyst libraries using array microreactors and mass spectrometry*, Angew. Chem. Int. Ed. 38 (1999b) 2794-2799

Senkan, S., Combinatorial heterogeneous catalysis-A new path in an old field, Angew. Chem. Int. Ed. 40 (2001) 312-329

Senkan, S., Kahn, M., Duan, S., Ly, A., L., Eidholm, C., *High-throughput metal nanoparticle catalysis by pulsed laser ablation*, Catal. Today 117 (2006) 291-296

Sinha, A. K., Seelan, S., Tsubota, S., Haruta, M., *Catalysis by gold nanoparticles: epoxidation of propylene*, Top. Catal. 29 (2004) 95-102

Somorjai, G. A., *Introduction to Surface Chemisty and Catalysis*, 1994, John-Wiley, New York

Song, Z., Mimura, N., Bravo-Suarez, J. J., Akita, T., Tsubota, S., Oyama, S. T., *Gas-phase epoxidation of propylene through radicals generated by silica-supported molybdenum oxide* Appl. Catal. A-Gen. 136 (2007) 142-151

Souza, M.F., Batistaa, P.S., Regiania, I., Liborio, J.B.L., Souza, D.P.F., *Rice Hull-Derived Silica: Applications in Portland Cement and Mullite Whiskers*, Mater. Res. 3 (2000) 25-30

Stangland, E.E., Stavens, K. B., Andres, R. P., Delgass, W. N., *Characterization of gold-titanium catalysts via oxidation of propylene to propylene oxide,* J. Catal. 191 (2000) 332-347

Su W., Wang S., Ying P., Feng Z., Li C., *A molecular insight into propylene epoxidation on Cu/SiO*$_2$ *catalysts using O*$_2$ *as oxidant*, J. Catal. 268 (2009) 165-174

Suo, Z. Jin, M., Lu, J., Wei, Z., Li, C., *Direct gas-phase epoxidation of propylene to propylene oxide using air as oxidant on supported gold catalyst*, J.Nat. Gas Chem. 17 (2008) 184–190

Takahashi, A., Hamakawa, N., Nakamura, I., Fujitani, T., *Effects of added 3d transition-metals on Ag-based catalysts for direct epoxidation of propylene by oxygen*, Appl. Catal. A-Gen. 294 (2005) 34-39

Takezawa N., Kobayashi H., Kamegai Y., Shimokawabe M., *Characterization of copper/silica catalysts in reduction states*, Appl. Catal. 3 (1982) 381-388

Thomas, J. M., Thomas, W. J., *Principle and Practice of Heterogeneous Catalysis*, 2nd Ed., VCH, Weinheim, 1997

Torres, D., Lopez, N., Illas, F., Lambert, R. M., *Low-basicity oxygen atoms: a key in the search for propylene epoxidation catalysts,* Heterogen. Catal. 46 (2007) 2055-2058

Trapp, O., *Gas chromatographic high-throughput screening techniques in catalysis*, J. Chrom. A, 1184 (2008) 160–190

van Santen, R. A., Neurock, M., *Molecular Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2006

Vaughan, O. P. H., Kyriakou, G., Macleod, N., Tikhov, M., Lambert, M. R., *Copper as a selective catalyst for the epoxidation of propene*, J. Catal. 236 (2005) 401–404

Wang, R., Guo, X., Wang, X., Hao, J*., Propylene epoxidation over silver supported on titanium silicalite zeolite,* Catal. Lett. 90 (2003) 57-63

Wang, R., Hao, J., Guo, X., Wang, X., Liu, X., *Propylene epoxidation over Ag/Ts-1 catalysts*, Stud. Surf. Sci. Catal. 154 (2004) 2632-2938

Wang, Y., Chu, H., Zhu, W., Zhang, Q., *Copper-based efficient catalysts for propylene epoxidation by molecular oxygen*, Catal. Today 131 (2008) 496-504

Weinberg, W. H., Jandeleitt, B., Self, K., Turners, H., *Combinatorial methods in homogeneous and heterogeneous catalysis*, Curr. Opin. Solid St. M. 3 (1998) 104-110

Wolf, D., Buyevskaya, O.V., Baerns, M., *An evolutionary approach in the combinatorial selection and optimization of catalytic materials*, Appl. Catal. A-Gen. 200 (2000) 63–77

Yao, W., Lu, G., Guo, Y., Guo, Y., Wang, Y., Zhang, Z., *Promotional effect of* Y_2O_3 *on the performance of* $Ag/\alpha\text{-}Al_2O_3$ *catalyst for epoxidation of propylene with molecular oxygen*, J. Mol. Catal. A- Chem. 276 (2007) 162–167

Zemichael, F. W., Palermo, A., Tikhov, M.S., Lambert, R.M., *Propene epoxidation over K-promoted Ag/CaCO3 catalysts: the effect of metal particle size*, Catal. Lett. 80 (2002) 93-98

Zhu, W., Zhang, Q., Wang, Y., *Cu(I)-catalyzed epoxidation of propylene by molecular oxygen*, J. Phys. Chem. C 112 (2008) 7731-7734

APPENDIX A

THERMO GRAVIMETRIC and DIFFERENTIAL THERMAL ANALYSIS (TGA-DTA) OF SOME CATALYST SAMPLES

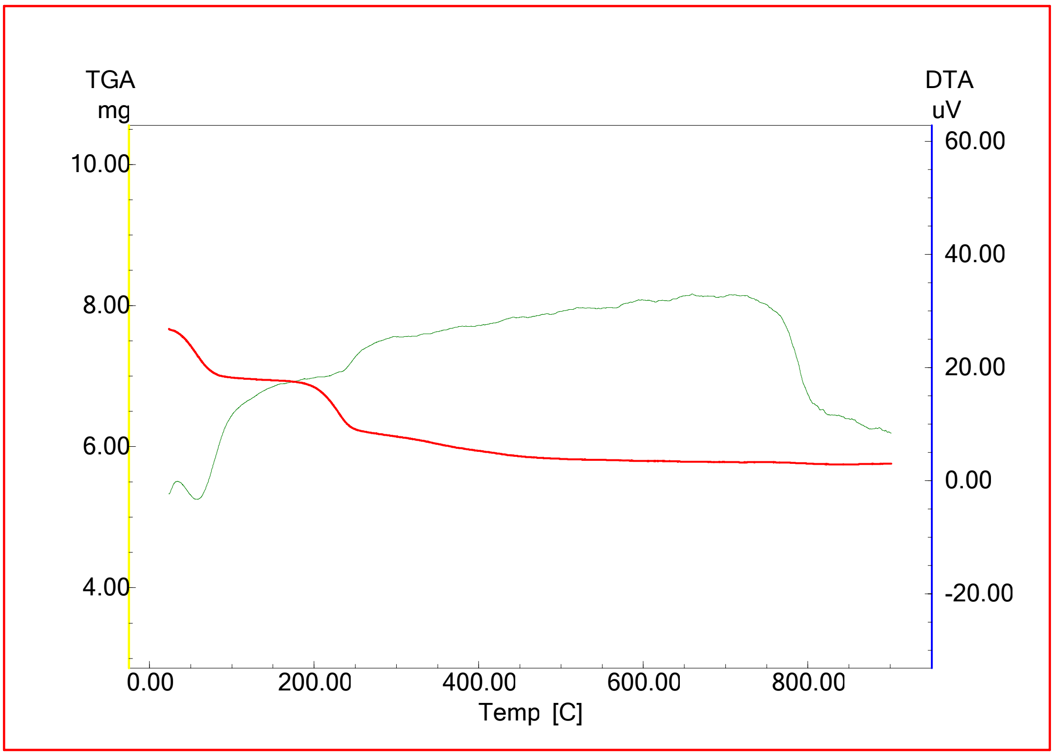


Figure A.1. TGA-DTA result of 10% Ag/SiO_2

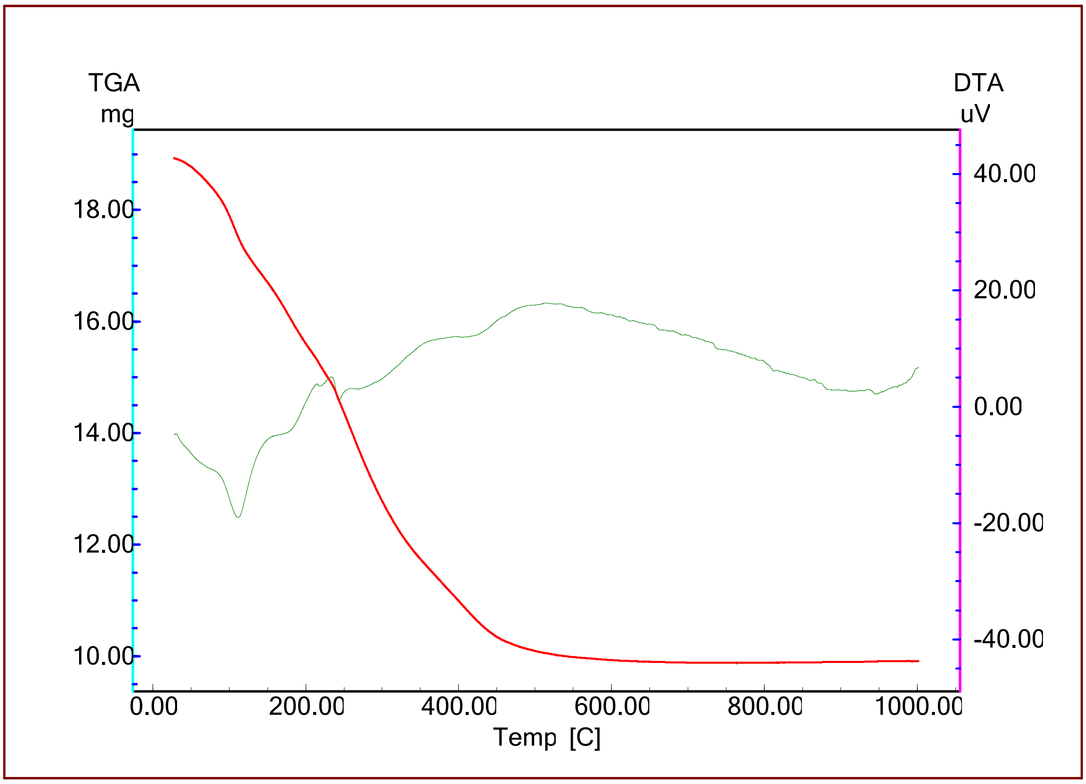


Figure A.2. TGA-DTA result of 20% Cu/Al_2O_3

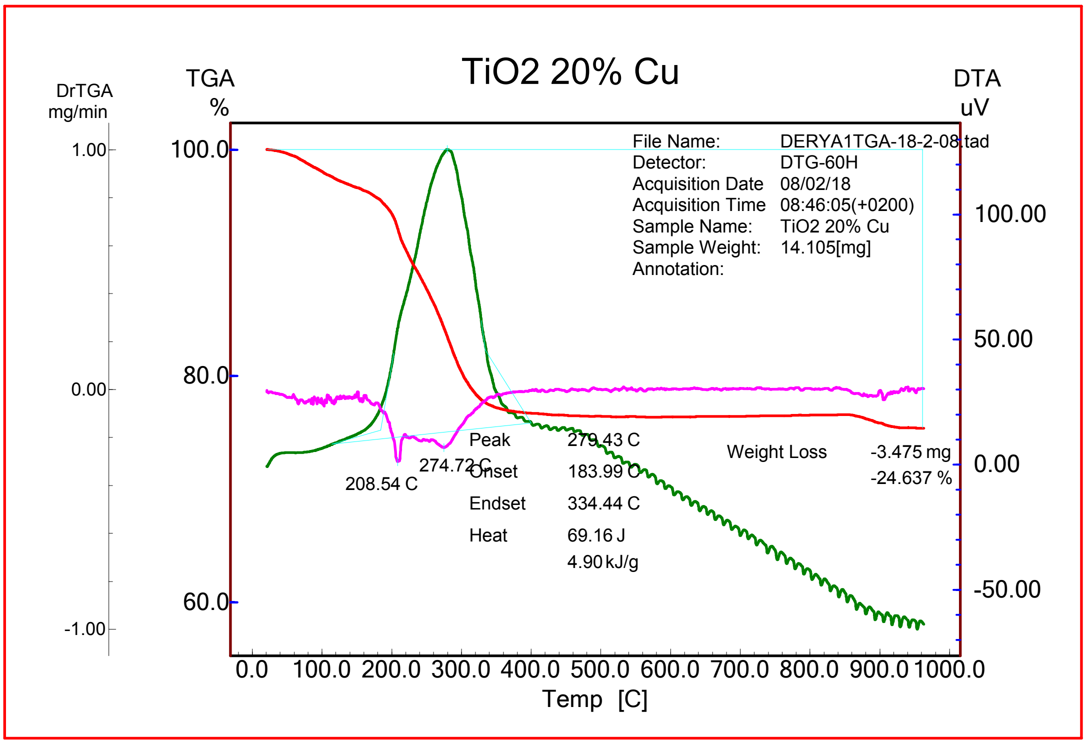


Figure A.3. TGA-DTA result of 20% Cu-TiO_2

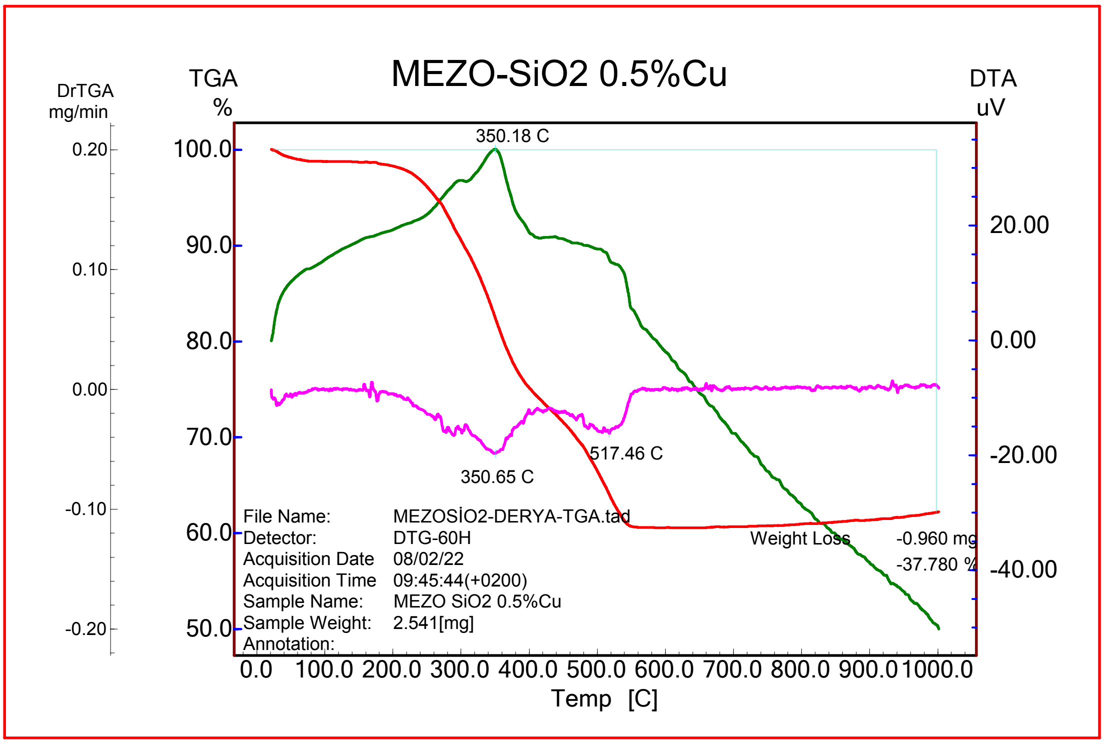


Figure A.4. TGA-DTA result of 0.5% Cu-m-SiO_2

APPENDIX B

AN EXPERIMENTAL FLOW SHEET

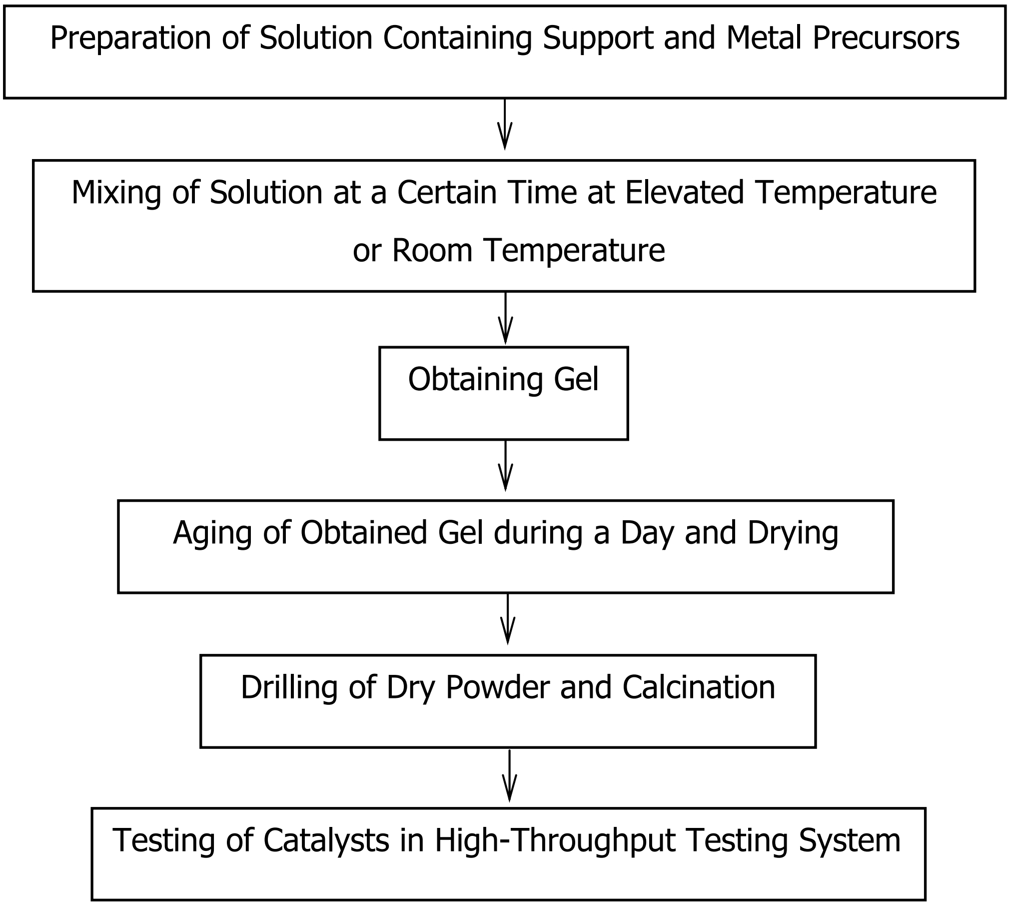


Figure B.1 A simple flowsheet for the experimental procedure

APPENDIX C

SCHEMATIC TESTING UNIT

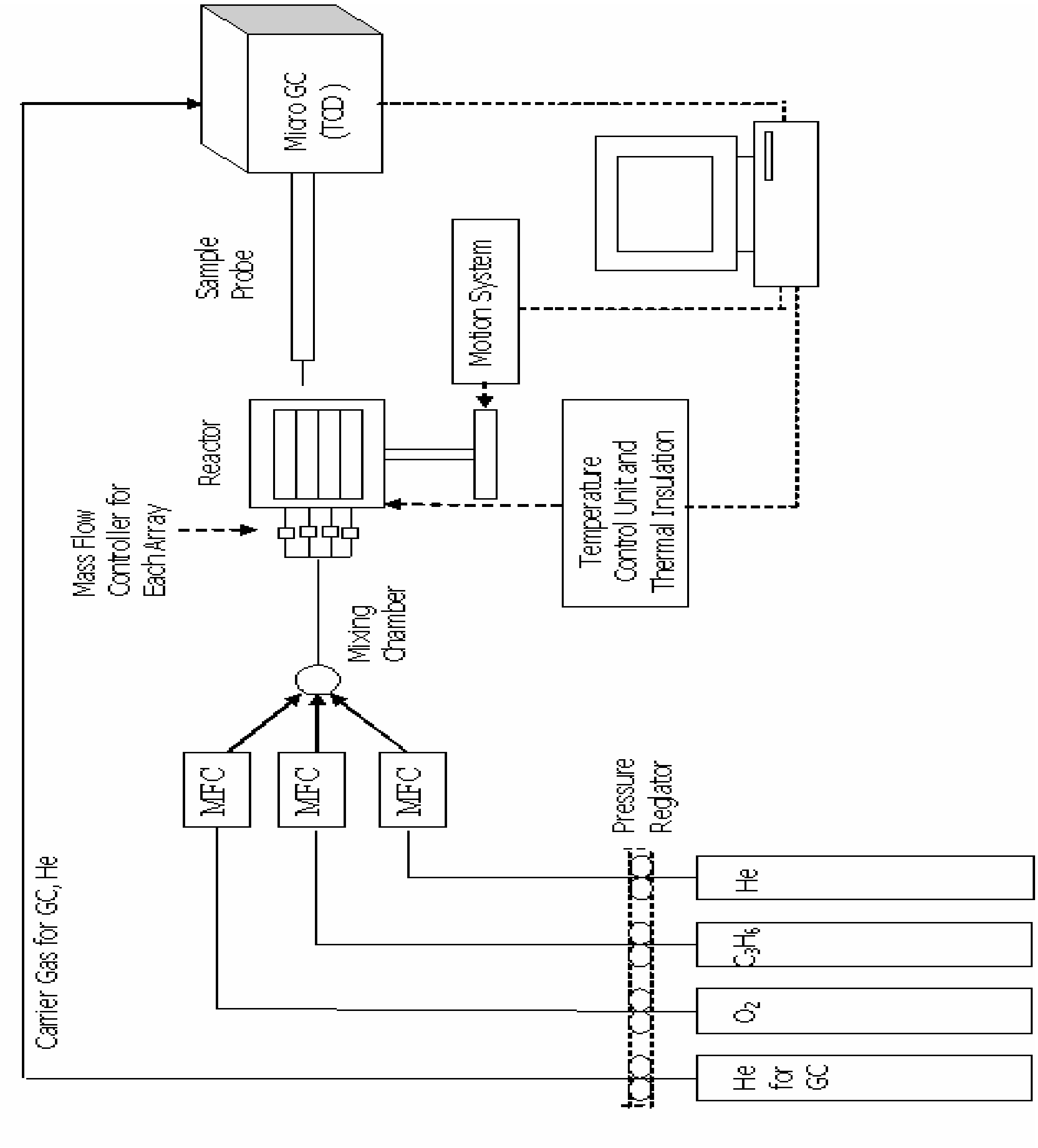


Figure C.1 Schematic representation of high throughput testing unit

APPENDIX D

REACTION PRODUCTS and SAMPLE CALCULATION

The products formed during reaction:

Propylene oxide (PO) formation reaction:

$$[CH_2CHCH_3] + \tfrac{1}{2} O_2 \rightarrow [C_3H_6O] \tag{D.1}$$

Propionaldehyde (PaL) formation reaction:

$$[CH_2CHCH_3] + \tfrac{1}{2} O_2 \rightarrow [CH_3CH_2CHO] \tag{D.2}$$

Acrolein (AC) formation reaction:

$$[CH_2CHCH_3] + \tfrac{1}{2} O_2 \rightarrow [CH_2CHCHO] \tag{D.3}$$

Acetone (AC) formation reaction:

$$[CH_2CHCH_3] + \tfrac{1}{2} O_2 \rightarrow [CH_3COCH_3] \tag{D.4}$$

Acetaldehyhde (AD) formation reaction:

$$[CH_2CHCH_3] + O_2 \rightarrow [CH_3CHO] + [CH_2O] \tag{D.5}$$

Carbondioxide (CO_2) formation reaction:

$$[CH_2CHCH_3] + \tfrac{9}{2} O_2 \rightarrow 3[CO_2] + 3[H_2O] \tag{D.6}$$

Definition of conversion and selectivity

Conversion = 100 x (moles of all products containing carbon detected by GC analysis)/(moles of propylene fed)

Selectivity = 100 x (moles of carbon in PO/ (moles of all products containing carbon detected by GC analysis)

Moles of CO_2 formed were divided by three.
Moles of AD formed were divided by two over three.

Sample Calculation

Reaction parameters:

Feed gas content: 14% C_3H_6: 28% O_2: 58% He

Volumetric flow rate of feed gas: 100 ml min^{-1}
Number of channel in an array: 20
Volumetric flow rate through a channel: 100/20 = 5 ml min^{-1}

Mass of catalyst tested=5 mg

P=1 atm
Molar flow rate of feed gas was calculated from ideal gas equation.

$$PV=nRT$$

R=0.082 atm.L/mol.K
GC column temperature during analysis: 120 °C

$(1\ \text{atm})*(5\text{x}10^{-3}\ \text{L min}^{-1}*0.14) = n*(0.082\ \text{atm.L/mol.K})*(120+273)\ \text{K}$

$n = 2.172\text{x}10^{-5}$ mol/min C_3H_6

The conversion and PO selectivity obtained for 3%Cu-2.25%K-m-SiO_2 catalyst from GC analysis at 300 °C reaction temperature;

% Conversion = 0.94

% PO selectivity= 21.00

The consumption rate of C_3H_6 = Conversion*Molar flow rate of C_3H_6/mass of catalyst

= [(0.94/100)* $2.172\text{x}10^{-5}$ mol/min] / (0.005 g cat.)

= $4.09\text{x}10^{-5}$ mol/min g cat.

= 40.9 μmol/min g cat.

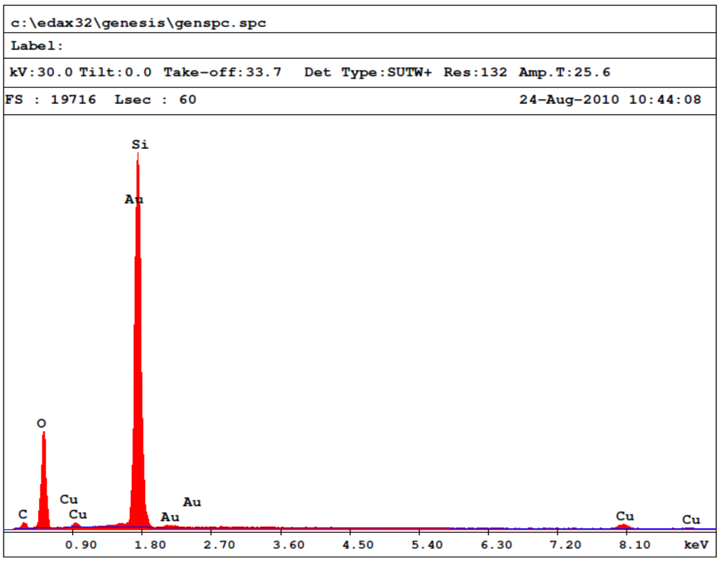
The PO production rate = Consumption rate * Selectivity

= 40.9 μmol/min g cat. * (21/100)

= 8.60 μmol/min g cat.

APPENDIX E

ELECTRON DISPERSIVE X-RAY SPECTROSCOPY (EDX) ANALYSIS OF CATALYST SAMPLES



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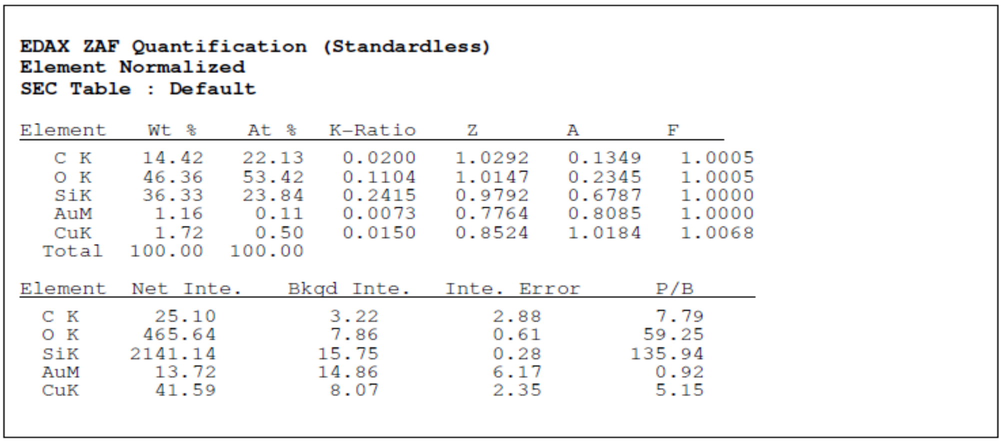

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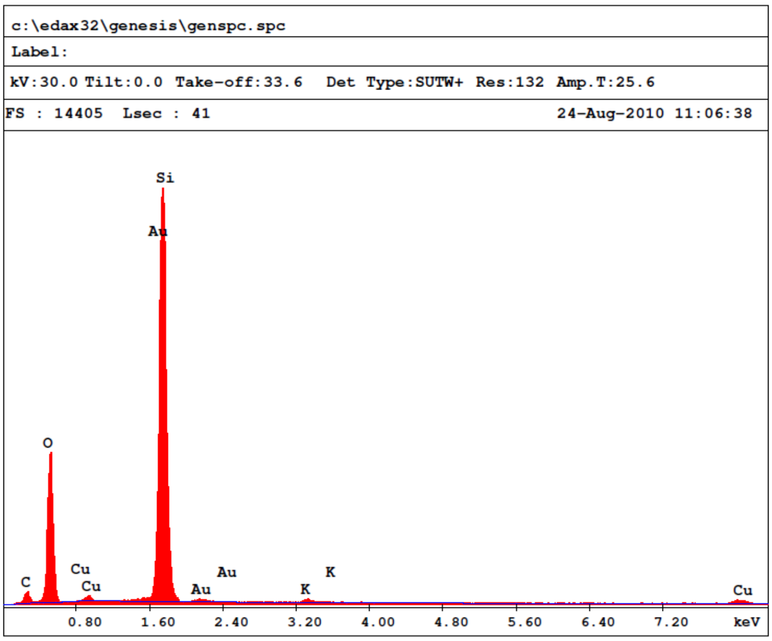
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

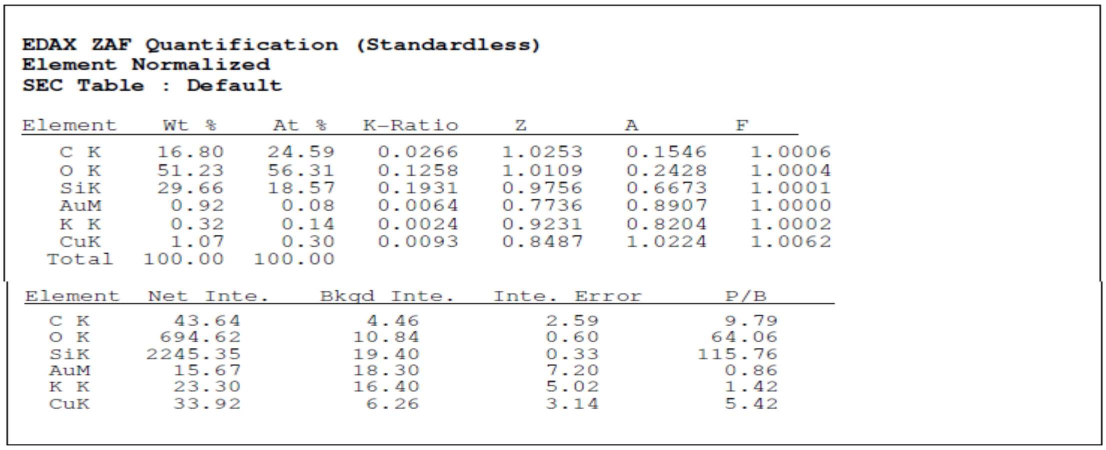
Element    Wt %     At %   K-Ratio     Z        A        F
   C K    14.42    22.13   0.0200   1.0292   0.1349   1.0005
   O K    46.36    53.42   0.1104   1.0147   0.2345   1.0005
   SiK    36.33    23.84   0.2415   0.9792   0.6787   1.0000
   AuM     1.16     0.11   0.0073   0.7764   0.8085   1.0000
   CuK     1.72     0.50   0.0150   0.8524   1.0184   1.0068
  Total  100.00   100.00

Element  Net Inte.    Bkgd Inte.   Inte. Error      P/B
  C K       25.10         3.22         2.88          7.79
  O K      465.64         7.86         0.61         59.25
  SiK     2141.14        15.75         0.28        135.94
  AuM       13.72        14.86         6.17          0.92
  CuK       41.59         8.07         2.35          5.15
```

Figure E.1 EDX result of 3%Cu-m-SiO_2 catalyst



```
c:\edax32\genesis\genspc.spc
Label:
kV:30.0 Tilt:0.0  Take-off:33.6   Det Type:SUTW+  Res:132  Amp.T:25.6
FS : 14405   Lsec : 41                              24-Aug-2010 11:06:38
```



```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %    At %   K-Ratio     Z        A        F
   C K     16.80   24.59   0.0266   1.0253   0.1546   1.0006
   O K     51.23   56.31   0.1258   1.0109   0.2428   1.0004
   SiK     29.66   18.57   0.1931   0.9756   0.6673   1.0001
   AuM      0.92    0.08   0.0064   0.7736   0.8907   1.0000
   K K      0.32    0.14   0.0024   0.9231   0.8204   1.0002
   CuK      1.07    0.30   0.0093   0.8487   1.0224   1.0062
  Total   100.00  100.00

Element  Net Inte.    Bkgd Inte.    Inte. Error        P/B
  C K       43.64        4.46          2.59            9.79
  O K      694.62       10.84          0.60           64.06
  SiK     2245.35       19.40          0.33          115.76
  AuM       15.67       18.30          7.20            0.86
  K K       23.30       16.40          5.02            1.42
  CuK       33.92        6.26          3.14            5.42
```

Figure E.2 EDX result of 3%Cu-2.25%K-m-SiO$_2$ catalyst

CURRICULUM VITAE

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WORK EXPERIENCE

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1999-2002	Anadolu Universtiy, Chemical Eng.	Research Assistant

FOREIGN LANGUAGES

Advanced English

PUBLICATIONS

1. **Düzenli, D.,** Önal, I., Şeker, E., Senkan, S., Epoxidation of Propene by High-throughput Screening Method over Combinatorially Prepared Cu Catalysts Supported on High and Low Surface Area Silica, Int. Jour. Chem. Reac. Eng. (submitted)

2. Önal, I., **Düzenli, D.,** Seubsai, A., Kahn, M., Şeker, E., Senkan, S., Propylene epoxidation: High-throughput screening of supported metal catalysts combinatorially prepared by rapid sol-gel method, *Topics in Catalysis* 53 (2010) 92-99

3. Beis, S. H., **Düzenli, D**., Onay, Ö., Koçkar, Ö., Fixed-Bed Pyrolysis of Daphne *(Laurus nobilis L.)* Seed, Energy Source 25 (2003) 1053-1062

HOBBIES

Swimming, riding horse, movie