CATALYTIC REACTION OF PROPYLENE TO PROPYLENE OXIDE ON VARIOUS CATALYSTS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ŞULE KALYONCU

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

SEPTEMBER 2012

Approval of the thesis:

CATALYTIC REACTION OF PROPYLENE TO PROPYLENE OXIDE ON VARIOUS CATALYSTS

submitted by **ŞULE KALYONCU** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences** ________________________

Prof. Dr. Deniz Üner
Head of Department, **Chemical Engineering** ________________________

Prof. Dr. Işık Önal
Supervisor, **Chemical Engineering Dept., METU** ________________________

Assoc. Prof. Dr. Erol Şeker
Co-Supervisor, **Chemical Engineering Dept., IIT** ________________________

Examining Committee Members:

Assoc. Prof. Dr. Görkem Külah
Chemical Engineering Dept., METU ________________________

Prof. Dr. Işık Önal
Chemical Engineering Dept., METU ________________________

Asst. Prof. Dr. Serkan Kıncal
Chemical Engineering Dept., METU ________________________

Assoc. Prof. Dr. Ayşen Yılmaz
Chemistry Dept., METU ________________________

Dr. Derya Düzenli
Maden Analizleri ve Teknolojisi, MTA ________________________

Date: September 14, 2012

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: ŞULE KALYONCU

Signature:

ABSTRACT

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Kalyoncu, Şule
M.Sc., Department of Chemical Engineering
Supervisor: Prof. Dr. Işık Önal
Co-Supervisor: Assoc. Prof. Erol Şeker

September 2012, 127 pages

Throughout this thesis work, various catalysts were investigated with combinational approach to develop highly active and selective novel catalysts for direct epoxidation of propylene to PO using molecular oxygen.

The promoted and un-promoted silver (Ag), copper (Cu), ruthenium (Ru), manganese (Mn) mono and multimetallic catalytic systems over different silica supports were prepared via sol-gel method and incipient wetness method. In addition to support effect, the effects of different promoters on the catalytic performances of these catalyst candidates were investigated. The study showed that commercial silica (c-SiO_2) is the most effective support when compared to silica (SiO_2) and silica synthesized with templete (t-SiO_2). Among bimetallic catalytic systems containing Ag, Ru, Mn and Cu metals, c-SiO_2 supported Cu-Ru catalyst was determined as the most active catalytic system. In addition, the most effective catalyst and promoter in the epoxidation reaction was determined as NaCl promoted Cu-Ru catalyst supported over c-SiO_2 with 35.98% selectivity& 9.55% conversion (3.44% yield) at 300^{0}C and 0.5 feed gas ratio (C_3H_6/O_2)..

In the study, the selected catalysts showed low and high PO productivity were also investigated by characterization techniques such as XRD, XPS, BET and FTIR.It was inferred from characterization tests that bimetallic systems reveal a synergistic behavior by exposing more active sites on the silica support material with respect to their monometallic counterparts. Besides, NaCl catalytic promoter has a strong interaction particularly with the Cu sites on the Cu/Ru/SiO_2 catalyst surface, altering the electronic structure of Cu sites that favors to PO production.

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

ÖZ

PROPİLENİN PROPİLEN OKSİTE DÖNÜŞÜMÜNÜN KATALİTİK OLARAK ÇEŞİTLİ KATALİZÖRLER ÜZERİNDE İNCELENMESİ

Kalyoncu, Şule
Yüksek Lisans, Kimya Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Işık Önal
Ortak Tez Yöneticisi: Doç. Dr. Erol Şeker

Eylül 2012, 127 sayfa

Bu tez çalışmasında, moleküler oksijen kullanarak propilenin gaz fazı oksitlenmesi tepkimesi için aktif ve yüksek seçiciliğe sahip yeni katalizörlerin geliştirilmesi amacıyla hızlı sonuç veren katalitik aktivite test sistemi ile birçok katalizör incelendi.

Farklı silika destek maddeleri üzerine yüklenmiş modifiye edilmiş ve modifiye edilmemiş gümüş (Ag), bakır(Cu), rutenyum (Ru) ve manganez (Mn) tekli ve çoklu metalik katalizör sistemleri çöz-pel ve emdirme yöntemleri kullanılarak hazırlandı. Destek maddenin etkisi yanında, farklı modifiye maddelerinin bu katalizör adaylarının katalitik performansları üzerine etkileri de incelendi. Çalışma, ticari silikanın (c-SiO_2) , silika (SiO_2) ve templete kullanılarak hazırlanan silikaya (t-SiO_2) göre daha etkili bir destek maddesi olduğunu gösterdi. Ag,Ru,Mn ve Cu metallerinin ikili kombinasyonlarından oluşan metalik sistemler incelendiğinde ise Cu-Ru sisteminin en aktif ikili katalizör sistemi olduğu belirlendi. Ayrıca epoksidasyon reaksiyonunda en etkili katalizör ve en etkili modifiye maddesinin 300˚C sıcaklıkta ve 0.5 oranındaki gaz oranı ile yapılan aktivite testi sonucunda 35.98% seçicilik ve 9.55% dönüşüm ile (3.44% PO verimi) NaCI ile modifiye edilmiş Cu-Ru katalizör sisteminin olduğu belirlendi.

Çalışmada ayrıca düşük ve yüksek PO üretimi gösteren seçilmiş katalizörler, XRD,XPS,BET ve FTIR tekniklerini içeren çeşitli karakterizasyon yöntemleri ile incelendi. Karakterizasyon sonuçlarından ikili metalik sistemlerin silika destek maddesi üzerinde tekli sistemlere göre daha çok aktif bölge oluşturarak sinerjik etki sergilediği anlaşılmıştır. Ayrıca, modifiye maddesi olan NaCI'nin Cu-Ru/SiO_2 katalizörü üzerindeki Cu bölgeleri ile güçlü etkileşim halinde olduğu ve Cu bölgelerinin elektronik yapısını değiştirdiği bu yüzden de PO üretimini desteklediği düşünülmektedir.

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

To My Family

ACKNOWLEDGEMENTS

I would like to thank my supervisor Prof. Dr. Işık Önal for giving me the opportunity to work with him, and for all his valuable advice, guidance and encouragement during my study.I would also like to thank tomy co-supervisor Assoc. Prof. Dr. Erol Şeker for his guidance, advice, encouragements throughout the research.

I would like to thank to Prof. Dr. Selim Senkan for providing high throughput catalytic testing facilities at UCLA. Also I would like to thank Assoc. Prof. Dr. Emrah Özensoy and Assoc. Prof. Dr. Ayşen Yılmaz for providing characterization experiments facilities.

I would also like to special thanks to Dr. Derya Düzenli for sharing their knowledge on catalysis, for her helps, for her friendship and all of the times we spent together. I am especially thankful to Dr. Anusorn Seubsaifor his help and advices. Also I would like to thank toCansın Badan and Zafer Say for their help.

Also I would like to thank İlker Tezsevin for his friendship and quick solutions to technical problems. I thank and acknowledge my friends, Duygu Gerçeker, Gökhan Çelik, Yasemin Coşkun, Nisa Ilgaz and Ceren Kasapoğlu for their friendship and all of the times we spent together.

And I am grateful to my parents, İkram Kalyoncu and Raziye Kalyoncu ,my brother Salih Kalyoncu and Güldane Kalyoncufor their endless love, encouragement, support and make my life meaningful.I especially thank Mehmet İner for his love, supportive attitude, encouragement and patience.

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ABBREVIATIONS

AC	Acrolein
AD	Acetaldehyde
ASF	Atomic Sensitivity Factor
AT	Acetone
BE	Binding Energy
c-SiO_2	Commercial Silica
$E_{electron}$	Electron Energy
$I_{emission}$	Electron Current
KAc	Potassium Acetate
PaL	Propionaldehyde
PO	Propylene Oxide
SiO_2	Silica
t-SiO_2	Silica Synthesized With Template

CHAPTER 1

INTRODUCTION

1.1. Catalysis Phenomena

The importance of catalysis in modern life is great that they take very deep and effective roles in it. They are included in the production process of many modern life needs such as plastics, synthetic fibers, food and many other everyday commodities (Lloyd, 2011).

Catalysis is the modification of the rate of a chemical reaction due to the participation of a substance called a catalyst. The usage of catalysts is very common that they are used during the production of almost 90% of all industrial chemicals (Lancaster, 2010). They are required for the production of 30 of the top 50 chemical commodities produced in the U.S. (Sheldon& van Bekkum, 2001).

Catalyst market is a dramatically emerging market. At the end of the 20th century, the whole value of catalyst world market was about 10 billion USD with ¼ refining, ¼ polymers, ¼ chemicals and ¼ environments. The value of catalysis could increase about 200 to 300 times of its own value, when they are used in the production of goods and services via petrochemistry, refining and polymerization catalysis (Baerns, 2004).

The realization of the importance of the catalysts leads the annual growth rate of this market to 3% (Morbidelli et al., 2005). Catalysts also owe their economic benefit to their high activity because they can convert tens of millions times of chemicals compared to their own weights (Lancaster, 2010).

A catalyst is commonly defined as a substance that changes the rate of reaction but emerges from the reaction unchanged. On the other hand, a catalyst does not change the thermodynamic equilibrium of a reaction during the process. Rather, it alters the rate of attainment of equilibrium. The goal then is the adaptation of the active catalysts structure to convert reactants directly to the target product without producing any by-products which is usually waste. So, catalysts eliminate most waste by nature (van Santen and Neurock, 2006). At the same time, most of the pollution control devices like catalytic converters for automobiles require catalysis. Hence, catalysis is extremely important with its economical and environmental advantages (Morbidelli et al., 2005).

1.1.1. Classification of Catalysts

Many catalysts known today can be classified according to the various criteria; structure, composition, or state of aggregation. Depending on the state of aggregation in which they act, catalysts can be classified into three categories; homogeneous catalysts, heterogeneous catalysts and an intermediate group, including biocatalysts.

Homogeneous catalysts are those in the same phase with the reactants. They are involved in reactions taking place in uniform gas or liquid phase. Generally, homogeneous catalysts are well-defined chemical compounds or transition metal complexes, which are molecularly dispersed in the reaction medium (End and Schoning,2004).

Biocatalysts, which are specific kind of catalysts, have similar features of homogeneous and heterogeneous catalysts. Enzymes are classified as bio catalysts and biological reactions need enzymes in order to occur at rates sufficient for life (Chorkendorff and Niemantsverdriet, 2003).

Most widely used catalysts in industrial processes are heterogeneous catalysts.

Heterogeneous catalysts are in different phase from that of the reactants. In most instances of heterogeneous catalysis, solid catalyst is brought into contacts with the reactants as either liquids or gases.

Reaction mechanism on a heterogeneous catalyst has consecutive steps. The entire cycle starts with the diffusion of reactants from feed stream to the catalyst surface. Reactants diffuse to the pores of the catalysts as internal diffusion and reach active site, where the reactants are adsorbed and interact with each other. After the reaction, products desorb from active site and diffuse to catalyst surface through pores. Finally, the reaction products diffuse into the surrounding medium (Le Page, 1987).

Industrial importance of the heterogeneous catalysis can be demonstrated by its wide range of products, from gasolines and plastics to fertilizers. Solid catalysts are very important for petroleum chemistry because they are used in most of the critical reactions. Their broad role includes many processes as the chemistry of evaluation of life and the control of automobile exhaust (National Research Council (U.S.), 1996).

1.1.2. Promoters and Poisons

The effectiveness of a catalyst is determined by its ability of formation desired products by increasing selectivity of them. Catalyst studies focus on promoters due to their notable impact on overall reactivity and selectivity of the catalyst. Promoters may not be catalytically active on their own, but they increase the efficiency of catalysts when mixed in small quantities with them.

The role of promoters in heterogeneous catalysis is very important for the design of successful commercial catalysis. They can be classified as structural promoters and electronic promoters. Structural promoters improve and help to stabilize the dispersion of active phase of a catalyst support, whereas electronic promoters influence the catalytic properties of the active phase itself. Electronic promoters significantly modify the chemisorptive properties of the catalyst surface. They affect the catalyst activity by changing the bond strength of the reactants and intermediates, therefore binding characteristics of the surface(Vayenas et al., 2001).

Many substances, called catalyst poisons, decrease the catalytic activity of the catalyst by blocking its active cites. Catalytic poisoning can be temporary or permanent. In temporary poisoning, the poisons are not adsorbed too strongly and gradually destroyed or eliminated from the reaction system, whereas in permanent poisoning, chemical forces hold the poisons at the active sides on the surface and the adsorption is strong (Patra and Samantray, 2011).

1.2. Propylene Oxide

Propylene oxide (PO), known as methyloxirane or 1,2-epoxypropane,is one of the most important organic chemical with a molecular formula CH_3CHCH_2O. It is a versatile chemical intermediate used in the production of a wide range of industrial products (Kirk-Othmer, 1997).

PO is a colorless and a highly volatile liquid. It has high miscibility with most common organic solvents, but forms a two-phase system with water. The compound exists as two optical isomers, and the commercial PO is racemic mixture. Some of the physical properties of PO showed in Table 1.1. PO forms azeotrope with dichloromethane,diethyl ether, cyclopentene, isoprene, cyclopentane, 2-methyl-1-butene, pentene, pentane, cyclohexane, hexene, and hexane (Ulleman, 1993).

Table1.1: Some physical properties of propylene oxide, C_3H_6O (Ulleman,1993)

Physical Property	**Constant**
Molecular weight	58.08 g/mol
Boling point (101.3 kPa)	34.23 ˚C
Melting point	-111.93˚C
Flash point	-37˚C
Critical temperature	209.1˚C
Critical pressure	4920 Kpa
Critical density	312 kg/m^3
Critical compressibility factor	0.2284
Heat of combustion (25˚C,101.3Kpa)	-33035 kJ/kg
Heat of polymerization	-1500 kJ/kg
Heat of fusion	112.6 kJ/kg
Heat of solubility in water at 25˚C	-45 kJ/kg
Solubility of PO in water at 20˚C	40.5 wt%
Solubility of water in PO at 20˚C	12.8 wt%

PO is a highly reactive compound used in the manufacturing of thousands of everyday products. Its high degree of reactivity arises from the strained, three-membered oxirane ring (Kirk-Othmer, 1997). Although most reactions of PO need acidic or basic catalyst, PO can reacts readily with hydrogen halides, chlorine and ammonia.

PO is mainly converted to polyether polyols(65%), propylene glycols(30%) and propylene glycol ethers (4%). Commercially, the most important reaction of PO is its polymerization to form polyether polyols which are used for the synthesis of (polyurethane) fumes. Polyols are produced by the reaction of epoxide and compounds or initiators, which are substances that contain active hydrogens such as alcohols or amines. The hydration of propylene oxide to form propylene glycol is also commercially important reaction that catalyzed by acids or bases to enhance reaction rates. However, the heat and the pressure are applied normally without catalyst in industrial processes. Propylene glycols are mainly used in the production of polyesters while propylene glycol ethers are usually used as solvents. Isopropanolamine, propylene carbonate, allyl alcohol, acetone and propanal are also products of the most important PO reactions(Kirk-Othmer, 1997;Nijhuis,2006).

1.3. Manufacture of Propylene Oxide

Propylene oxide has worldwide production value of over 8 million tons per year (Seubsai et al., 2011). PO is manufactured traditionally by chlorohydrin processes and indirect oxidation processes in industrial scale.

1.3.1. Chlorohydrin Process

The manufacture of propylene and ethylene oxide was historically maintained by the chlorohydrin process.

Today, this route is rarely used to synthesis ethylene oxide because of the development of more efficient direct epoxidation process, but it is still used as an important process for the manufacture of propylene oxide in industrial scale. Significant propylene oxide capacity is based on this process, which nearly accounts for about half of the world propylene oxide production (Yudin, 2006).

Commercial chlorohydrin process is carried out mainly in two reaction steps, which are synthesis of propylene chlorohydrin (chlorination) and dehydrochlorination of propylene chlorohydrin (epoxidation or saponification). These steps are followed by product purification.

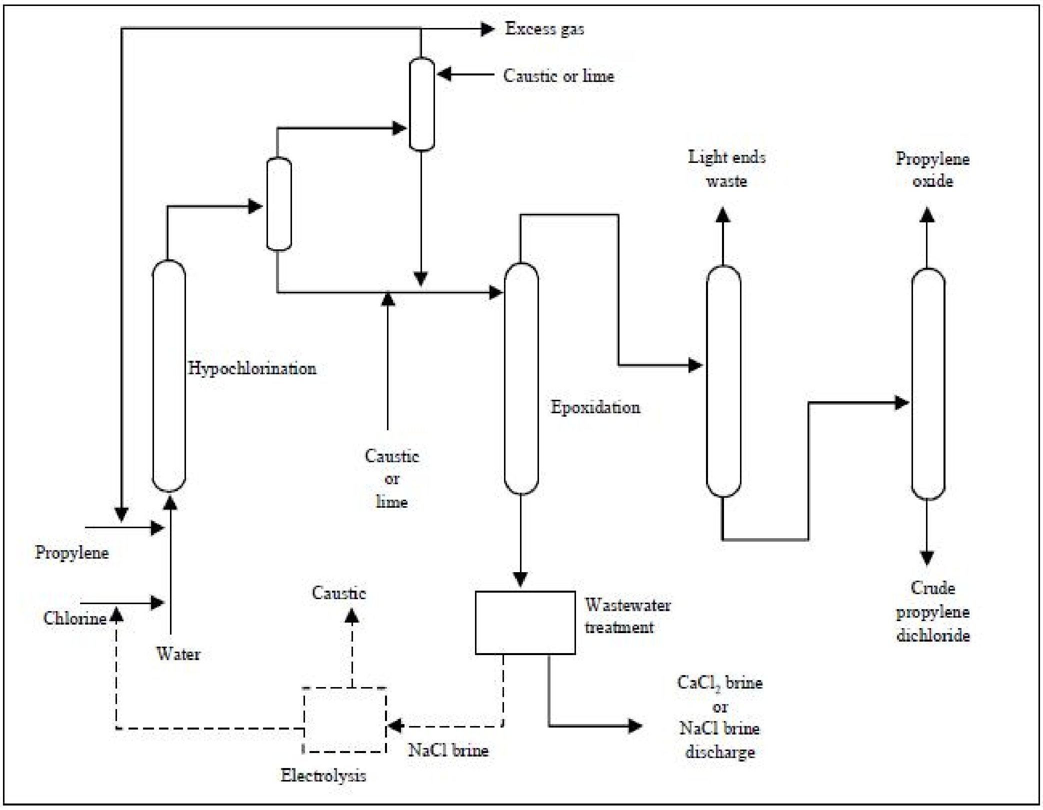


Figure 1.1: Flow scheme for PO production with chlorohydrin process (Kirk-Othmer, 1997)

In the first reactor shown in flowchart, the first reaction step of the chlorohydrin process, namely chlorohydrination, is shown. In chlorohydration, propylene gas and chlorine are mixed in aqueous solution to generate a propylene-chloronium complex.

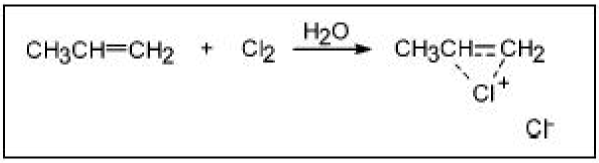


Figure 1.2: Chloronium production reaction in chlorohydrin process
(Kirk Othmer,1997)

This complex is then reacts with water to generate two propylene chlorohydrin isomers (1-chloro-2-propanol, 2-chloro-1-propanol) and hydrochloric acid. The first isomer in Figure 1.3 (1-chloro-2-propanol) represents 90% of the chlorohydrin produced and the second (2-chloro-1-propanol) represents 10% of chlorohydrin produced.

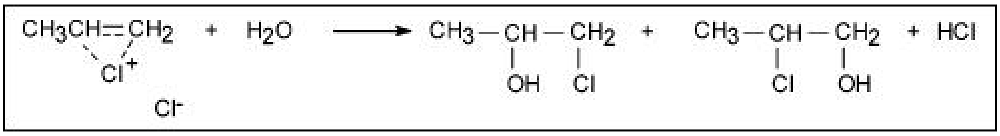


Figure 1.3: Chlorohydrin isomers production reaction in chlorohydrin process
(Kirk Othmer,1997)

The propylene-chloronium complex can also react with chloride ion to form 1.2-dichloropropane or react with propylene chlorohydrin to form dichloroisopropyle ethers as byproducts. The excess water used in the chlorohydrination is an effective method that minimizes the byproduct formation (Ulleman,1993).The chlorohydrination reaction is usually performed in one or more parallel reactors depending upon the capacity of the plant. The reaction temperature is in the range of 45 to 90˚C and the operating pressure is slightly above the atmospheric pressure

(1.1-1.9 bar).Besides, the selection of brick, rubber or plastic lined equipment as construction material is important because of the corrosive nature of the reactant mixture.

The other reaction step of the chlorohydrin process is the dehydrochlorination (epoxidation or saponification), taking place in the second reactor shown in the flow chart. In dehydrochlorination, propylene chlorohydrin reacts with a base, usually aqueous sodium hydroxide or calcium hydroxide, to produce crude propylene oxide and a dilute calcium chloride or sodium chloride brine stream. Figure 1.4 shows the dehydrochlorination reaction with the base $Ca(OH)_2$.

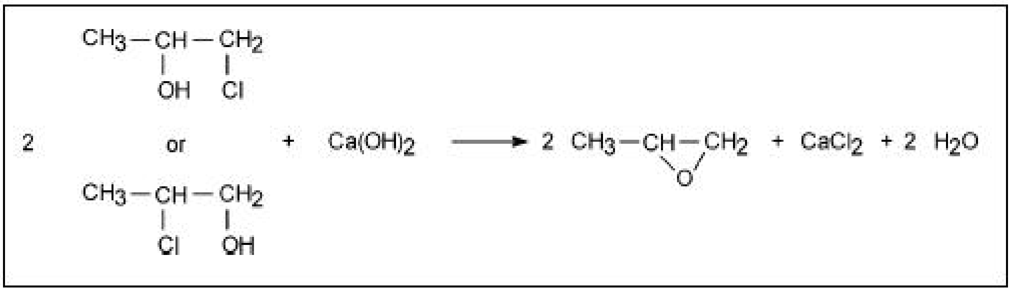


Figure 1.4: Epoxidation of chlorohydrin isomers with calcium hydroxide
(Kirk Othmer,1997)

In a subsequent reaction, PO undergoes hydrolysis to propylene glycol. In order to avoid this side reaction, PO is steam stripped from the reactor. The brine leaving the bottom of the reactor is then treated by biological oxidation to remove glycols and small amounts of other hydrocarbons present prior to discharge. Crude PO coming from the reactor as an overhead stream also contains some organic by-products and water. PO is further purified to sales specifications in packed or trayed distillation column.

Environmentally unfriendly chlorinated side products and large salty waste water are two main disposal problems that make the process unprofitable. So currently new chlorohydrin plants are not built and old ones are closed instead of modernized (Nijhuis et al., 2006).

1.3.2. Hydroperoxide Processes

The hydroperoxide process is the other commercial route that for PO production. The process is based on epoxidation of propylene with alkyl-hydroperoxide generated by peroxidation of an alkane. Propylene oxide and alcohol, products of epoxidation reaction, are then purified and the co-product alcohol is converted to a useful product for sale. In the view of economy, the hydroperoxide process is highly dependent on market of the co-product that usually 2-4 times of propylene oxide produce (Nijhuis et al., 2006). In current industry, two hydroperoxide routes are used, these are the propylene oxide-styrene monomer (PO-SM or SMPO) process and the propylene oxide- tert-butyl alcohol (PO-TBA) process.

1.3.2.1. PO-SM Process

In the PO-SM process, ethylbenzene (EBHP) is used for the peroxidation step and co- product styrene monomer is generated. In the first reactor, ethylenbenzene is noncatalytically converted to ethyl-hydroperoxide by liquid phase oxidation in air atmosphere. The oxidation is usually performed at 146˚C and 2 bars.

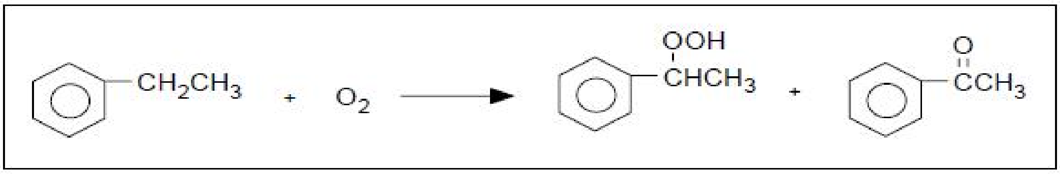


Figure 1.5: Ethylenzene hydroperoxide generation reaction in PO-SM process (Kirk Othmer,1997)

In the second reactor, the resulting peroxide stream is catalytically reacted with propene to produce PO.The epoxidation of propene is usually performed at 100˚C and 35 bars.The other reactor products are ∞-phenylethanol, acetophenone, and other organic impurities.

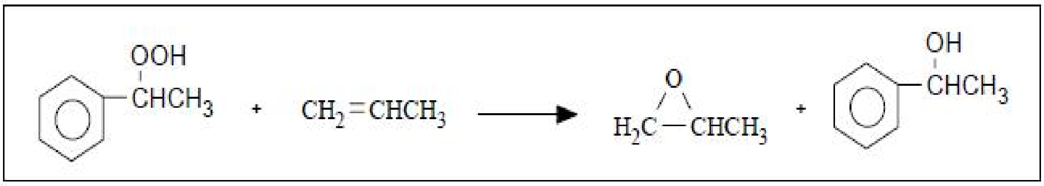


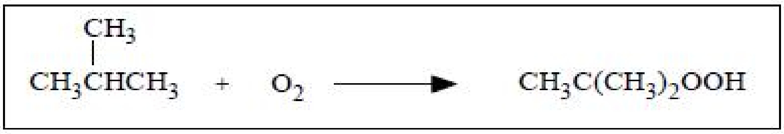
Figure 1.6: Propylene epoxidation reaction in PO-SM process (Kirk Othmer,1997)

In PO-SM process, there are two alternatives with respect to the type of the catalyst used in the epoxidation of propene.These are Halcon Process and Shell Process that uses homogeneous molybdenum catalysts and heterogeneous titanium based catalysts, respectively. The heterogeneous catalyst is recovered easier than homogeneous, so Shell process is more preferential.

Crude PO is purified in a distillation column. The remaining ∞-phenylethanol-rich mixture at the bottom of the distillation column is fed to a dehydration reactor. The dehydration occurs at 270˚C and 0.35 bar in the presence of alumina catalyst and triphenylmethane as solvent (Ulmann, 1993).

1.3.2.2. PO-TBA Process

In the PO-TBA process, isobutane is used for the peroxidation step and co-productsisobutene and methyl-tert-butyl ether are generated. In the process, isobutane, generated by is noncatalytically converted to tert-butyl hydroperoxide (TBHP) by liquid phase oxidation. TBHP is partially decomposes to tert-butyl alcohol. The oxidation is usually performed at 120˚C -140˚C and 25-30 bars.



$$CH_3\overset{\overset{CH_3}{|}}{C}HCH_3 + O_2 \longrightarrow CH_3C(CH_3)_2OOH$$

Figure 1.7: Oxidation of isobutene of tery-butyl hydroperoxide in the presence of tery-butyl alcohol (Kirk Othmer,1997)

The resulting peroxide stream is catalytically reacted with propene to produce PO and co-product tert-butyl alcohol.

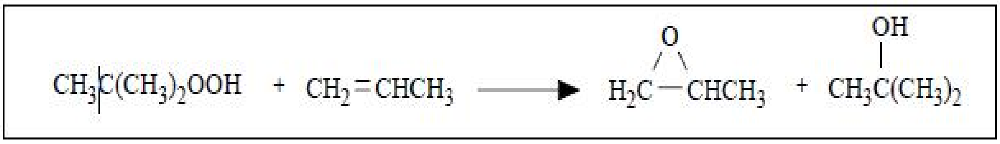


Figure 1.8: Propylene epoxidation reaction in PO-TBA process (Kirk Othmer, 1997)

The epoxidation of propene is achieved in a reaction system including up to five consecutive reactors. The preferred catalyst is generally an organometal in most cases vanadium,molybdenum with molybdenum complexes with napthenatesor carboxylates (Kirk-Othmer, 1997).

After epoxidation step, PO is then separated by distillation from the crude PO mixture consisting of tert-butyl alcohol, catalyst and medium and high boiling components. Co-product tert-butyl alcohol is purified for further utilization. This can be dehydrated to isobutene or can be used with methanol to generate methyl tert-buthyl ether which is important as a fuel additive for lead free gasoline (Ulleman, 1993).

The hydroperoxide possesses advantages that they are more selective and produce much less waste then the chlorohydrin process. However, the hydroperoxide processes always produce a fixed amount of co-product, which is the main disadvantage. The problem arises from the different markets for PO and the co-products.All of the latest plants using hydroperoxide process prefer PO-SM type instead of PO-TBA because of the decline in usage of methyl tert buthyl ether as a fuel additive (Nijhius et al., 2006).

1.3.3. Other Processes

1.3.3.1. Epoxidation of Propylene with Hydrogen Peroxide (H_2O_2)

A recent advance in propylene epoxidation is the production of PO using hydrogen peroxide (H_2O_2) as an oxidizing agent. In the process, epoxidation of propylene is accomplished catalytically by H_2O_2 in methanol as the solvent. The preferred catalyst is titanium silicate catalyst in the reaction. The other catalysts such as molybdenum oxide or tungsten oxide can be used for the reaction; however these are all very sensitive to presence of water. The propylene epoxidation with titanium silicalite-1 (TS-1) is carried out in a fixed-bed reactor at 313 K and atmospheric pressure. Crude PO is then purified by simple separation steps. The market value of H_2O_2 is comparable to PO, this limits the operationability of process for the epoxidation of propylene (Nijhius et al., 2006).

1.3.3.2. Epoxidation of Propylene with Nitrous Oxide (N_2O)

Nitrous oxide (N_2O) has been also widely explored as an oxidizing agent for the epoxidation of propylene. This method would be considered as an effective way to propylene epoxidation with the PO selectivity of up to 80% at conversions of up to 5% obtained over the potassium- promoted iron oxide on SBA-15 catalyst (Wang, 2004). However, the absence of N_2O commercially in large amounts limits the production of propylene using N_2O in industrial scale (Nijhius et al., 2006).

1.3.3.3. Epoxidation of Propylene with Molten Salts

In the late 1980's, The Olin Co. was piloted a process using molten alkali nitrate salts for the epoxidation of propylene. In the process, the propylene air mixture is flowed through the molten alkali salt mixture and the epoxidation reaction is carried out at a pressure of 20 bar and a temperature of 473 K. PO selectivity of 65% at 15% propylene conversion is obtained and the byproducts of this reaction are acethaldehyde, acrolein, carbon monoxide and carbon dioxide. Increase in selectivity is accomplished by recirculation of the aldehyde or by adding NaOH to the molten salt.The main problem of the performing of propylene epoxidation in a homogeneous gas-phase reaction is that it is very sensitive to reactor and operation conditions. This causes high differences in conversions and selectivities obtained. In addition, the side products in large quantities cause high separation costs (Nijhius et al.,2006).

1.3.3.4. Homogeneous Catalysts

Although numerous homogeneous catalysts are presented in epoxidation of alkenes, almost all of these catalysts only use hydroperoxides as oxidant. Through these hydroperoxides, high selectivities (>90%) at 10% propylene conversion can be obtained. The disadvantage of more selective homogeneous catalysts is that the catalyst is consumed during the reaction. This can be explained by two reasons. First, the catalyst cannot be reoxidized by molecular oxygen, after it oxidizes to propylene. Second, while the catalyst absorbs a molecular oxygen, it epoxides propylene with one of these oxygen atoms. The other oxygen atom remains bonded to the catalyst. This unreacted oxygen is not active in epoxidation of propylene, so it causes the decrease in active sites of the catalyst. Reactivation of the catalyst can be achieved by reduction in the second reactor.

Some of the homogeneous catalysts explored are performing better than most heterogeneous systems. However, processes based on these homogeneous catalysts are not preferred for application, because extra separation of the catalyst from the liquid stream is required in homogeneous systems. This causes also loss of the catalyst and ligands during separation process.

Furthermore, because of the high vapor pressure of propylene, the process is operated at high pressure in homogeneous system or the solvent for the reaction is required. Therefore, homogeneous process for propylene epoxidation shows some limitations due to its extra separation and pressure costs. Homogeneous processes are still valuable because of their successful application in other selective oxidation.

Regarding to economical and environmental concerns, many alternative methods including epoxidation using photochemically activated oxygen, electrochemical processes and biocatalytic systems have been mentioned in literature in order to develop a new propylene epoxidation process. However, so far, these alternative approaches, have produced insufficient propylene oxide yields to be able to consider soon as a feasible alternative for the existing processes (Nijhius et al., 2006).

1.4. Supported Catalysts

Supported catalysts are widely used in many industrial processes since they combine high dispersion with a high degree of thermostability of the catalytic component. The support is a thermostable, highly porous and usually inert material, to which active component is dispersed. The role of the support material is to allow the formation of a large particle of catalyst, which is comprised of very small easily sinterable crystals of catalysts. Sintering and agglomeration of these catalytic species are prevented by the help of support material. Supports are utilized in two ways. Firstly, a support may be utilized as a refractory surface to which catalyst crystals are affixed. This method is usually applied for catalysts in which valuable metals are used, because the volume of support is significantly greater than the volume of catalytic species. Such catalysts are preferentially prepared by the method of impregnation. Secondly, the support may be utilized as finely divided refractory crystals sited between particles of catalytic species by this way the contact of such species is prevented.

The selection of proper support is based on its attractive features, which are mainly chemical inertness, surface area, thermal stability under conditions of reaction and regeneration, porosity, low cost in industrial scale, and outstanding mechanical properties such as attrition resistance, hardness and compressive strength. Considering combination of these desirable features mentioned,alumina, silica and activated carbon are mostly used supports in industry (Caralo, 1997).

1.4.1. Methods for Preparation of Supported Catalysts

1.4.1.1. Co-precipitation

In the co-precipitation method, the reaction occurs between catalytically active metal salt solution, support material salt solution and a precipitating agent, generally hydroxide, alkali carbonate or bicarbonate. After a while, precipitation of hydroxides or hydroxyl salts start and resulting precipitate form a homogeneous mixture. The homogeneous mixture is then filtered off. The solids dried and calcined to convert desired metal oxides. The control of this process is usually difficult. The solution should be kept homogeneous in order to allow two components to precipitate at the same time and change in pH throughout the solution should be prevented (Chorkendroff and Niemantsverdriet, 2003).

1.4.1.2. Impregnation, Ion Exchange and Adsorption

Impregnation is one of the widely used methods for preparing supported porous catalysts. Among all the heterogeneous catalyst preparation methods, the impregnation is known as the simplest, cheapest and most commonly used method. In the impregnation method, the metal-containing solution is contacted with the support material for a certain period of time. The support is then dried in order to remove imbibed liquid. The catalyst is finally activated by calcination, reduction or other proper treatment. The amount of the active element in the catalyst depends on the concentration of active element solution and its penetration into the catalyst.

Impregnation methods can be applied either with excess solution or with repeated application of solution depending on the total amount of solution. In the first method, namely wet impregnation, the metal-containing solution is added in excess amount to the support and contacted with support for the time needed for total impregnation. The solid is then drained, dried and calcined. In the second method, the support is contacted with the metal-containing solution, which is in the volume corresponding to total known pore volume or slightly less. This is a more controllable method that also called dry impregnation, also called incipient wetness impregnation.

For both methods, temperature is the major factor that affects both the solubility of precursor and viscosity of the solution, consequently, wetting time (Caralo, 1997).

Ion-exchange method, used in preparation of various metal support combinations, involves replacing of ion species in an electrostatic interaction with the surface of a support. Support including ion A is exposed to an excess volume of solution including ion B, which gradually diffuses into the pores of the support material and takes the place of ion A. This continues until distribution of the two ions between support and the solution comes to equilibrium(Perego and Villa, 1997).

Adsorption is used to define all processes in which an electrostatic attraction occurs between the ionic species from aqueous solution and charged sides on a solid surface. There is a characteristic difference between ion-exchange and adsorption.

Ion-exchange is applied for the systems that require charge compensating ions, such as zeolites, cationic clays or layered double hydroxides. Instead a pH-dependent surface charge is created by most oxide supports when they are placed in an aqueous solution. These oxides tend to adsorb cations (SiO_2–Al_2O_3, SiO_2) or anions (ZnO, MgO). In addition to these, some oxides tend to adsorb both cations in basic solutions and anions in acid solutions (TiO_2, Al_2O_3). The surface can be positively charged or negatively charged, which is controlled by its isoelectric point, at which net charge on the support is zero, as well as by the pH and ionic strength of the solution (Campanati, 2003).

1.4.1.3. Deposition-precipitation

Deposition precipitation involves two steps, which are precipitation from bulk solutions and interaction with the support surface. Powders or particles of the salt in desired amount are used for the formation of slurries, and then alkali solution in sufficient amount is added to precipitation. In order to avoid deposition outside the pores of the support, precipitation in the bulk solution should be prevented. Uniformly distributed and homogeneous active phase is obtained by the direct interaction of OH− groups of the support with the ions present in the solution. The nucleation rate at the surface must be higher compared to the nucleation rate in the bulk solution and the solution homogeneity must be preserved. As a source of OH- the urea is preferred to use in order acquire uniform precipitation. The use of urea, which is solvable in water and decomposes slowly at 90˚C, gives a uniform OH− concentration in both the bulk and pore solutions (Campanati, 2003). After the deposition-precipitation step, solid is filtered, washed,dried, shaped and finally calcined. If necessary, reduction or sulfidation is used additionally for activation (Chorkendroff and Niemantsverdriet, 2003).

1.4.1.4. Sol-Gel Method

The sol-gel processing is widely used in catalyst preparation owing to its versatility and precise control over the product characteristics. It is a wet chemical technique that applied for the production of widely used materials, such as fibers, powders, monolits and composites. The intrinsic advantages of the method are a high degree of homogeneity and purity, controlled porosity, processing at low temperature, uniform phase distribution in multicomponent systems, and high pore size distribution. With the sol-gel method, preparation of new crystalline and non-crystalline materials can also be prepared; additionally the method enables easy preparation of thin films and coatings.

The process is called “sol-gel”, because a sharp increase in viscosity occurs at a particular point in the series of process steps. A sudden increase in viscosity indicates the beginning of gel formation. In the process, the inorganic oxides are produced from inorganic or organometalic precursors. Typical precursors are metal alkoxides since they can react easily with water.

The sol-gel process incorporates several physical and chemical steps. First step is called hydrolysis, which begins with formation of a solution with a mixture of metal alkoxides and water in a mutual solvent, generally alcohol. The reaction takes place at ambient temperature in the presence of a mineral acid or base as a catalyst.

For instance, the hydrolysis of tetraethylortosilicate (TEOS,$Si(OC_2H_5)_4$) causes to formation of silanol groups (Si-OH) via the attachment of hydroxyl group(OH) to the silicon atom. The hydrolysis reaction is completed depending on adequate amount of water and appropriate catalyst used in the reaction.

In the next step, the condensation reaction of adjacent molecules occurs, where partially hydrolyzed molecules are linked together. For the formation of silica based materials, siloxane bonds (Si-O-Si) are formed in condensation reactions. In addition, water or alcohol is released during the reaction. Repeated reaction causes macromolecule formation from the silicon molecule by the process of polymerization.

The following step is gelation, in which interconnected three dimensional network is formed by the linkage of polymeric networks throughout the liquid (Tskalakos et al., 2001).

The viscosity of the clear solution increases suddenly at a particular point called gelation point, and the solution is appeared like an elastic solid. After the gelation point the change in structure and properties of the gel continues during aging process. Syneresis which is called the shrinkage of the gel and the expulsion of liquid from the pores is observed during aging. Aging process may include further condensation or other bond forming processes. Increase in the degree of cross-linked network and gel viscosity occurs during aging process, so mechanic strength and rigidity of the gel are improved with aging (Brinker and Scherer, 1990).

The next steps of the sol-gel process are drying, dehydrating and densification. In drying, water and alcohol are removed at a temperature less than 470 K., leaving hydroxylated metal oxide with residual organic content .During dehydration, organic residues and chemically bounded water is removed at temperatures between 670 K and 1070 K and a glassy chemically stable ultraporous solid is produced. The last step is densification, in which formation of dense oxide product takes place at temperatures above 1270 K.

1.5. Combinatorinal Catalysis

Drug development faced important change in the 1990s via the fast synthesis and various formulations on fully automated working stations and analytics. This method which is called “combinational method” began to be used in other research areas. Emerging technology for automation, micromechanics and computation made the automation of high throughput screening of considerable solid catalysts possible. Therefore, fully automated robots designed for fast catalyst synthesis and multiple parallel reactors for parallel for catalytic testing can now be used.

Combinatorial catalysis is a sophisticated methodology in which large diversities of distinct catalytic materials are synthesized and tested in parallel. The methodology involves coordinating high throughput methods for synthesis, characterization and reactivity testing of catalyst, managing large amount of data, and optimizing methods for design of experiments rapidly. Combinational approach allows discovery of potentially high performing catalysts in a short time by increasing the examination of many variables. Indeed, this methodology enables to research diverse effects such as promotion and synergy between catalyst and support and the influence of these effects on the performance of the catalyst for a specific reaction.

The invention of heterogeneous catalysts is a milestone because differently than 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 definite detection of a specific molecule in the area of small catalyst sites. Various methods have been applied to screen heterogeneous catalyst libraries so far (Senkan and Ozturk, 1999).

Optical Methods: Color indicator method is the appropriate optical screening for liquid phase reactions. The initial application of this method was held to analyze the relative activity of a range of conventional hydrosilation catalysts.

Infrared (IR) Techniques: The easily applicable infrared (IR) thermography is generally used to screen the activities of various catalytic materials. Solid state catalytic materials can also be screened by Fourier transform infrared (FTIR) spectrometry.

Laser Induced Fluorescence Imaging (LIFI): This technique uses the changing function of fluorescence properties of molecules as a result of the breakage and the formation of chemical bonds. This technique has a limited application because it can only be applied to screen (detect) fluorescent species.

Resonance-Enhanced Multiphoton Ionization (REMPI): Contrary to former techniqueLaser Induced Fluorescence Imaging (LIFI) technique, this technique is highly applicable to gas phase species. It is based on the in situ ionization of reaction products by UV lasers. Then it detects the photoions or electrons by spatially addressable microelectrodes which are in the area of the laser beam.

Photothermal Deflection (PTD): New optical techniques are expected to be raised to screen libraries of catalytic materials ın a case by case basis. The photothermal deflection (PTD) method has recently been observed to detect ethylene in an ethane background.

Mass Spectrometry Methods: Mass spectrometry is a broadly used detection technology to detect complex gaseous mixtures. Lately, a quadrupole mass spectrometer (QMS) based systemhas been reported to screen heterogeneous catalyst libraries sequentially.

Gas Chromatography Method (GC): This method is used to apply quantitative analysis on complex mixtures however chromatographic separations are usually the time limiting part of high-throughput screening. To analyze reaction mixtures and evaluate data in real-time, offline and online gas chromatographic separations covering chromatography has been held to find out an ideal work flow.

1.6. The Objective of the Study

Propylene oxide (PO) is one of the most important commodity chemicals produced by two major industrial processes; the chlorohydrin process and the inorganic hydroperoxide process. These processes are complex and expensive. However the direct epoxidation of propylene by molecular oxygen has long been the most desirable as well as challenging goal of production of PO in view of environmental friendliness, simplicity and operating costs.

In the study, the object is to investigate various catalysts with combinational approach for the advance of highly active and selective novel catalysts for direct epoxidation of propylene to PO with molecular oxygen at atmospheric pressure. Oxide based metal catalysts including Cu, Ru, Ag, Mn monometallic and multimetallic systems supported on different silica supports were synthesized via impregnation method and sol-gel method. Indeed, the effects of different promoters on the activity of these catalyst candidates were investigated. The performance of these catalysts were tested and ranked in macro amounts in a high throughput activity and selectivity testing apparatus. The selected catalysts were reranked in a normal speed activity test unit in which higher amount of catalyst were tested. These catalysts were structurally characterized by X-ray diffraction (XRD), X-ray photonelectron spectroscopy (XPS), the multipoint Brunauer, Emmett and Teller (BET) method, AND Fourier transform infrared (FTIR) spectrometry in order to draw meaningful correlations between catalytic activity and physico-chemical structure of catalysts.

CHAPTER 2

LITERATURE SURVEY

The heterogeneously catalyzed epoxidation of alkenes, especially ethylene and propylene, is an important goal in chemical industry, since epoxides are commercially important intermediates used in the manufacturing of many industrial products (Lambert et al., 2005).

Propylene oxide (PO) is one of the extremely important organic chemicals for the manufacturing of a wide range of products, mainly polyether polyols, propylene glycol and propylene glycol ethers. Currently, PO is produced by two conventional methods, which are chlorohydrin and organic hydroperoxide processes. In the chlorohydrin process, equipment corrosion and environmental problems arises from stoichiometric amounts of waste salts and some chlorinated by-products. While in the hydroperoxide process, equimolar amounts of co-product appears together with desired products, so the method has the co-product limitation (Lu et al., 2002). Because of the deficiencies of these processes, researchers have developed many novel methods of producing PO by oxidizing propylene directly using proper catalytic systems combined with proper oxidant. Some of these novel methods are, for example, TS-1/H_2O_2 system, in situ-generated H_2O_2 systems such as gold supported on titania (Au/TiO_2), and using N_2O as the oxidant. However, these oxidants are costly and H_2 utilization is not efficient that restricts to commercialize these processes. Therefore, the direct gas-phase epoxidation of propylene to PO by molecular oxygen has been under intense research as the most attractive process in view of the economy and green chemistry (Su et al., 2009).

In 1998, Haruta and coworkers reported gold catalysts supported on titania as highly selective catalysts for direct epoxidation of propylene to propylene oxide. Above 99% selectivity and 1% conversion were achieved when Au/TiO_2 catalyst was tested at relatively low temperatures and atmospheric pressure with the presence of H_2 and O_2 in the reaction environment It was also reported that H_2 in reactant stream enhances the oxidation of propylene over Au/TiO_2 catalyst (Hayashi et al., 1998).

The discovery of the high activity of Au on titania catalyst triggered other studies about Au supported on titania catalysts. The test of Au/TS-1 reported that the selectivities between 60-85% and activities between 2.5-6.5% were obtained. In these studies, activity and selectivity values were changeable based on the Au composition between 0.06-0.074wt% and Ti/Si ratio which is between 33 and 48. It was observed that catalysts have higher stability and higher activity if they contain low amount of Au and Ti (Yap, Andres et al. 2004). However, Au with its high selectivity value is not useful for industrial reasons because of the need for hydrogen co-feeding and low propylene conversion (Suo et al., 2008).

The silver catalyzed epoxidation of ethylene by molecular oxygen has been commercialized for many years. In the process, ethylene oxide (EO) is produced by using Ag catalyst supported on α-alumina. Addition of alkalis and halides as promoters increases EO selectivity near 90%. On the other hand, epoxidation of propylene over Ag/α-alumina is not successful for commercial application. The yield and selectivity are lower than those for ethylene oxide as a result of the existence of allylic hydrogens in propylene. The allylic C-H bonds are much more active toward oxidation than vinyl C-H bonds in ethylene which clarifies the lower selectivity in propylene epoxidation (Wang et al., 2008). However it is also remarkable that, silver catalyst could be also successful for epoxidation of propylene by modification of the catalyst which would cause the adsorbed oxygen species with proper electronic properties.

Therefore many studies about the activity of modified and unmodified Ag based catalysts on propylene epoxidation have been reported with different support materials and modifiers. Some of these studies about the effectiveness of supported Ag catalysts on the propylene epoxidation were expressed below:

Lu and coworkers (Lu et al., 2002a) investigated the effect of NaCl promoter on the catalytic performance of Ag catalysts. After the comparison of different Ag catalysts, it was stated that Ag_2O, Ag and AgCl cannot be the right phase for propylene epoxidation. For Ag catalyst it was reported that PO selectivity was only 0.35% at 32.5% propylene conversion. Addition of NaCl increased the PO selectivity up to 29.1% at 11.2% propylene conversion for NaCl/Ag (5 wt %) catalyst. Different types of promoters, Na and K salts (Cl,Br,F salts),were loaded to the Ag catalysts and their effect of the catalytic performance were also investigated. Among these promoters, highest selectivity was obtained by modification of Ag with 10 wt% NaCl (31.6% selectivity at 12.4% propylene conversion). In the study, it was also reported that AgCl formed in the preparation step modify the electronic property of Ag catalysts, so inducing the adsorbed oxygen species to become electrophilic, which is efficient for epoxidation of propylene. In the study, proper propylene to oxygen ratio (C_3H_6:O_2) was also investigated and the highest selectivity was obtained with the ratio C_3H_6:O_2=0.5 in the feed gas.

Palermo and coworkers (Palermo,2002) studied supported Ag based catalysts for the epoxidation propylene. In the study, Ag catalysts were supported on different oxide, which are α-alumina, K promoted β-alumina and $CaCO_3$. In addition to supports, the effect of the modifiers (K, NO, Cl and their combinations) on the catalytic performance of the Ag catalysts was also investigated. The research group concluded from the results that $CaCO_3$ is the most effectual support material and K is the most effectual modifier among the investigated modifiers in the study in spite of low PO selectivity and propylene conversion.

Ag catalysts supported on $CaCO_3$ with different loading levels was also investigated in another study in order to state the effect of particle size of a metal on ethylene epoxidation and propylene epoxidation. $Ag/CaCO_3$ catalysts were prepared with loading levels of 0.5-56 wt%. In the study, it was observed that epoxidation of ethylene is enhanced 3-5 fold at 473-493 K by large particle, but epoxidation of propylene is not affected by particle size significantly. In addition, XRD and UV-vis spectroscopy results showed that bulk of particles contain silver in Ag0 state, but small particles contain silver in Ag+ state. It was also reported that lower silver loading increase the Ag+ / Ag0 ratio. The research group concluded that the layer of Ag_2O possibly cover the small particles, which causes lower selectivity for epoxidation for both propylene and ethylene oxidation in the small size system (Lue et al., 2005).

After that, the same research group also investigated the effect of different supports on the catalytic performance of Ag catalysts. The best results were obtained for medium surface area support such as α-Al_2O_3 and low surface area supports such as $CaCO_3$ which gave high TOF values for PO formation. In the study they concluded that PO formation is favored by large silver particles. On the other hand, the effect of the particle size on propylene epoxidation reported as low in their previous study. Beside the different support materials, various promoters loaded on $Ag/CaCO_3$ catalysts were also investigated in the research, and NaCI was reported to be an successful promoter for the epoxidation of propylene. Addition of 1wt% NaCI to unpromoted catalyst (56%$Ag/CaCO_3$) caused a dramatic decrease in propylene conversion from 60% to 1-3%, but a high increase in PO selectivity from <2% to 39.2%.It was explained that loading NaCI modify the electronic characteristics of the catalyst, leading to adsorbed oxygen species to become electrophilic and increase the Ag size of the Ag particles. While the maximum distribution was at 370 nm for the unpromoted Ag catalyst (56%$Ag/CaCO_3$ sample), it was at 800 nm with more regular shape for the 56%$Ag/CaCO_3$ catalyst modified with 1wt% NaCI (Lu et al., 2006).

Wang and coworkers investigated Ag catalysts supported on titanium silicate (TS), which is commonly used as a support in the presence of oxygen and hydrogen to generate peroxide for Au catalysts. In the study, the efficiency of the parameters of Ag loading, support material, Si/Ti ratio of TS-1, and calcination temperature were researched. According to the results, these parameters were reported as highly effective on the performance of the catalyst. The effect of support materials were observed by using TiO_2, SiO_2, HZSM-1 and TS-1 as support materials. Among these supports, TS-1 was reported as the best support. Over Ag/TS-1 catalyst, optimum activity was obtained as 91.21% PO selectivity at 0.92%propylene conversion when Ag loading was 2.0wt% and Si/Ti ratio was 64. In addition, calcination of the catalysts at 450˚C in air exhibited the optimum catalytic performance (Wang et al., 2003)

The research on propylene oxide (PO) has been also performed by bimetallic Ag containing catalytic systems in order to enhance selective propylene epoxidation to PO.

Takahashi and coworkers are one of the many groups studied the catalytic effect of bimetallic systems for the issue. They studied Ag-based catalysts including Mn, Fe, Co and Ni and reported that Ag based catalysts containing Ni showed highest PO yield. Over Ag-Ni catalyst at 33 mol% Ni, PO selectivity was obtained as 11.8% at 6.5% propylene conversion, and that was obtained as 2.5% at 7.9% conversion for the Ag single catalyst. From XRD and TEM results, the research group showed that increase of Ag particle dispersion in Ag-Ni catalyst was parallel with the Ni content which indicates that Ni atoms controlled the Ag particle size by repressing the sintering of Ag particles. In the study, it was also suggested that oxygen species on the terrace sites (nucleophilic) and defect sites (electrophilic) on the Ag surface worked in cooperation for catalyzing epoxidation of propylene (Takahashi et al., 2005).

For the epoxidation of propylene, Ag-$MoNO_3$ catalyst was also investigated by the Jin and coworkers. In the study, they observed firstly the activity of the unsupported $MoNO_3$ modified Ag catalysts with different $MoNO_3$ loading levels. Over MoO_3-free Ag catalyst, PO selectivity was obtained as 0.8% at 58.9% O_2 conversion, and that was obtained as 34.3% at 7.1% O_2 conversion over the 50%Ag- 50% MoO_3 catalyst. In addition, the effects of different support materials ($CaCO_3$, CaF_2, SiO_2, TiO_2, ZrO_2, TiO_2-ZrO_2 and TiO_2-SiO_2) were investigated and the highest PO selectivity was obtained for ZrO_2 which improved the catalytic performance of Ag-MoO_3 catalyst. After that, the effects of the parameters reaction temperature and space velocity were also researched over 20%Ag-4%MoO_3/ZrO_2 catalyst. It was suggested that low reaction temperature or high space velocity increase the PO selectivity by hindering the deep oxidation of propylene. The catalysts with larger particle size of Ag-MoO_3 (300-500 nm) showed higher PO selectivity (Jin et al.,2004;2005).

Although studies generally reported that Ag particles with larger or proper size (20-40 nm) is required for high activity (Lu et al. 2006; Ji et al.,2005), Lei and coworkers showed in their study that unpromoted size-selected Ag^3 clusters and ~3.5 nm Ag nanoparticles supported on alumina achieved higher PO formation rate with insignificant amount of CO^2 than for any previously studied Ag catalysts. In the study, they also showed that for oxidation activity and selectivity of oxidized silver trimers were higher than extended Ag surface with density functional calculation (Lei et al., 2010).

The efficiency of Cu based catalysts for epoxidation of propylene was investigated by many research groups after determining selectivity of Cu is higher than Ag for the epoxidation of alkenes (Cowell et al., 2000).

Lu and coworkers studied on NaCl modified VCexCu1-x (x=0-1) catalysts for epoxidation of propylene. They reported that VCe-NaCl (20) is inactive for epoxidation reaction and Cu content has an important effect on the catalytic performance of the catalyst by comparison of the activity results of VCe-NaCl (20) and VCexCu_{1-x}-NaCl (20) catalysts. In the study, they obtained the highest selectivity with $VCe_{0.2}Cu_{0.8}$-NaCl(20) (43.4% at 0.19% conversion).From the XPS results, they also stated that Cu^0 may be the active phase for epoxidation of propylene(Lu et al., 2002b).

Vaughan et al. studied on 1% and 5% cupper loaded Cu/SiO_2 catalysts. For 1%Cu/SiO_2, PO selectivity reached its maximum (53% at 0.25% propylene conversion) at 225˚C and decreased to a negligible value at 275˚C (1.26% of propylene conversion).The behavior of 5%Cu/SiO_2 was similar to 1%Cu/SiO_2 ,but PO selectivity was significantly lower (15% PO selectivity and 0.24% conversion at 225˚C).In the study, they also investigated the effect of various alkaline and chlorine additives on the catalytic performance of 5%Cu/SiO_2 catalyst. The results of 5 wt% NaCI-modified and 5wt%CI-modified catalysts synthesized with impregnation method showed that PO selectivity decreased with these additives. From the XPS and Auger spectroscopy results, they also stated that Cu^0 is the active phase in highly dispersed atomic like form (Vaughan et al., 2005).

Lambert and coworkers performed surface chemistry studies about the oxidation chemistry of allylbenzene, trans-methyl stryrene and α-methyl stryrene on Ag and Cu single crystal surfaces and investigated the variations in their oxidative behavior on these surfaces. They stated that Cu is more selective than Ag for epoxidation of alkenes because Cu surface maintains to catalyze selective oxidation successfully when the alkene contains allylic hydrogen atoms, but Ag burns these alkenes. They also reported that epoxidation degree strongly related with the closeness of C=C bond to the Cu surface (Lambert et al., 2005).

Cu and Ag surfaces were also investigated by Torres and coworkers. In the study, they used DFT quantum chemical calculation method on Cu(111) and Ag(111) surfaces for determination of thermochemistry and activation-energy barriers. From the periodic slab calculation results, the reason behind the higher epoxidation activity of Cu than Ag was explained by the lower basicity of oxygen adsorbed over Cu. The catalytic performance of Ag on propylene epoxidation is disfavored by the basic character of adsorbed oxygen causing allylic hydrogen stripping and combustion,while catalytic performance of Cu is favored by lower basicity of cupper providing metallacycle formation then epoxide production (Torres et al., 2007).

Epoxidation reaction of propylene was investigated in another surface chemistry study, where Cu and Ru-Cu surfaces were studied by Kizilkaya et al. In the study, they used periodic density functional theory (DFT) calculations on metallic Cu(111) and bimetallic Ru-Cu(111) surfaces. From the calculation results on Cu(111), it was reported that Cu (111) favored the oxametallacycle (OMMP) formation over AHS. On the other hand, the results obtained on Ru-Cu (111) surfaces showed that the energy barrier for the stripping of the hydrogen atom is lowered, whereas energy barrier for OMMP formation was increased on the Ru-Cu(111) surface when compared to the Cu (111) surfaces. This result indicated that Ru-Cu (111) surface would inefficient for PO production. The reason of that was investigated by Bader charge analysis and chemisorptions of the probe sulfuric acid molecule on the oxygenated metal surfaces.From the results, they concluded that because of the higher basicity of atomic oxygen adsorbed over Ru-Cu (111) surface, the subtraction of allylic hydrogen of propylene occurs instead of formation of PO intermediate (Kizilkaya et al., 2010).

Chu and coworkers studied on the CuOx/SBA-15 catalysts and their catalytic performance after modified with potassium (at K/Cu=7). Without K+ modification, they reported that PO selectivity was 9.9% at 0.77% propylene conversion (at 498 K) and acrolein was the main product. After modification, PO formed as a main product and its selectivity increased to 59% at 0.40% propylene conversion (at 498 K) and 46% at 0.95% propylene conversion (at 523 K). For the epoxidation of propylene at oxygen-rich atmosphere, they concluded that catalytic performance of the halogen-free K^+–modified CuOx/SBA-15 catalysts was higher than Cu-based catalysts reported so far (Chu et al., 2006).

Wang and coworkers performed NH3-TPD measurements and observed that amount of K^+ reduced the strength and the amount of the acid sites. From these and the XPS results, they also stated that Cu^I or Cu^{II} is the active phase for the epoxidation of propylene by O_2 (Wang et al., 2008).

Their further study was conducted with the purpose of determination the exact state of Cu obviously. From in-situ XRD and FT-IR measurements of K^+-5wt%CuO_x-SiO_2 (K/Cu=0.2) catalyst, they reported that Cu^I is the active phase for the epoxidation of propylene by O_2 (Zhu et al.,2008).

In the study belongs to Su et al., catalytic effects of various promoters on Cu/SiO_2 system for propylene epoxidation were investigated. As a result of the experiments conducted at different reaction conditions halogen-free K was stated as the best promoter for Cu/SiO_2 system. In addition to these, they reported that both Cu^0 and Cu^I particularly Cu^0 in the small cluster are essential for epoxidation of propylene (Su et al.,2009).

Modifying effect of various transition metals and metal oxides on the catalytic performance of the unsupported Cu catalysts was investigated in another study.It was observed that the modification by vanadium increased the activity of the Cu catalysts and highest PO formation was obtained for catalyst with V/Cu atomic ratio of 0.11-0.20. Characterization results revealed that the dispersion of Cu was enhanced by the presence of vanadium, which might increase the catalytic performance. It was also reported that higher performance was obtained by pre-reduction of the VO_x-Cu catalyst when compared to the oxidation pretreatment and an induction stage was observed for PO formation over the reduced catalysts. In situ XRD analysis showed that the presence of VO_x promoted the partially transformation of Cu^0 in the reduced catalyst to the Cu_2O in propylene epoxidation. From the structure-performance correlations, it was also suggested that Cu^I was the active site for epoxidation of propylene. In addition, activation of oxygen was promoted by the vanadium species at lower valance states(V^{III} and V^{IV}) .From the H_2–TPR and C_3H_6–TPR studies, the existence of VO_x was revealed to suppress the reactivity of the lattice oxygen in the working catalyst (Yang et al.,2010).

In addition to study on Cu catalyst modified with alkali metals as promoter, the research on propylene oxide (PO) has been also performed by bimetallic or multimetalic Cu containing catalytic systems in order to enhance selective propylene epoxidation to PO.

Liu et al. investigated the effect of alone or binary combination of different additives (KNO_3, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Ba(NO_3)_2$, $CaCl_2$, $LiNO_3$, NaCl) on the Ti and Al containing hexagonal mesoporous silicates. In the study, the highest activity was observed with the $Ca(NO_3)_2$- and KNO_3- modified Ti-Al-HMS catalyst, obtained 19% PO yield for the epoxidation of propylene at 523 K, which was 14.6% for of Ti-Al-HMS catalysts (Ti/Al/Si = 4/1/100 (molar ratio)). Although high PO yield was obtained with the Ti-Al-HMS catalysts, these catalysts deactivated rapidly because of the carbonaceous deposit on the catalyst surface. Addition of a little amount of H_2 to the feed gases decreased the deactivation speed to a great extent, but could not fully suppress catalyst deactivation (Liu et al. 2006).

Recently, Bracey and coworkers investigated the efficiency of the binary combination of Au and Cu catalysts supported on SiO_2 for gas phase propylene epoxidation. In their experimental study, they stated low interaction between Au and Cu species by the visible spectroscopy .Pretreatment with H_2 led to catalyst reduction that caused to triggered formation of Cu-Au alloy in which interaction between the Cu and Au metals is higher. Besides, implementation of the XPS analysis revealed the presence of Cu_2O species and metallic Au. From the activity tests, PO selectivity was obtained up to 70% while conversion was generally less than 1% (Bracey et al.,2011).

In a recent study, supported Ag-based bimetallic catalysts with low Ag loading of 3.0 wt% were explored for epoxidation of propylene. Among these catalysts, prepared by surfactant-protected colloidal method, the highest catalytic performance was obtained for the $BaCO_3$ supported bimetallic Ag-Cu catalyst. In the study, the highest activity was observed with the Ag_{95}-Cu_5/$BaCO_3$ bimetallic catalyst, obtained 55.1% PO selectivity at 3.6% conversion. From the XRD and TEM analysis, it was indicated that Cu can act as a regulating factor for the size of Ag crystallites to restrict their agglomeration. XPS analysis showed that Cu makes Ag electropositive by withdrawing electrons from nearby Ag, which provides production of more active sites where electrophilic oxygen species can be absorbed to increase the PO selectivity. Besides, H_2-TPR analysis conducted for Ag/$BaCO_3$, Ag_{95}-Cu_5/$BaCO_3$ and Cu/$BaCO_3$ catalysts showed that presence of the synergistic effect between Ag and Cu increases the activity by regulating the reactivity and the amount of the oxygen species adsorbed on Ag surface (Zheng et al.,2012).

In heterogeneous catalysis, the development of potentially high performing multicomponent catalytic systems requires more effective methods when compared to conventional approach in which high time effort required for synthesizing and screening potential solid catalysts. Over the past decade, more modern and sophisticated methodologies were designed for high throughput experimentation (HTE). In these methodologies, large diversities of distinct catalytic materials are synthesized and tested in parallel using special purpose devices. The improvement and application of special-purpose methods for HTE has been the subject of various studies in heterogeneous catalysis.

Senkan and co-workers used combinational methodology to investigate the catalytic performance of Pt and Pd catalysts in dehydration of cyclohexane into benzene by resonance-enhanced multiphoton ionization (REMPI) detection technique. They also studied the activity of catalysts including Pt, Pd and In metals by REMPI and quadrupole mass spectroscopy (QMS) techniques. Detection of benzene with these two techniques showed that combinational method was effective in determination of activity of the catalysts in a short time (Senkan, 1998; Senkan and Ozturk, 1999).

Combinational method was also applied by Miyazaki and coworkers to discovery active catalyst for epoxidation of propylene by molecular oxygen as an oxidant.
They investigated the performance of alone or binary combination of 34 metals supported on γ-Al_2O_3. They used three metal loading level (0.1%, 1% and 10wt%) and reported that highest PO level (1000 ppm) was obtained for 1.0%Rh at 1% conversion among unimetalic systems. Among binary systems, they reported that highest PO level (2000 ppm) was obtained at 1% conversion. They observed high PO levels with Rh-V, Rh-Cr, Rh-Sn, Rh-In, Rh-Mo and Rh-Sm catalytic systems although substantial CO_2 product was formed. Besides, Rh-Ag, Rh-Zn and Rh-Cr combinations were reported to the most active catalysts regarding high PO levels and low CO_2 products (Miyazaki et al., 2003).

In the study of Senkan and coworkers, high-throughput laser ablation (HT-PLA) method was used to synthesis of unimetallic Rh, bimetallic Rh-Pt andtrimetallic Ph-Pt-Au catalysts for the epoxidation of propylene (Senkan et al., 2006) .In the study, these catalysts (over 40 catalysts in number) supported on γ-Al_2O_3, CeO_2, TiO_2, SiO_2 and γ-ZrO_2 in a short time with distinct particle size and loading level. They reported that highest PO plus acetone yield was obtained for TiO_2 supported Rh nanoparticles with 77.2% PO+AT selectivity at 16.9 % conversion (at 275 ˚C, 100 pulse loading and C_3H_6/O_2= 1). They also stated that combinational methodology (HT-PLA together with high-throughput catalysts screening method) was an effective way to determine potentially high performing catalysts in a short time by increasing tempo of the research (Senkan et al., 2006). Besides, they studied by micro-GC with thermal conductivity detector (TCD) for qualification of reaction products and stated that (Rh/TiO_2) was not an effective catalyst for PO formation differently from their previous study (Duan et al., 2007).

Similarly, Onal and coworkers explored the efficiency of a large number of unimetallic and bimetallic supported catalytic systems for gas phase oxidation of propylene via high throughput catalyst preparation and screening tools. In the study, the effects of metal loading, support-metal and metal-metal interactions for PO formation were investigated. Among various support materials based on silica,alumina and titania, silica synthesized with dodecylamine (DDA) template was reported as most appropriate support. From the investigation of the performance of Ag,Cu or Mn unimetallic catalysts for epoxidation of propylene, the most promising PO activity was obtained for Cu metal at low loadings. It was also reported in the study that Cu^{II} ionic species and large metallic Ag particles are necessary for propylene epoxidation. Besides, Ag-Cu and Cu-Mn bimetallic systems were stated as promising catalytic systems for epoxidation of propylene. They reported that PO yield is increased by several folds because of the synergistic effect of multimetallic systems particularly for Ag-Cu bimetallic catalysts supported on SiO_2 synthesized without template and Cu-Mn bimetallic catalysts supported on a-Al_2O_3 (Onal et al.,2010).

They also investigated the modifying effect of alkali promoters such as K and Li on the catalytic performance of Cu containing high and low surface area silica at different reaction conditions. The highest PO yield (55.1% PO selectivity at 3.6%

conversion) was observed for 2.25%K-3%Cu catalyst supported on high surface area silica. In the study, XRD, TEM and XPS analysis showed that modification with K resulted in no noticeable change in structural and chemical properties of catalysts. With K addition, activation energy in PO production was similar to 3%Cu catalyst without modification (77 vs. 75 kJ mol^{-1}), whereas lower activation energy observed in propylene consumption rate (71 vs. 92 kJ mol-1). It was concluded that K neutralized the acid sites of silica (Duzenli, 2012).

Kahn and coworkers investigated catalytic performance of 35 metals supported on silica, prepared by high throughput pulsed laser ablation method. Among these metals, they reported that Cr, Mn, Cu, Ru, Pd, Ag, Sn, and Ir were the most favorable metals for PO production. Because the PO yield was not high for these unimetallic catalysts, they tried bimetallic systems of these metals in order to increase PO selectivity and production rate. They started with the investigation of Mn-Cu bimetallic systems, which were prepared by sequential deposition process. In the study, they reported that the highest catalytic performance was obtained for Cu-on-Mn/SiO_2 catalyst with PO formation rate which was higher by a factor of 5 than the unimetallic Cu and Mn catalysts (Kahn et al.,2010).

As a result of the investigation of various metals and their combinations via high throughput screening methods, Senkan and co-workers reported the discovery of a new SiO_2- supported trimetallic RuO_2-CuO_x-NaCl catalysts with highest PO yield (40%-50% PO selectivity at 10-20%conversion) for the direct epoxidation of propylene by molecular oxygen at 240˚C-270˚C under atmospheric pressure. XRD and TEM analysis conducted for most active catalysts showed that they are composed of nanocrystalline domains of the three phases of RuO_2, CuO_x and NaCl. In addition, effect of the NaCl on PO mechanism was reported to be come from chlorine's electronegativity that changes the surface electronically (Seubsai et al., 2011). Basing on the results of this research, we also decided to prove and improve the catalytic performance of RuO_2-CuO_x-NaCl catalysts for propylene epoxidation studies in this research.

CHAPTER 3

EXPERIMENTAL

In the study, a large number of silica supported mono- and multimetallic heterogeneous catalysts and support materials containing silica and silica synthesized with template were synthesized by impregnation and sol–gel method in a combinatorial fashion. In order to be able to synthesize supported catalysts in a combinatorial fashion, a commercial synthesis apparatus was used. This synthesis apparatus contains 24 cells where catalysts can be concurrently synthesized. Magnetic stirring is provided for each cell. The synthesis block is also capable of reflux by circulating cold water, this reflux system is used effectively during preparation of the catalysts that require high temperature conditions. Catalyst candidates were synthesized according to the following procedures.

3.1. Synthesis of the Catalysts

3.1.1. Synthesis Procedure for Metal Containing Catalysts Supported on Silica (SiO_2)

The chemicals used in preparation of metal containing catalysts supported on silica were tetraethyl orthosilicate (TEOS) as a silica source with 99% purity supplied from Fluka, ethanol (EtOH) as a solvent with 99.8% purity, 1 M of nitric acid (HNO_3) solution, 0.5 M of ammonium hydroxide (NH_4OH) solution, deionized water and metal precursors. In the case of copper (Cu), potassium (K), sodium (Na), and ruthenium (Ru), the precursors were $CuNO_3$, KNO_3, KAc, $NaNO_3$, NaCl, $RuCl_3.XH_2O$). The corresponding molar ratios of chemicals are shown in Table 3.1.

Table 3.1: The corresponding molar ratios of chemicals with respect to Si

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

1 g SiO_2 was taken as a basis for the synthesis of metal containing silica catalysts and amount of chemicals were determined on this basis.

TEOS, HNO_3, EtOH and water were put together in the glass tube at room temperature and heated to temperature of 80 ˚C. During the heating period, the solution was stirred under reflux condition. After the solution was kept at temperature of 80˚C for 2 h, the desired amount of metal precursor was added into the solution and the mixture was kept under vigorous stirring and reflux condition for 1 h. In the case of preparation of catalysts promoted with metal like K, Li etc., the metal nitrates were added after another 1 h. Then, NH_4OH was added into the metal containing solution and gel was obtained. The obtained gel was aged at room temperature during a day and dried overnight at 120˚C and calcined at 550˚C for 5 h.

In the preparation of bimetallic or multimetallic catalysts using metal nitrates and metal chlorides (LiCl, KCl, NaCl) together as precursors, metal containing catalysts firstly prepared by sol-gel method decribed above without adding metal chloride salts. Loading of metal chloride was provided by impregnation method as a last step of the preparation process. Desired amount of metal chloride was dissolved in desired amount of distillated water and added to the calcined catalyst. The mixture was heated while stirring (50˚C to 80˚C) until all the water was evaporated. Finally the prepared sample was dried at 120˚C for 12 h and calcined at 350˚C for 3 hour.

In the study, promoted and unpromoted Cu catalysts supported on silica were prepared with this method. Only silica support was also synthesized to be used for preparation of SiO_2 supported Cu-Ru bimetallic catalysts by impregnation method.

3.1.2. Synthesis Procedure for Catalysts supported on Silica Synthesized with Template (t-SiO_2)

The chemicals used in preparation of metal containing catalysts supported on silica synthesized with template were TEOS, 15.8 M of stock HNO_3 solution, dodecylamine (DDA) supplied from Fluka, EtOH, water, and metal precursors. ($CuNO_3$, KNO_3, KAc, $NaNO_3$, $LiNO_3$, LiCl, NaCl). The corresponding molar ratios of chemicals are shown in Table 3.2.

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Table 3.2: The corresponding 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 %

1 g SiO_2 was taken as a basis for the synthesis of metal containing silica catalysts and amount of chemicals were determined on this basis.

The desired amount of metal precursor was dissolved with deionized water in the glass tube. DDA and HNO_3 were introduced into the solution and the mixture was stirred for 1 h. Then, the prepared solution of TEOS and EtOH was added to the mixture. Stirring continued during 4 h at room temperature and then the magnetic stirrer was closed. The mixture was aged at room temperature during 18 h and then filtered. The resultant product was dried overnight at 70˚C to prevent ignition of filter paper and calcined at 650˚C for 3 h.

In the preparation of bimetallic or multimetallic catalysts using metal nitrates and metal chlorides (LiCI, KCI, NaCI) together as precursors, metal containing catalysts firstly prepared by sol-gel method decribed above without adding metal chloride salts. Loading of metal chloride was provided by impregnation method as a last step of the preparation process. Desired amount of metal chloride was dissolved in appropriate amount of distillated waterand added to the calcinated catalyst. The mixture was heated while stirring (50˚C to 80˚C) until all the water was evaporated.

Finally the prepared sample was dried at 120˚C for 12 h and calcined at 350˚C for 3 hour.

In the study, promoted and unpromoted Cu catalysts supported on silica synthesized with template (t-SiO_2) were prepared with this method. Only t-SiO_2 was also synthesized to be used for preparation of SiO_2 supported Cu-Ru bimetallic catalysts by impregnation method.

3.1.3. Synthesis Procedureof Incipient Wetness Method

Beside the direct sol-gel method, some catalysts supported on SiO_2, t-SiO_2 and commercial silica (SiO_2, Alfa Aesar, surfacearea 97 m^2g^{-1}) were prepared with co-impregnation method. According to the method, the water pore volume of calcined silica was 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 (for 2 g silica basis: 7ml water for low surface area silica; 15 ml water for high surface area silica; 25 ml water for commercial silica). The desired amount of metal nitrate was dissolved in distillated water, and the solution was added to the support material. The mixture was heated while stirring (50˚C to 80˚C) until all the water was evaporated. Finally the prepared sample was dried at 120˚Cfor 12 h and calcined (for low surface area and commercial silica 550˚C& 5h; for high surface area silica 650˚C& 3h). In the synthesis of catalysts promoted with metal chloride (LiCl, KCl), catalysts firstly prepared by sol-gel or co-impregnation method decribed above without adding metal chloride salts. Then desired amount of metal chloride was dissolved in distillated water and added to the calcined catalyst. The mixture was heated again while stirring (50˚C to 80˚C) until all the water was evaporated. Finally the prepared sample was dried at 120˚Cfor 12 h and calcined at 350˚C for 3 hour.

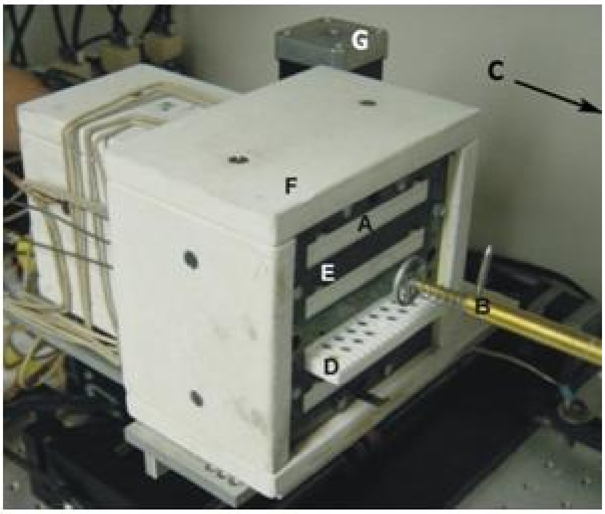
3.2. Catalytic Activity Tests

All of the synthesized catalysts candidates were tested for gas phase epoxidation of propylene with molecular oxygen in University of California Los Angeles (UCLA).The activity of the catalysts were investigated there with high throughput screening methods in a computer controlled array channel microreactor system. Besides, the selected catalysts were re-tested in Middle East Technical University (METU) with a normal speed activity test unit in which higher amount of catalyst were tested. These activity test systems were described in detail as follow.

3.2.1. Activity Test Unit in University of California Los Angeles (UCLA)

The catalyst screening test unit in University of California Los Angeles (UCLA) is a computer controlled array channel microreactor system in which up to 80 catalysts could be screened concurrentlyas shown in Figure 3.1. The system was also illustrated in Figure 3.2.

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 3.1: a) Arroy channel micro-reactor b) Catalytic activity test unit in UCLA

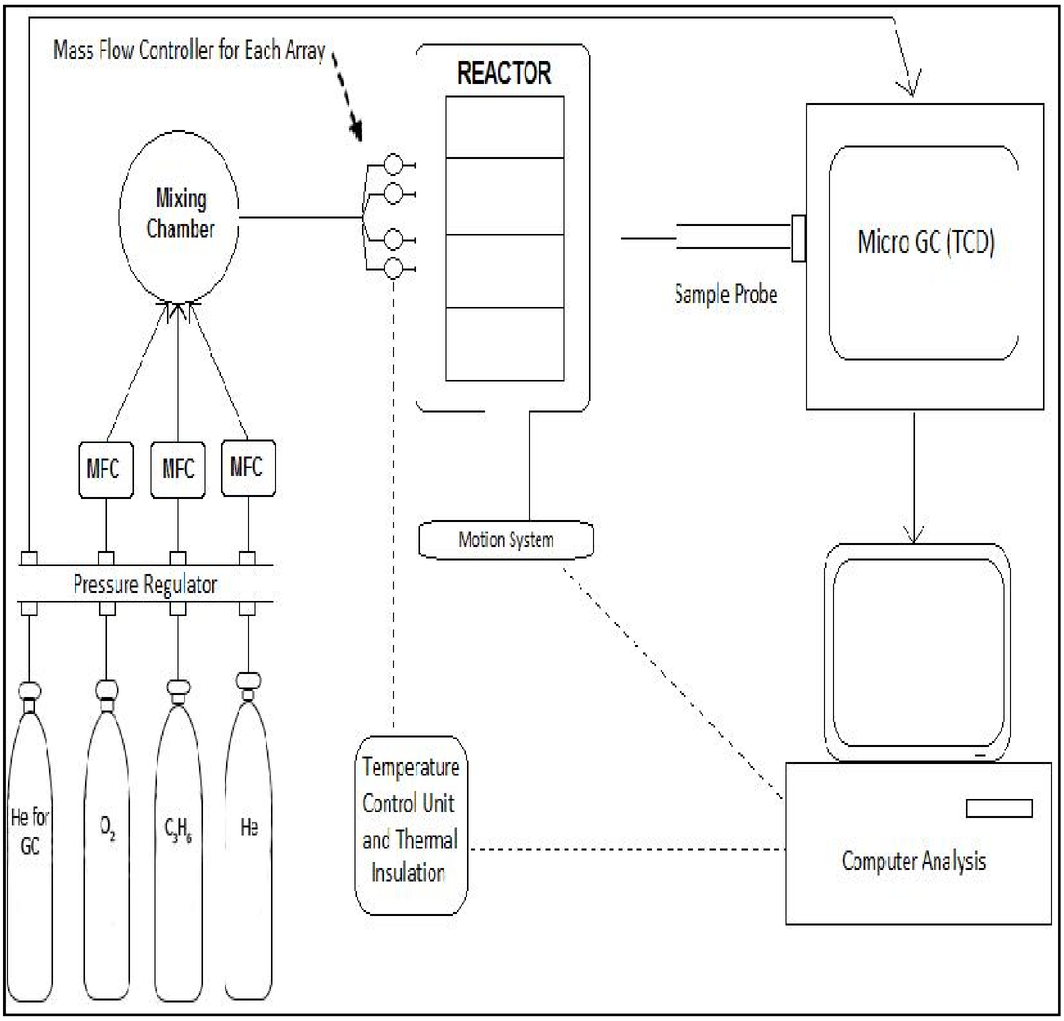


Figure 3.2: Flow chart of catalytic activity test unit in UCLA

The activity test of 20 catalyst candidates was completed in one screening experiment in this study. On average, one catalyst's screening took 3 minutes to have one data point. The synthesized catalyst candidates are placed into the wells of the ceramic array microreactors. In these microreactors, reactant gases flow over the flat surfaces of catalyst powder which are individually isolated within reactor channels. Reactor outflow streams were withdrawn by a heated capillary sampling probe and then analyzed by on-line gas chromatography (Varian CP-4900 Micro GC with thermal conductivity detector (TCD) with Porapak Q (10m) and Molecular sieve

13X (10m) columns). A Propak Q column was used to detect oxygenates (acetaldehyde, propylene oxide, propionaldehyde, acrolein, acetone, and alcohols) and propylene, while Molecular Sieve 13X column was used to detect CO,CO_2 and O_2.

All experiments were conducted by using 0.005 g of catalyst under atmospheric pressure and at a gas space velocity (GHSV) of 20,000 h^{-1} at different reaction temperatures. While the gas flow rates over each plate and over each channel were 100 cc min^{-1} and was 5 cc min^{-1}, respectively. The experiments were conducted using feed gas including 14% C_3H_6, 28% O_2 ($C_3H_6/O_2=0.5$) and balance helium (He) at 300˚C and 350˚C temperatures.

The percent of the amount of carbon in PO in all the products is defined as the selectivity of PO. The same calculation model is used for the selectivity of the other C_3 products such as propionaldehyde plus acrolein (PaL+AC), acetone (AT) and acetaldehyde (AD). The reaction pathway for propylene oxidation products, PO and other products (PaL, AC, AT, AD, CO_2, CO), were given in Appendix D where the sample calculation of PO selectivity and propylene consumption for 2%Cu-5%Ru-1,75 %NaCl/c-SiO_2 were also shown.

3.2.2. Activity Test Unit in Middle East Technical University (METU)

Catalytic activity test unit in METU Chemical Engineering Department is a fixed bed reaction system and tests higher amounts of catalysts at a normal test speed. This dynamic test system, illustrated in Figure 3.3, is completely computerized and basically composed of gas flow control unit, a split furnace, a quartz reactor and gas chromotography (GC).

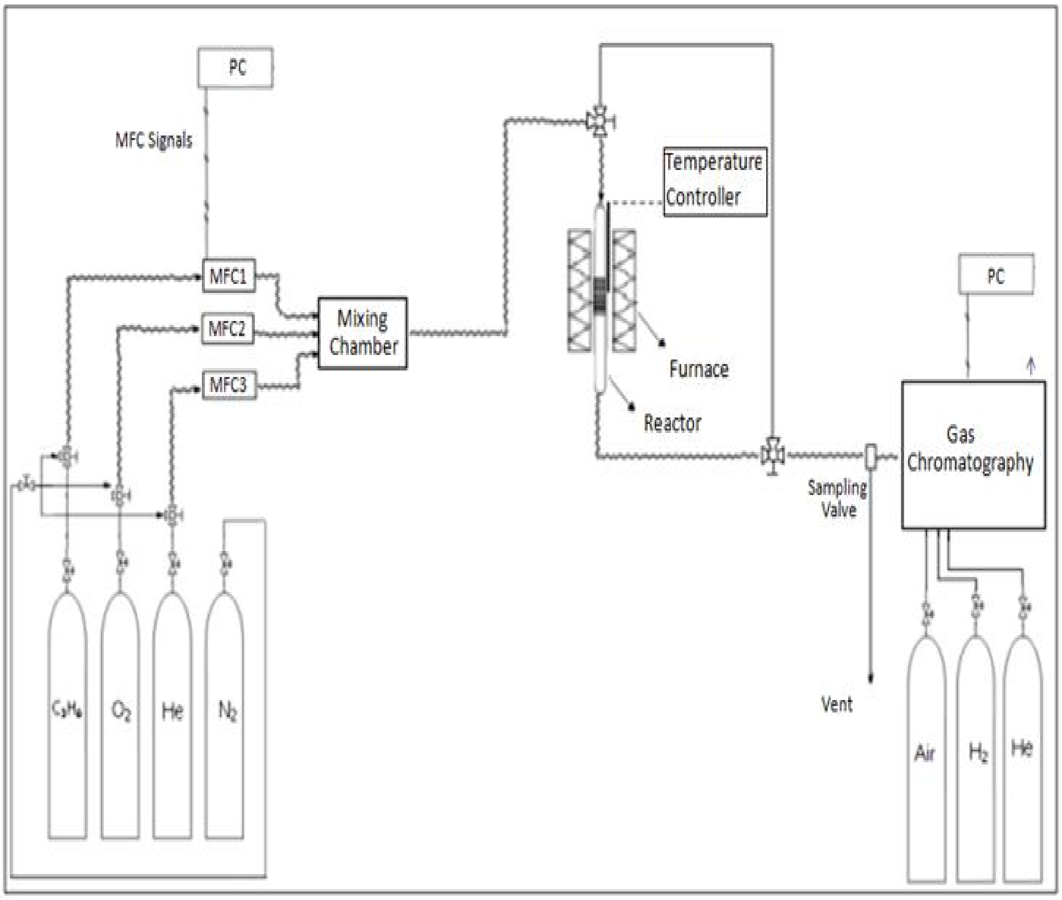


Figure 3.3: Flow chart of catalytic activity test unit in METU

In this unit, using a computer program the predefined values of propylene (C_3H_6), oxygen (O_2) and helium gas (He) flow rates are input and the flow rates of gases with desired concentrations are controlled by mass flow controllers (MFCs). All the gases from MFC1, MFC2 and MFC3 are mixed in a manifold. The feed gas including 14% C_3H_6, 28% O_2 ($C_3H_6/O_2=0.5$) and balance helium (He) with the gas flow rate of120cc/min^{-1}sent through the fixed bed reactor. The reaction section of the catalytic activity test unit consists of a quartz tube reactor (4 mm of inner diameter, 6 mm of outer diameter) placed in an electric furnace and connected with gas chromatograph. Amount of 0.2 g of catalyst (75-500 µm) placed into the central zone of the reactor and the experiments were conducted at 300˚C under atmospheric pressure. The temperature of reactor is controlled with reactor furnace temperature controller receiving data from thermocouple place at the exit of catalyst bed. The outlet gases were sent to the gas chromatography where reaction products were analyzed online by an FID detector with TRB-WAX capillary column (60mx 0.25mm) and a TCD detector with Carboxen capillary column (30mx0.32mm). A TRB-WAX capillary column was used to detect oxygenates (acetaldehyde, propylene oxide, propionaldehyde, acetone, and alcohols) and propylene, while Carboxen capillary column was used to detect CO,CO_2 and O_2. Gas chromatography analysis data are evaluated at computer via software and gas concentrations are calculated. Computer sets gas flow at desired value by commanding gas flow controllers. In addition, nitrogen gas (N_2) is also used for cleaning the gas lines of the test unit.

3.3. Characterization

Various methods were used for the characterization of selected catalysts investigated in this study. These methods were X-ray diffraction (XRD), BET surface area, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectrometry.

X-ray diffraction (XRD) method was employed for some of the selected catalysts which have high and low activity for epoxidation of propylene to determine the structure and morphology of them. The equipment used for the employment of this method was Rigaku X-ray Diffractometer (Model, Miniflex) with XuKα (30kV, 15mA, λ=1.54051 Å). The scans were run at 2θ of 5 to 90° at a rate of 0.1°.

BET surface area method was implemented to measure the BET surface area and the pore size of the catalysts with Quantachrome NOVA 2002 equipment. Initially samples were degassed at 300˚C. After the evacuation process of the sample at 300˚C to remove impurities and water, the samples reach to a constant weight. Then the sample adsorbs the nitrogen that is injected on the sample in the quartz tube at the liquid nitrogen temperature (-196˚C). The quantity of the adsorbed nitrogen gives the specific surface area of the sample. The Brunauer–Emmett–Teller (BET) method was used to determine specific surfaces area and the pore size of the catalysts were calculated using Barret-Joyner-Holenda (BJH) method.

FTIR spectroscopic measurements were carried out in transmission mode in a batch-type catalytic reactor coupled to an FTIR spectrometer (Bruker Tensor 27) and a quadruple mass spectrometer (QMS) (Stanford Research Systems, RGA 200) for TPD and residual gas analysis (RGA). FTIR spectra were recorded using a Hg-Cd-Te (MCT) detector, where each spectrum was acquired by averaging 128 scans with a spectral resolution of 4 cm^{-1}. The samples were mounted into the IR cell consisting of a five-way stainless steel chamber equipped with optically-polished BaF_2 windows. This IR cell was connected to a gas manifold (including a dual-stage rotary vane pump and two turbomolecular pumps) so that the pressure in the cell could be varied within 1000 Torr - 10^{-6} Torr. About 20 mg of finely ground powder sample was pressed onto a high-transmittance, lithographically-etched fine tungsten grid which was mounted on a copper sample holder assembly, attached to a ceramic vacuum feedthrough. A K-type thermocouple was spot-welded to the surface of a thin tantalum plate attached on the W-grid to monitor the sample temperature. The sample temperature was controlled within 298 K – 1100 K via a computer-controlled DC resistive heating system using the voltage feedback from the thermocouple. After having mounted the sample in the IR cell, sample was gradually heated to 373 K in vacuum and kept at that temperature for at least 12 h before the experiments in order to ensure the removal of water from the surface. In an attempt to minimize the effect of background water (i.e. re-adsorption of water on the sample from the reactor walls and the gas manifold), the system was frequently baked. Before acquisition of each spectral series, a background spectrum of the clean, adsorbate-free sample was obtained in vacuum at 323 K (with a residual reactor pressure ~1 x 10^{-5} Torr).

XPS data were recorded using a SPECS spectrometer with a PHOIBOS-DLD hemispherical energy analyzer and a monochromatic Al Kα X-ray irradiation (hν = 1486.74 eV, 400 W). The powder samples were settled on copper based conducting sticky tape. An e-beam flood gun was used for charge compensation during the XPS analysis. The flood gun parameters were chosen to be appropriate for binding energy (B.E.) shifts and peak width broadening.

CHAPTER 4

RESULTS and DISCUSSION

4.1. Catalytic Activity Test Results

In this study various silica materials with different morphological properties and metallic systems were investigated to determine the proper catalysts for direct epoxidation of propylene to PO.

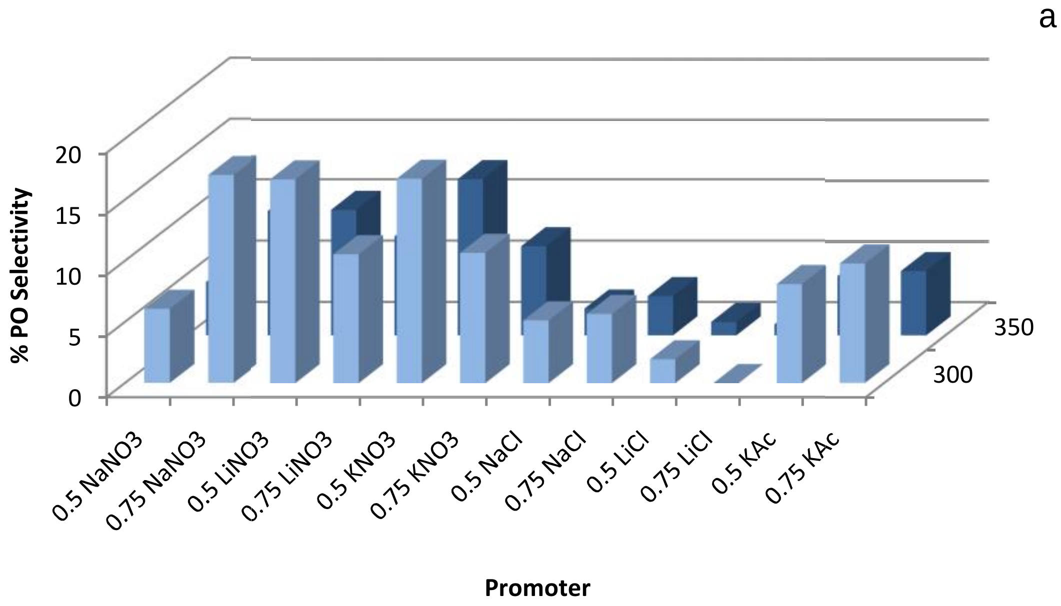
At the beginning of the study, catalytic performances of Cu catalysts promoted with different alkali salts were investigated based on the study of Onal and coworkers. In their study, Cu metal was loaded into the different support materials including SiO_2, t-SiO_2 (silica synthesized with template), TiO_2, γ-Al_2O_3, α-Al_2O_3 and titanium containing silica. Among these support materials, SiO_2 and t-SiO_2 were determined the most promising supports for PO production, however t-SiO_2 was found the most effective support material due to high propylene consumption and PO selectivity. After screening a large number of catalysts, the better performance was obtained for low Cu content catalysts supported over t-SiO_2 and promoted with $LiNO_3$ and KNO_3 salts (Duzenli,2012). Therefore this study was continued to investigate the effect of different alkaline salts on the performance of catalyst.

For this purpose, catalytic activities of 44 promoted Cu catalysts were investigated in the first part of the study. Silica was synthesized with template and promoted Cu catalysts were prepared by loading metal salts into the support material during synthesis. Then, these catalysts were screen with developed high throughput test unit in UCLA. The obtained results were presented in the following section.

4.1.1. t-SiO_2 Supported Cu Catalysts

At the beginning of this study %3, %5 and %7 Cu containing catalysts modified with different alkali salts such as $NaNO_3$, $LiNO_3$, KNO_3, NaCl, LiCl and KAc were prepared. After synthesis of the catalysts they were tested at a reaction temperature of 300˚C and 350˚C with propylene/oxygen ratio of 0.5. These optimum reaction conditions were also determined in the study of Onal et al. and the activity results of 3%Cu/t-SiO_2, 5%Cu/t-SiO_2 and 7%Cu/t-SiO_2 catalysts were summarized in Figure 4.1, Figure 4.2, and Figure 4.3, respectively.

When the results were evaluated based on the type of the precursor salts, it can be seen that the most effective promoter is sodium nitrate salt than chloride and acetate salts for catalysts supported into t-SiO_2. $NaNO_3$ promoted all the catalysts containing different amount of Cu most effectively. In addition, the effect of reaction temperature to the activity of the catalyst can be seen clearly. However propylene consumption increased with increasing temperature from 300˚C to 350˚C, for all the catalysts tested at 300˚C showed higher selectivity compared to catalysts tested at 350˚C. Among the catalysts the highest PO selectivity (0.16% yield: 21.77% PO selectivity at 0.74% conversion) was obtained for 7%Cu-5.25%$NaNO_3$ (P/Cu=0.75) catalyst at 300˚C but 3%Cu-2.75%$NaNO_3$ (P/Cu=0.75) catalyst showed optimum epoxidation of propylene (0.26% yield: 17.02% selectivity at 1.47% conversion). In the study of Duzenli et al., 3%Cu-2.75% KNO_3 catalyst gave the maximum PO yield among the all catalysts prepared.



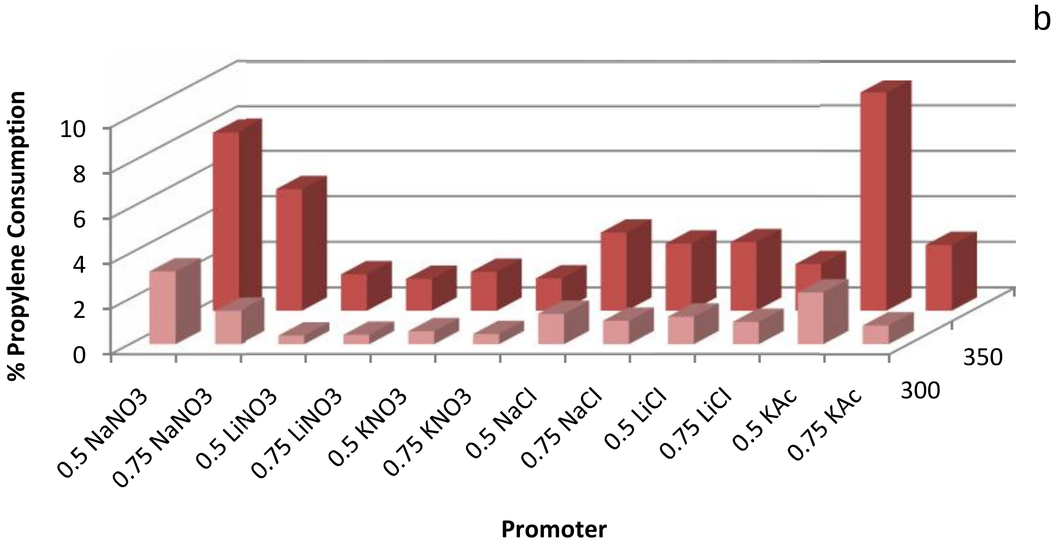


Figure 4.1: a) PO selectivity and b) Propylene consumption of 3%Cu/t-SiO_2 catalysts promoted with different alkaline salts ($NaNO_3$, $LiNO_3$, KNO_3, NaCl, LiCl, KAc) with the promoter/Cu weight ratio of 0.5 and 0.75 at 300˚C and 350˚C

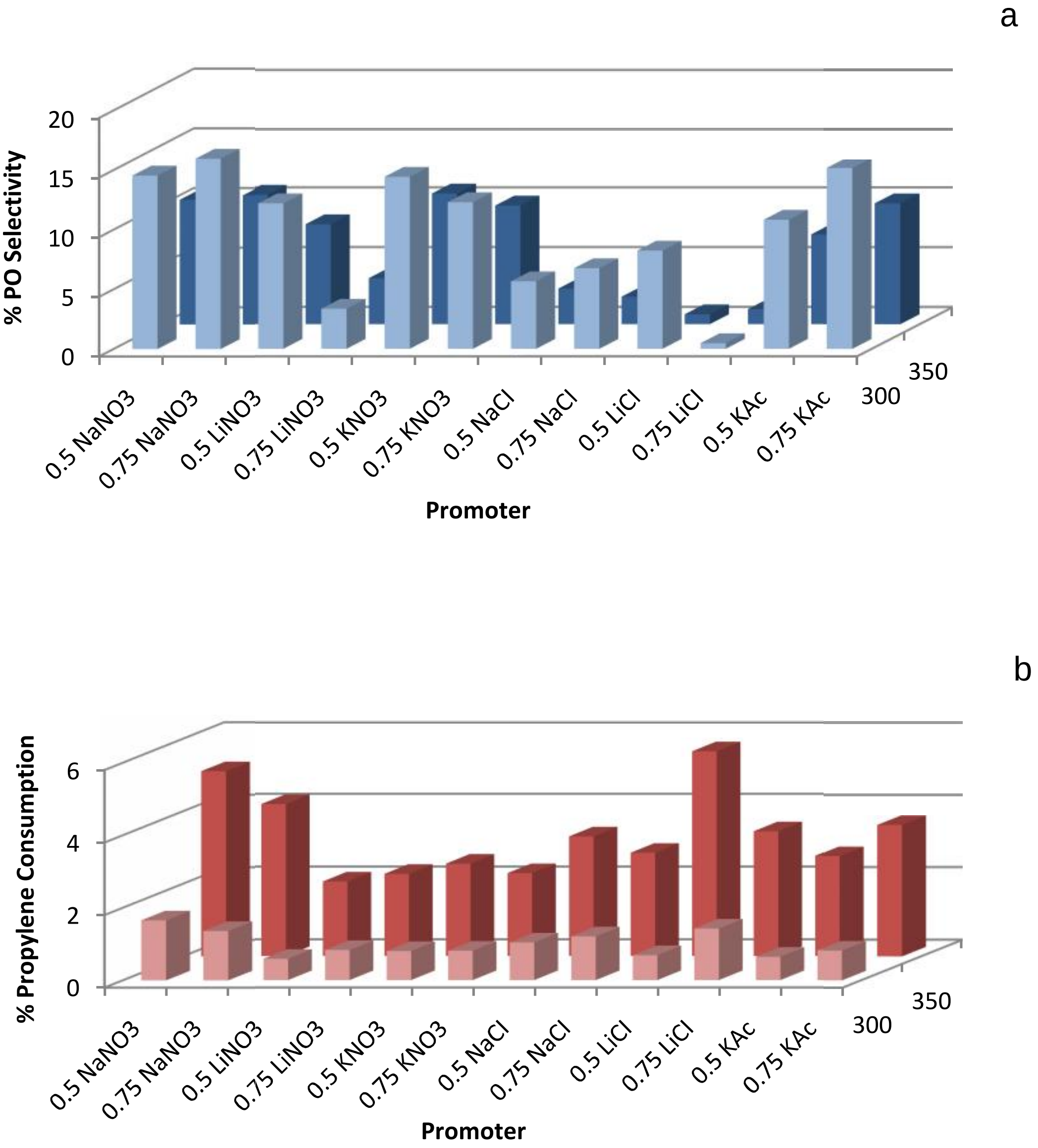
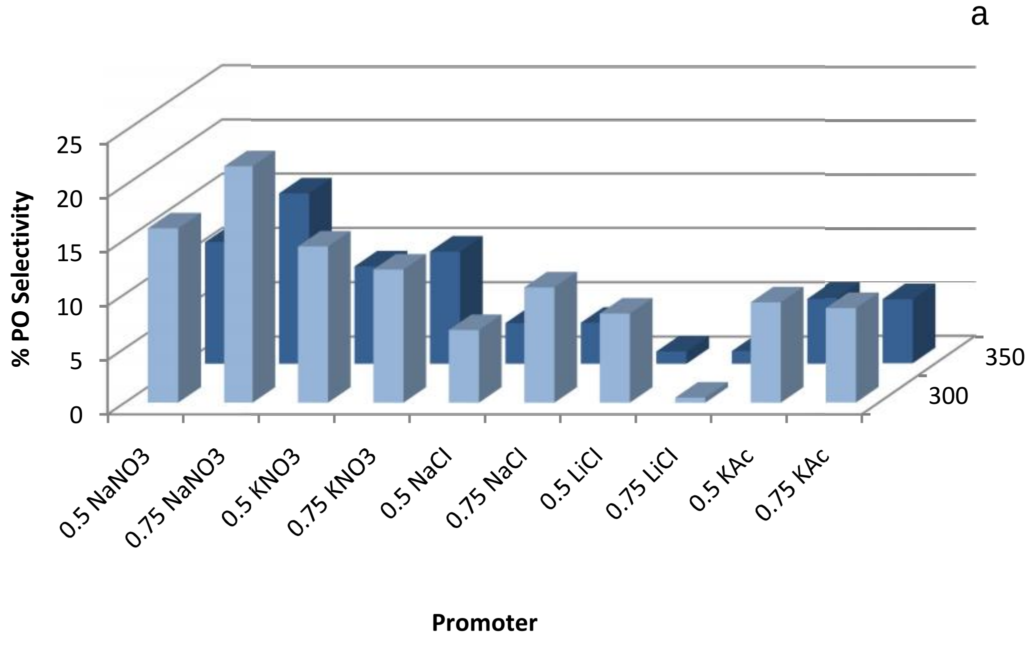


Figure 4.2: a) PO selectivity and b) Propylene consumption of 5%Cu/t-SiO_2 catalysts promoted with different alkaline salts ($NaNO_3$, $LiNO_3$, KNO_3, NaCl, LiCl, KAc) with the promoter/Cu weight ratio of 0.5 and 0.75 at 300˚C and 350˚C



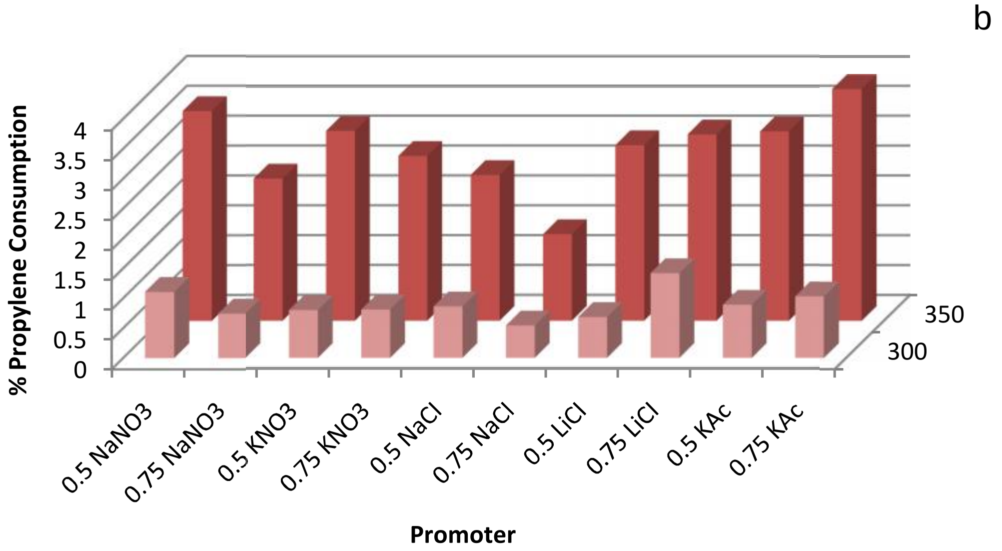


Figure 4.3: a) PO selectivity and b) Propylene consumption of 7%Cu/t-SiO_2 catalysts promoted with different alkaline salts ($NaNO_3$, $LiNO_3$, KNO_3, NaCl, LiCl, KAc) with the promoter/Cu weight ratio of 0.5 and 0.75 at 300˚C and 350˚C

The monometallic Cu catalysts promoted with various alkaline metal precursors did not give desired catalytic performance as expected. In the previous work reported in the literature bimetallic and trimetallic Cu catalysts was investigated to obtained high catalytic performance to produce PO from propylene and molecular oxygen at atmospheric pressure and without any co-reactant. In spite of these efforts there is no promising catalyst until Seubsai and coworkers study. They reached 40-50% PO selectivity at 10-20% propylene conversion over a new class of silica-supported multimetallic RuO_2-CuO_x-NaCl catalysts.

In the second part of the study we prepared Cu-Ru catalysts modified with various promoters and tested to observe the effect of different supports and modifiers. For this purpose, 50 catalysts were investigated and the obtained results were presented in the following section.

4.1.2. Supported Cu and Ru Catalysts

First monometallic Cu and Ru catalysts and bimetallic Cu-Ru catalysts supported on SiO_2 were synthesized by single step sol-gel method and these catalysts were tested with developed high throughput test unit in UCLA. The synergic effect between Ru and Cu metals can be seen in Figure 4.4 clearly. It can be seen that bimetallic Cu-Ru catalysts increased both propylene conversion and selectivity to PO when compared with monometallic Cu and Ru catalyst.

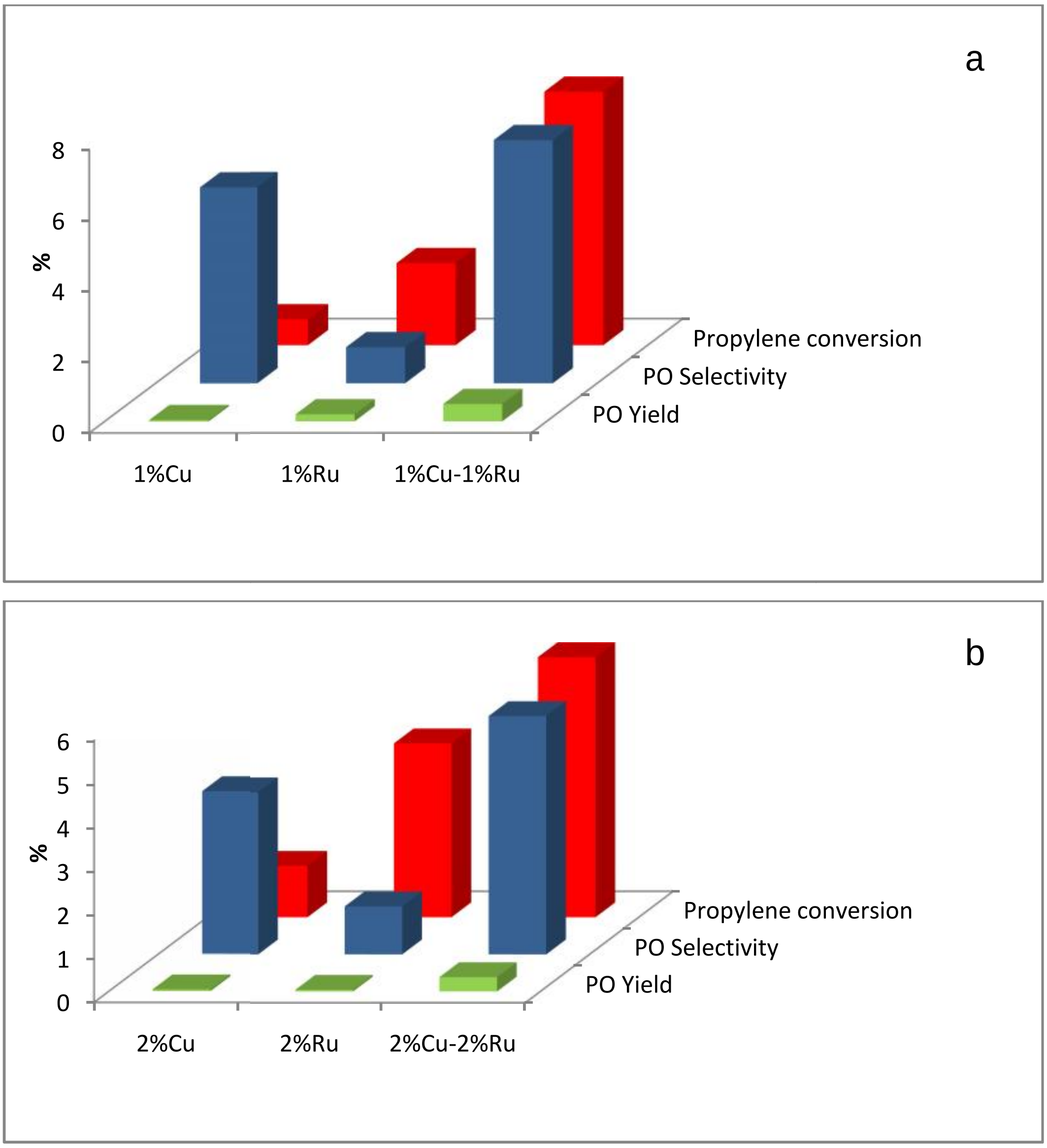


Figure 4.4: Comparison of the catalytic performances of Cu&Ru monometalic and bimetallic systems supported on SiO_2 with a) 1% and b)2% weight percentage of each metal at a reaction temperature of 300˚C (tested in UCLA)

Activities of Cu-Ru monometallic and bimetallic systems were also re-tested with a normal speed activity testing unit in Middle East Technical University (METU). Main differences of activity testing units in UCLA and METU are reactor types, speed of test and amount of catalyst tested. Activity testing system in UCLA is a high speed activity testing unit (high throughput screening) in which low amount of catalyst (0.005 g) were tested. In this system,array channel microreactor system is used and gas flows over the catalyst. However, activity testing unit in METU is a fixed bed reaction system which tests higher amounts of catalysts (0.2g) at a normal test speed. Because of speed of test and amount of catalyst tested, activity testing system in METU is more close to industrial application.Activities of Cu-Ru monometallic and bimetallic systems were tested in these two systems at 300°C and C_3H_6/O_2=0.5.The results (PO selectivity and propylene consumption) for the catalysts having 1% weight percentage of each metal were demonstrated in Figure 4.5 and Table 4.1. It was again observed from the activity results that bimetallic Cu-Ru catalyst increased PO selectivity significantly when compared with monometallic Cu and Ru catalysts. 1%Cu-1%Ru/SiO_2 catalyst showed optimum epoxidation of propylene (0.58% PO yield), which was consistent with the result observed in the high speed activity testing unit in UCLA (0.49% PO yield). Therefore, the effectiveness of Cu-Ru bimetallic systems compared to their monometallic systems was proved with the activity results obtained from each of the two test units.

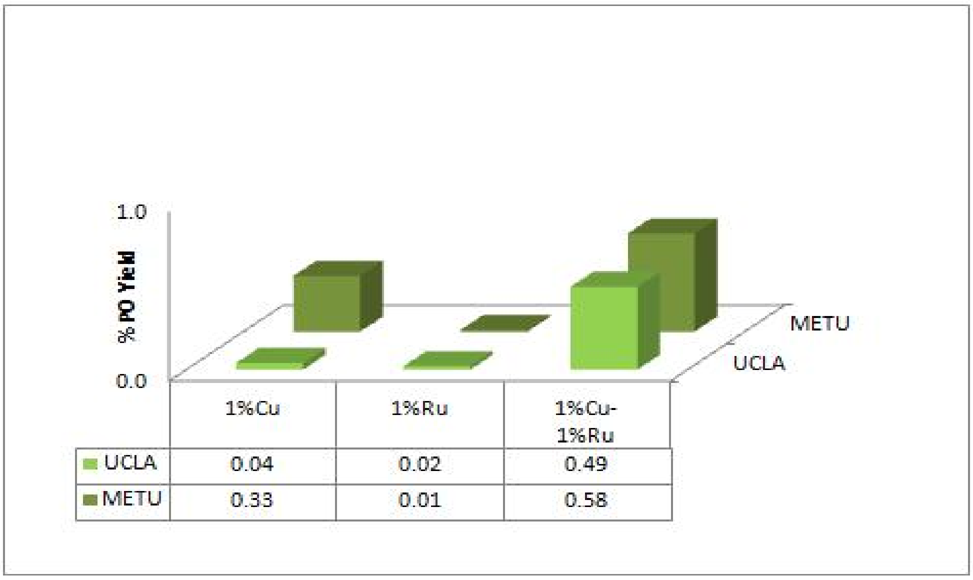
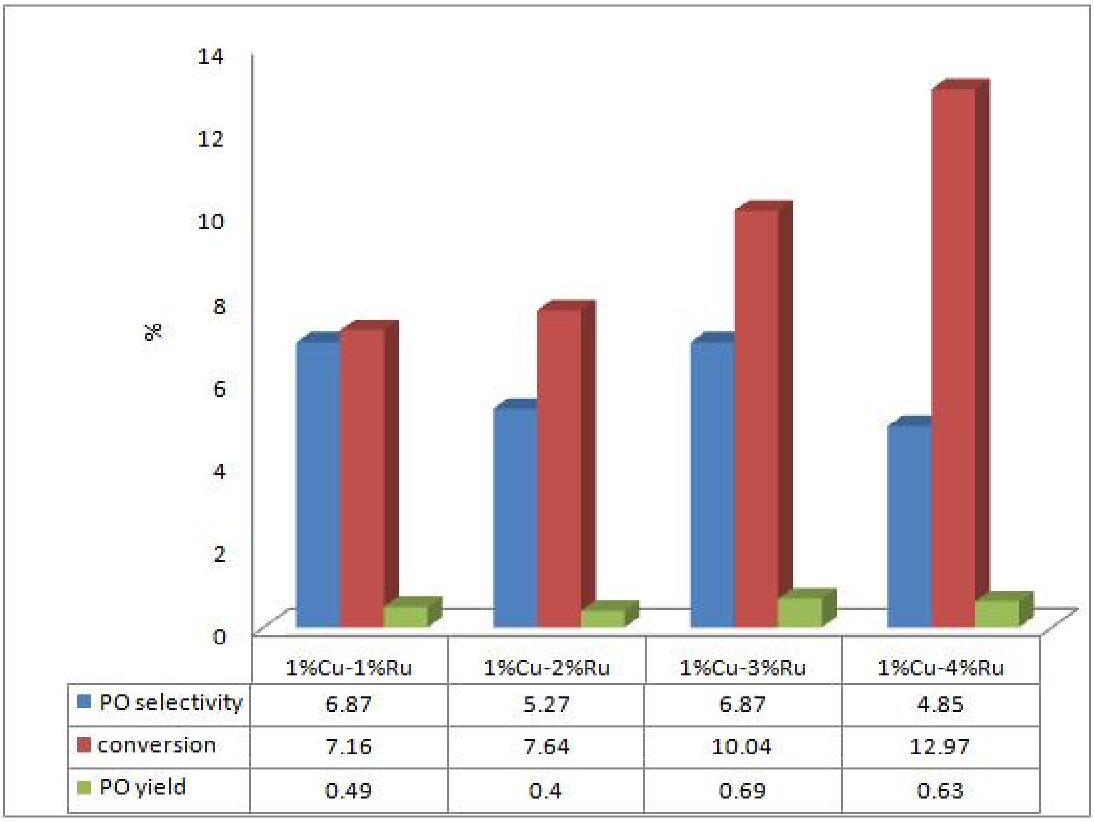


Figure 4.5: Comparison of trends for PO Yields of Cu&Ru monometallic and bimetallic systems supported on SiO_2 with 1% weight percentage of each metal at a reaction temperature of 300˚C (tested in METU and UCLA)

Table 4.1: Catalytic properties of Cu&Ru monometallic and bimetallic systems supported on SiO_2 with 1% weight percentage of each metal at a reaction temperature of 300˚C

Catalyst	**METU**			**UCLA**		
	PO Selectivity (%)	Propylene Conversion (%)	PO Yield (%)	PO Selectivity (%)	Propylene Conversion (%)	PO Yield (%)
1%Cu	0.69	47.44	**0.33**	5.54	0.73	**0.04**
1%Ru	0.01	79.28	**0.01**	1.02	2.32	**0.02**
1%Cu-1%Ru	1.71	33.84	**0.58**	6.87	7.16	**0.49**

After this observation, the study continued with the preparation of bimetallic Cu-Ru catalysts with different amount of metals. For 1%Cu-x%Ru (x=1-4 with 1wt.% interval) catalysts, the overall conversion increased continuously with Ru content whereas selectivity did not show a regular increase or decrease with an increase in Ru content as shown in Figure 4.6. After these observations, catalysts containing different Cu/Ru amount were prepared and screened combinatorially. Among various catalysts the best performance (yield) was obtained for 2%Cu-5%Ru/SiO_2 catalyst.

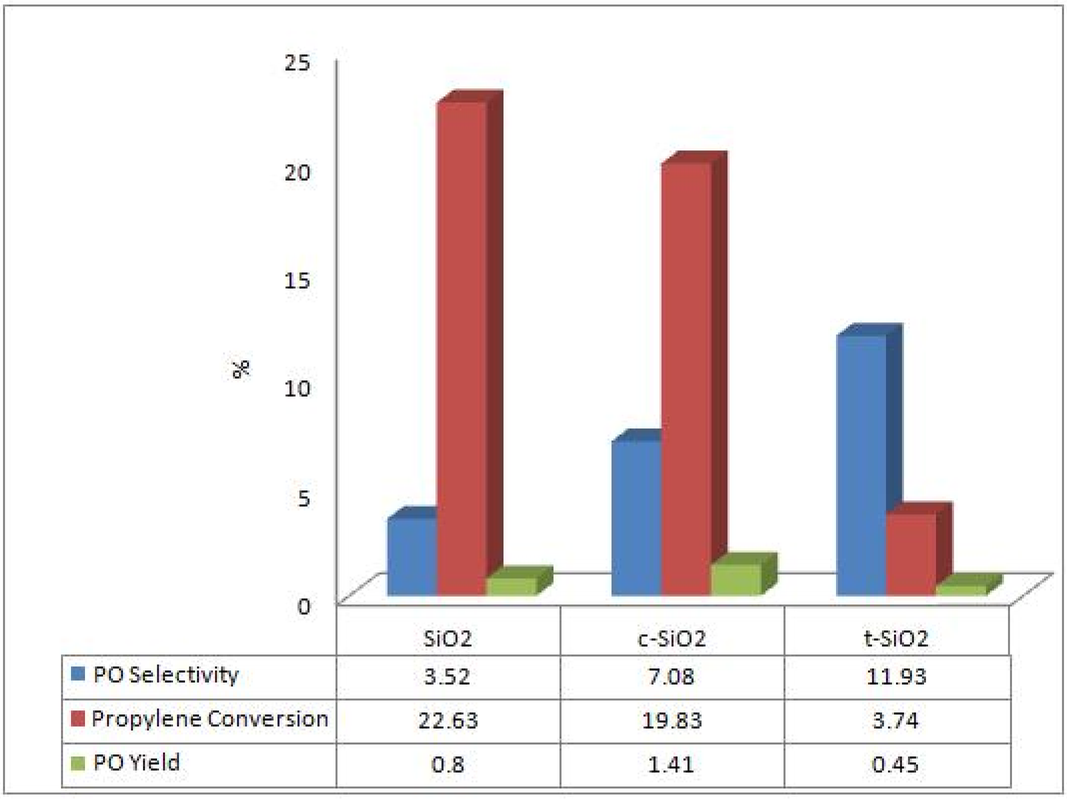


	1%Cu-1%Ru	1%Cu-2%Ru	1%Cu-3%Ru	1%Cu-4%Ru
🟦 PO selectivity	6.87	5.27	6.87	4.85
🟥 conversion	7.16	7.64	10.04	12.97
🟩 PO yield	0.49	0.4	0.69	0.63

Figure 4.6: Catalytic performances of bimetallic 1%Cu-x%Ru
(x=1-4 with 1wt.% interval) catalysts

The theoretical studies with Density Functional Theory (DFT) of conducting in our laboratory was also showed that when Cu_2O(001) and RuO_2(110) surface compared with each other for the epoxidation reaction, Cu_2O(001) surface is mainly favor the allylic hydrogen striping reaction. However RuO_2(110) surface is not active for the formation of PO and other oxygenated product such as acetone and PA. Our test results showed that 54.94% selectivity to acrolein was obtained for 2%Cu-c-SiO_2 catalyst and 5%Ru-c-SiO_2 catalyst caused almost combustion reaction and produced 95% CO_2. In addition to these two surface, when RuO_2(110)-Oγ surface was prepared, where Oγ represents weakly bonded oxygen atom over surface, the direct PO formation without any surface intermediate is favor with almost no activation barrier. In this theoretical study, bader charge effect was also applied to understand the electronic property of surface oxygen. Oγ species over RuO_2(110)-Oγ surface was determined as the most electrophilic species after bader charge calculation (Onay,2012).

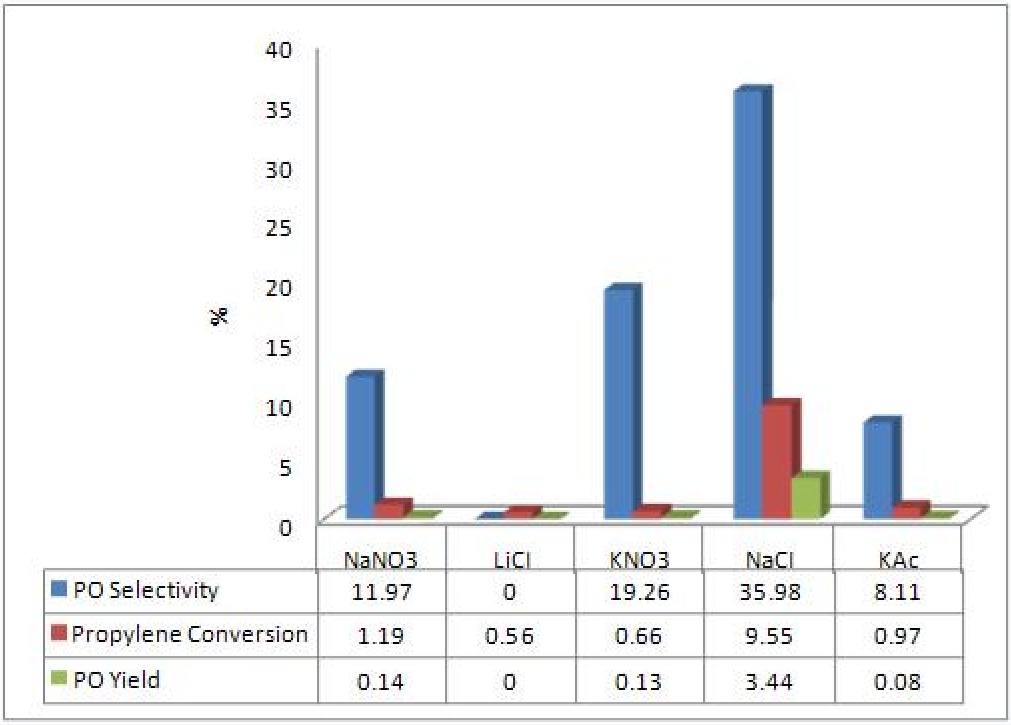
After determining the appropriate metal ratio, bimetallic catalyst was supported on the different silica materials (c-SiO_2, t-SiO_2 and SiO_2) to investigate the best metal-support interaction. All the catalysts were prepared by impregnation method. The catalytic performance of the different 2%wt Cu-5%wt Ru /support catalyst was shown in Figure 4.7.



	SiO2	c-SiO2	t-SiO2
🟦 PO Selectivity	3.52	7.08	11.93
🟥 Propylene Conversion	22.63	19.83	3.74
🟩 PO Yield	0.8	1.41	0.45

Figure 4.7: Catalytic performances of bimetallic 2%Cu-5%Ru catalysts supported on SiO_2, c-SiO_2 and t-SiO_2 at 300˚C

Despite of the high PO selectivity obtained for the t-SiO_2 supported catalyst (0.45% yield: 11.93% selectivity at 3.74% conversion), the optimum result was obtained for commercial silica(c-SiO_2) supported catalyst (1.41 % yield: 7.08% selectivity at 19.85% conversion). SiO_2 supported catalysts generally caused combustion reaction. So the effect of different promoters on the performance of the catalyst was investigated for commercial silica (c-SiO_2) supported catalyst. For this purpose alkaline promoters mostly reported in the literature were added into the metal catalysts by co-impregnation method.



	NaNO3	LiCl	KNO3	NaCl	KAc
🟦 PO Selectivity	11.97	0	19.26	35.98	8.11
🟥 Propylene Conversion	1.19	0.56	0.66	9.55	0.97
🟩 PO Yield	0.14	0	0.13	3.44	0.08

Figure 4.8: Catalytic performances of bimetallic 2%wtCu-5%wtRu/t-SiO$_2$ catalysts promoted with NaNO$_3$, LiCl, KNO$_3$, NaCl and KAc at 300˚C

As seen in the Figure 4.8, NaCl increased the PO yield of Ru-Cu catalyst more significantly than other promoters. The conversion of the 2%Cu-5%Ru/c-SiO$_2$ catalyst decreased from 20% to 9.55% while selectivity to PO increased from 7% to 35.98% with the addition of NaCl. The addition of KNO$_3$ also promoted PO selectivity but conversion remained at very low level (0.66%). To better understand the effect of NaCl over each metal, they were promoted separately.

As seen in Figure 4.9 (a),(b) and Figure 4.10, NaCl addition influenced Cu/c-SiO2 catalyst positively, but Ru/c-SiO$_2$ performance was depleted with promoter. The main product for un-promoted Cu/c-SiO$_2$ catalyst was AC and then CO$_2$. While AD formation was not observed, the PO formation was observed with a negligible amount. However PO selectivity was increased from 1.2% to 7.72% with the addition of NaCI. The increase in PO selectivity correlated with a noticeable decrease in the AC formation. It was also seen that propylene consumption was very low before and after the NaCI modification. For unpromoted Ru/c-SiO_2catalyst it was observed that mainly combustion reaction took place, but AC was second product with low selectivity (3.54%). Besides the amount of PO,AD and AT could be negligible. Modification of Ru/c-SiO_2 catalyst with NaCI did not show any improvement for PO and other oxygenated products, conversely formation of these products was depleted. It was also shown that Cu-Ru/c-SiO_2 bimetallic system enhanced significantly both propylene consumption and PO selectivity compared with un-promoted monometallic Cu/c-SiO_2 and Ru/c-SiO_2 catalysts. With the addition of NaCI to the Cu-Ru/SiO_2 bimetallic system, PO selectivity reached its maximum (36%), while propylene conversion decreased to 9.6%. In addition, there was no other oxygenated product with significant amount for promoted or un-promoted Cu-Ru/c-SiO_2 bimetallic systems.

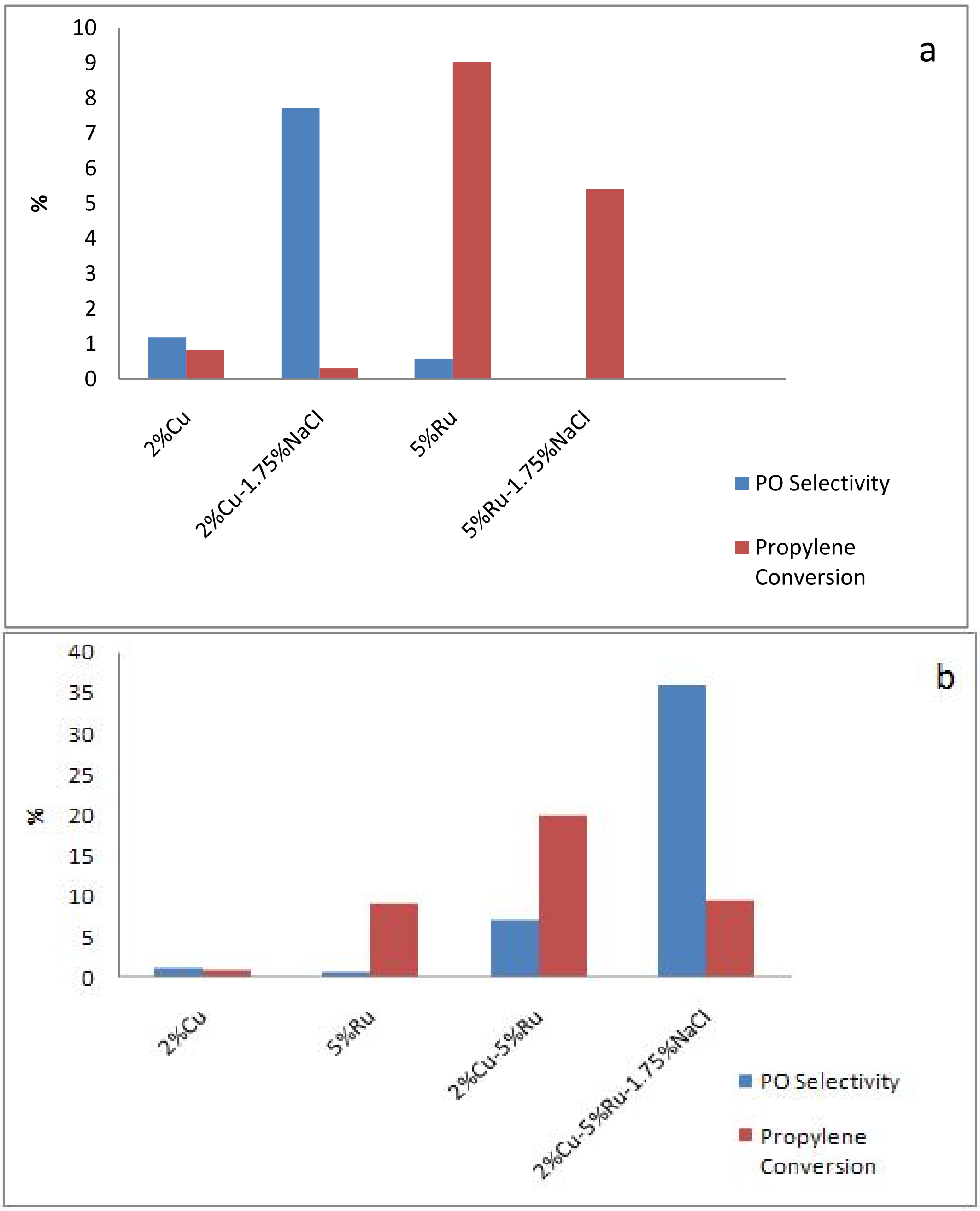


Figure 4.9: (a) and (b) PO selectivity and propylene conversion of Cu&Ru based catalysts at 300˚C

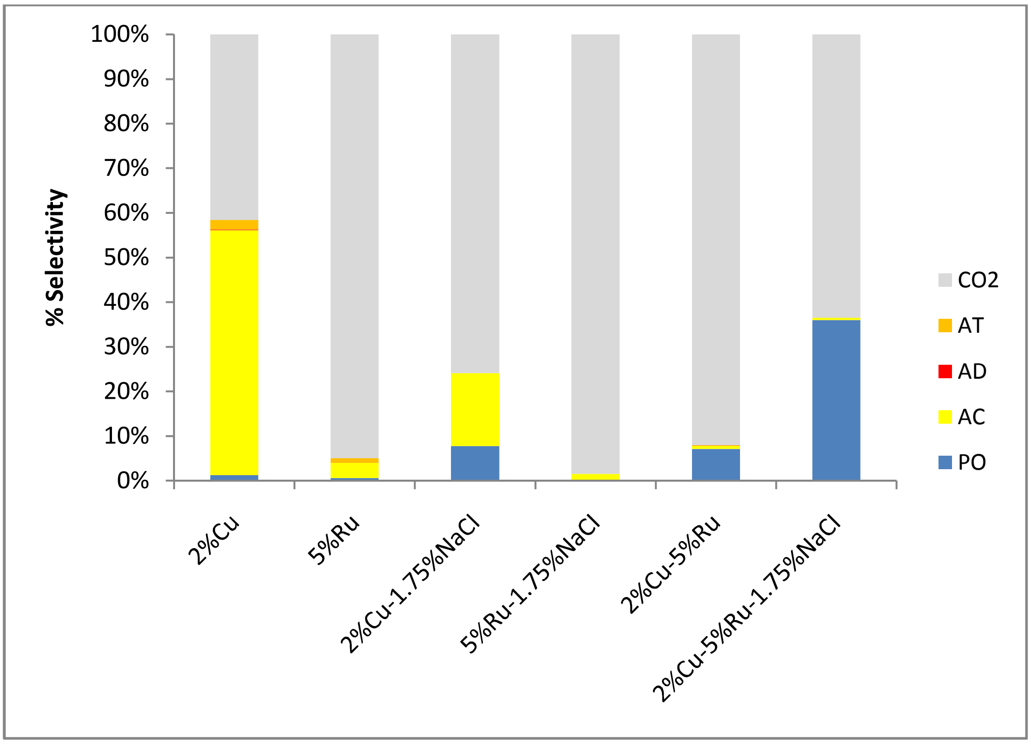


Figure 4.10: Selectivity of the products (carbon dioxide (CO_2), acetone (AT), acetaldehyde(AT), acrolein(AC), propylene oxide(PO)) of Cu&Ru based catalysts

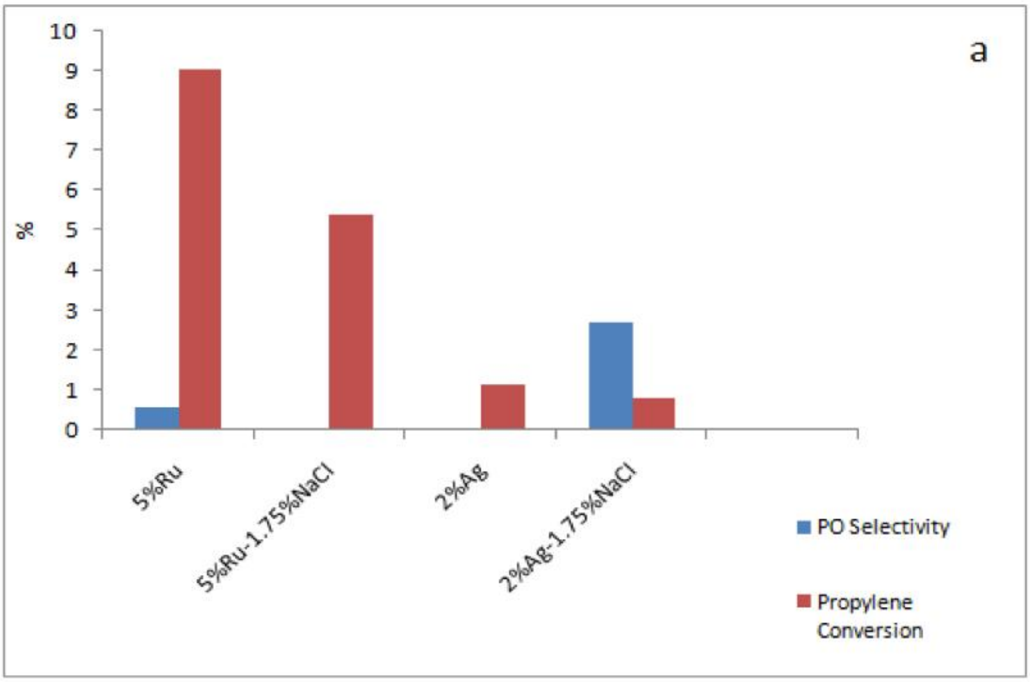
After the effectiveness of c-SiO_2 supported Ru-Cu-NaCl multimetallic system for direct epoxidation of propylene was observed, the study was continued with the investigation of NaCl effect on the other ruthenium containing bimetallic systems prepared with silver (Ag), manganese (Mn). These multimetallic systems prepared with the same metallic weight ratio of Ru-Cu-NaCl system (2%wt X- 5%wt Ru-1.75 wt%Na (where x=Ag,Mn; and NaCl used as sodium precursor).

For this purpose, 20 catalysts were investigated and the obtained activity test results were presented in the following section.

4.1.3. Supported Ag and Ru Catalysts

In the study, 2%wt Ag/c-SiO_2, 5%wt Ru/c-SiO_2 and 2%wt Ag-5%wt Ru/c- SiO_2 catalysts were prepared and the effect of NaCI on these monometallic and bimetallic systems was investigated separately.

It was shown in Figure 4.11 (a),(b) and Figure 4.12 that NaCl addition increased the performance of Ag/c-SiO_2 catalyst, but depleted the performance of Ru/c-SiO_2 catalyst. The main product for un-promoted Ag/c-SiO_2 catalyst was observed as CO_2 and then AC, while PO, AT and AD formation were not observed. With the addition of NaCl, Ag/c-SiO_2 catalyst was promoted to PO formation and 2.72% PO selectivity was obtained. Besides, the PO formation correlated with a noticeable decrease in the AC formation. When Ag-Ru/c-SiO_2 bimetallic system compared with un-promoted monometallic Ag/c-SiO_2 and Ru/c-SiO_2 catalysts, it was seen that Ag-Ru/c-SiO_2 bimetallic system significantly enhanced propylene consumption. However, mainly combustion reaction took place and PO selectivity and selectivity of other oxygenated products were obtained with a negligible amount. The addition of NaCI to the Ag-Ru/SiO_2 bimetallic did not affect PO selectivity and complete combustion reaction again taking place.



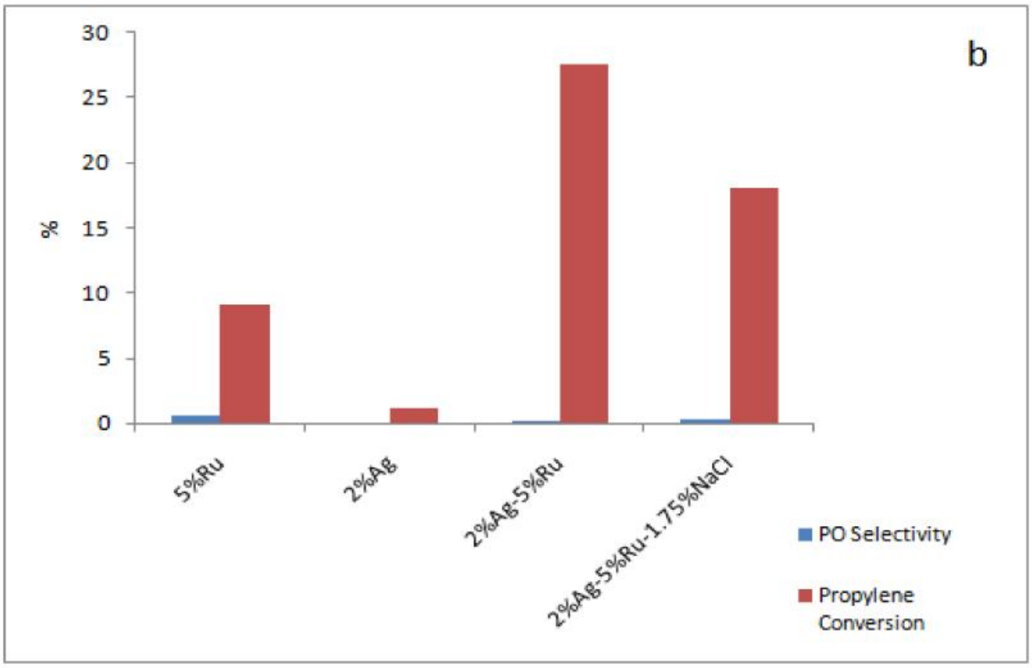


Figure 4.11: (a) and (b) PO selectivity and propylene conversion of Ag&Rubased catalysts at 300˚C

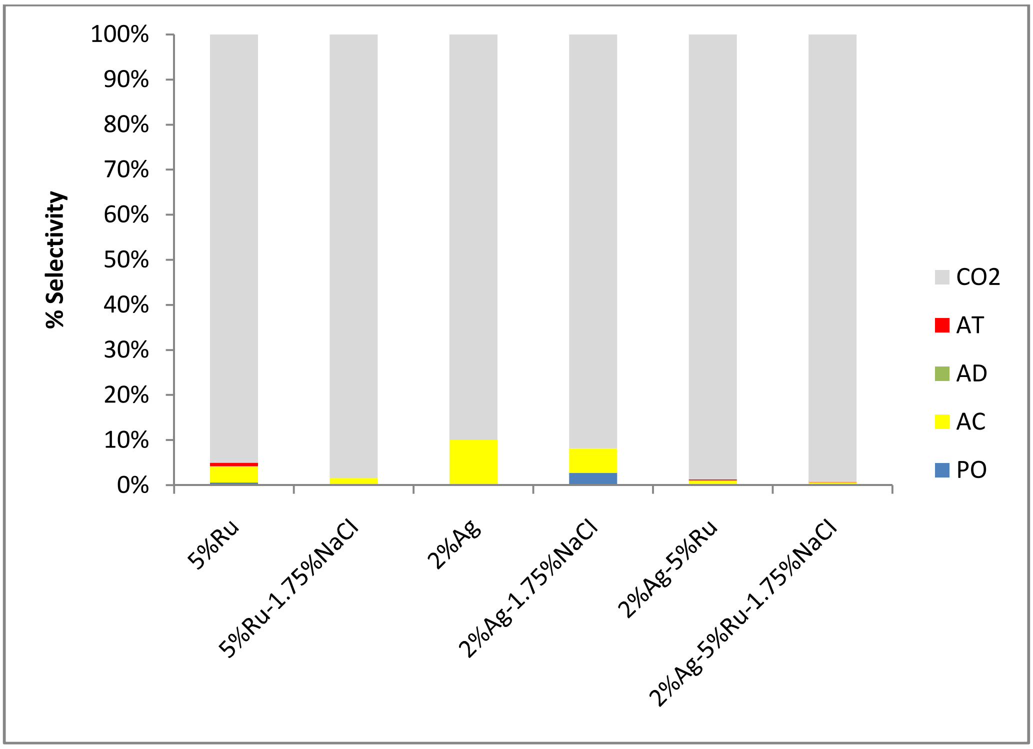


Figure 4.12: Selectivity of the products (carbon dioxide (CO_2), acetone (AT), acetaldehyde(AT), acrolein(AC), propylene oxide(PO)) of Ag&Ru based catalysts

4.1.4. Supported Mn and Ru Catalysts

In the study, 2%wt Mn/c-SiO_2, 5%wt Ru/c-SiO_2 and 2%wt Mn-5%wt Ru/c-SiO_2 catalysts were synthesized and the effect of NaCl on these monometallic and bimetallic systems was investigated separately.

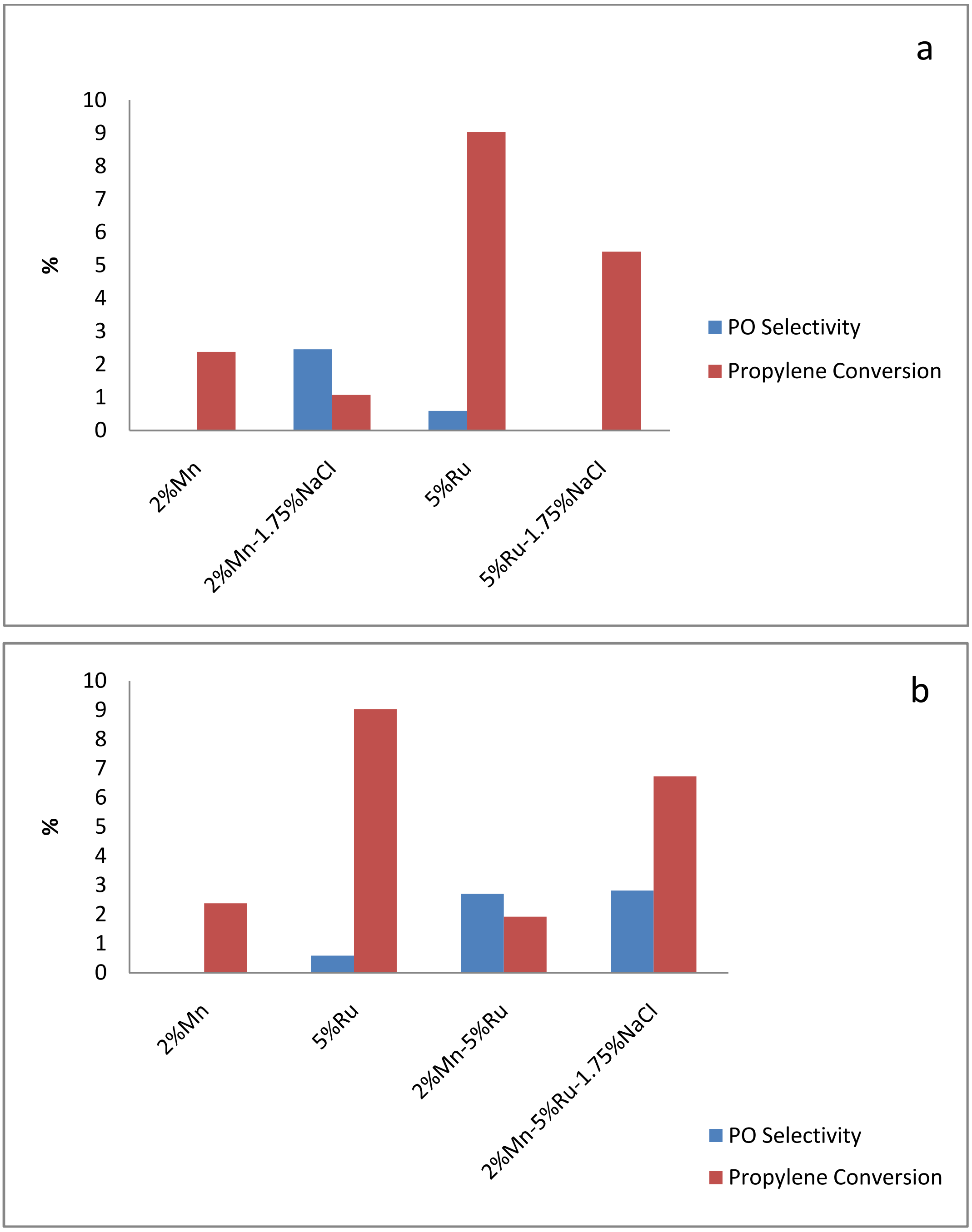


Figure 4.13: (a) and (b) PO selectivity and propylene conversion of Mn&Ru based catalysts at 300˚C

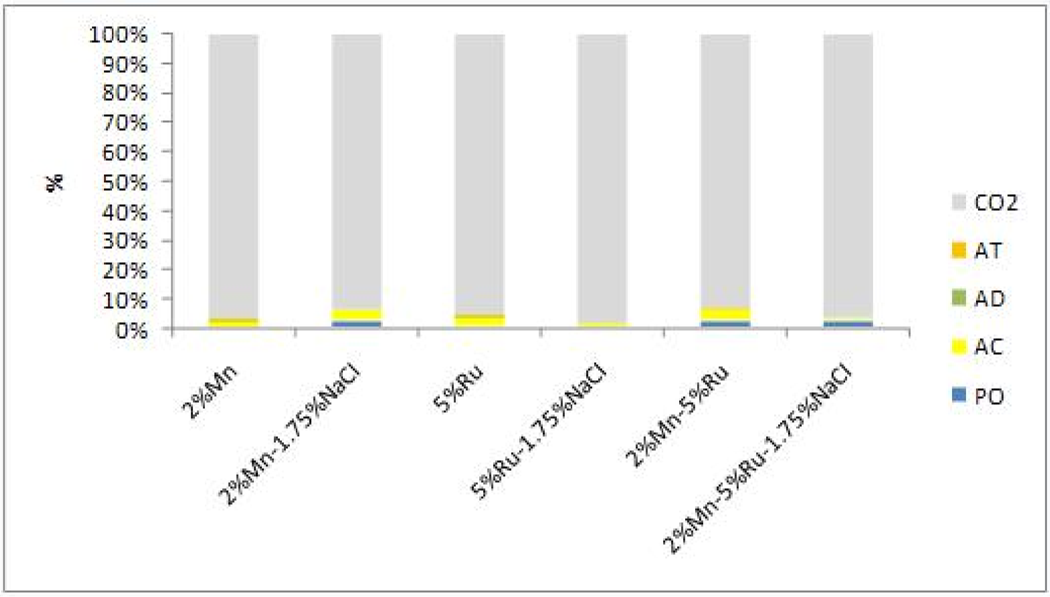


Figure 4.14: Selectivity of the products (carbon dioxide (CO_2), acetone (AT), acetaldehyde(AT), acrolein(AC), propylene oxide(PO)) of Mn&Ru based catalysts

As seen in Figure 4.13 (a)-(b) and Figure 4.14, the effect of NaCl addition on Mn/c-SiO_2 was similar with the effect of NaCl on Ag/c-SiO_2 catalyst. The main product for Mn/c-SiO_2 catalyst was observed as CO_2 and then AC, while PO formation was not observed. However, with the addition of NaCl, Mn/c-SiO_2 catalyst was promoted to PO formation and 2.46% PO selectivity was obtained. When Mn-Ru/c-SiO_2 bimetallic system compared with monometallic Mn/c-SiO_2 and Ru/c-SiO_2 catalysts, it was seen that Mn-Ru/c-SiO_2 bimetallic system increased PO formation (2.71% PO selectivity at 1.92% propylene conversion). Besides the addition of NaCl to the Mn-Ru/SiO_2 bimetallic system caused only a slight increase in PO selectivity. To summarize, Mn-Ru catalysts mostly caused combustion reaction and produced $CO_{2.}$

In the study, c-SiO_2 supported Ag-Cu and Mn-Cu bimetallic systems were also prepared for direct epoxidation of propylene and the effect of NaCl on these catalysts were investigated. The obtained activity test results were presented in the following sections.

4.1.5. Supported Ag and Cu Catalysts

2%wt Cu/c-SiO_2, 5%wt Ag/c-SiO_2 and 2%wt Ag-5%wt Cu/c-SiO_2 catalysts were synthesized and the effect of NaCl on these monometallic and bimetallic systems was investigated separately.

As seen in the Figure 4.15 (a)-(b) and Figure 4.16, addition of NaCl enhanced POselectivity only for Cu/c-SiO_2 catalyst. For 5%wt Ag catalyst, the main product was CO_2 with 62% selectivity and then AC with 38% selectivity, while PO formation was not observed. As shown before in Section 4.1.3, the same products were observed for 2%wt Ag/c-SiO_2 catalyst (shown in Figure 4.11 and Figure 4.12) with 90% CO_2 selectivity and 10% AC selectivity. When 2%wt Ag/c-SiO_2 and 5%wt Ag/c-SiO_2 was compared, it was seen that increase in silver amount promoted only AC formation, but did not affect the PO formation or propylene conversion. It was also shown in Figure 4.14 that modification of 5%wt Ag/c-SiO_2 catalyst with NaCl was ineffective for PO formation. Besides, desired improvement for PO production could not be obtained for Cu-Ag/c-SiO_2 bimetallic system before and after NaCl modification.

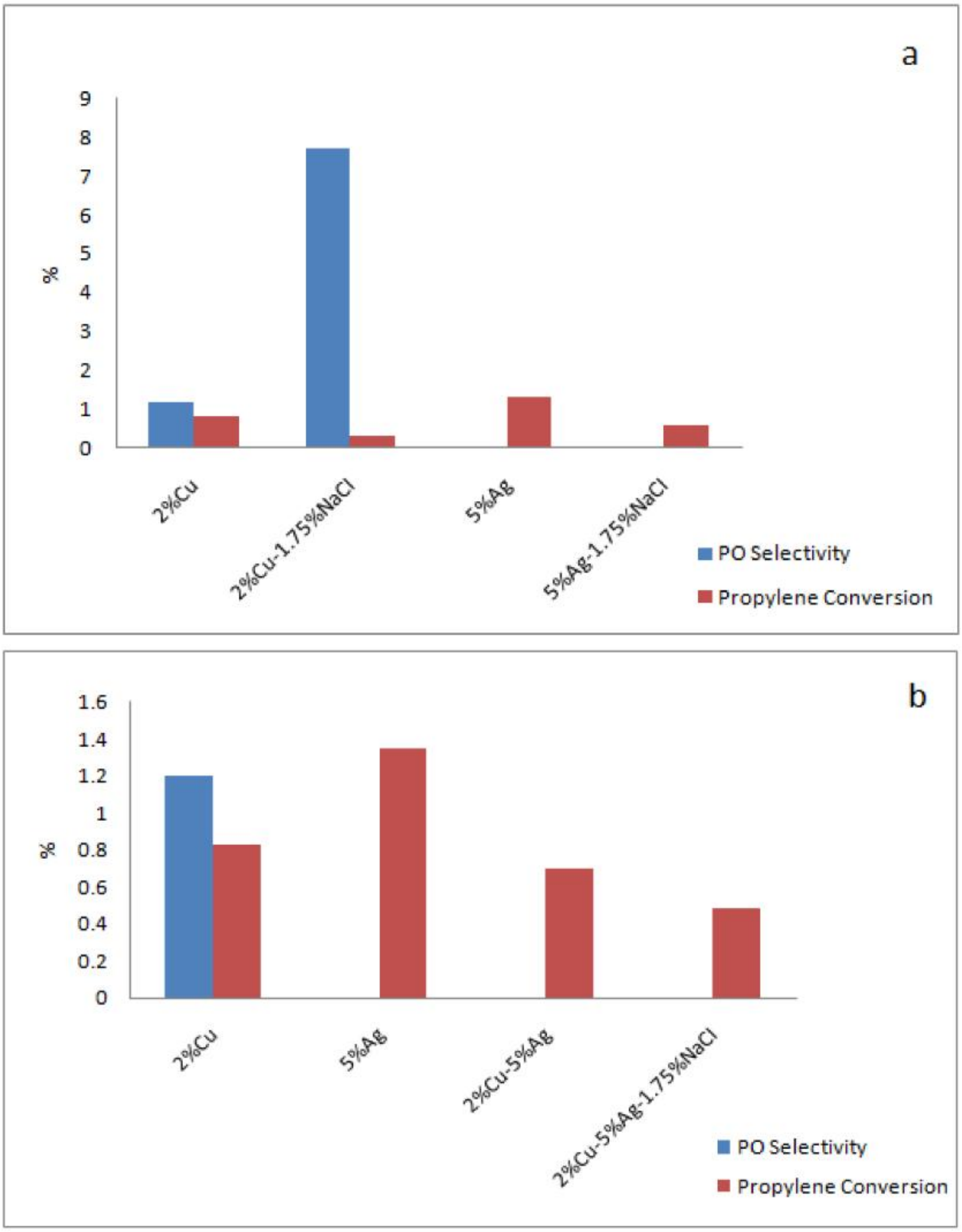


Figure 4.15: (a) and (b) PO selectivity and propylene conversion of Mn&Ru based catalysts at 300˚C

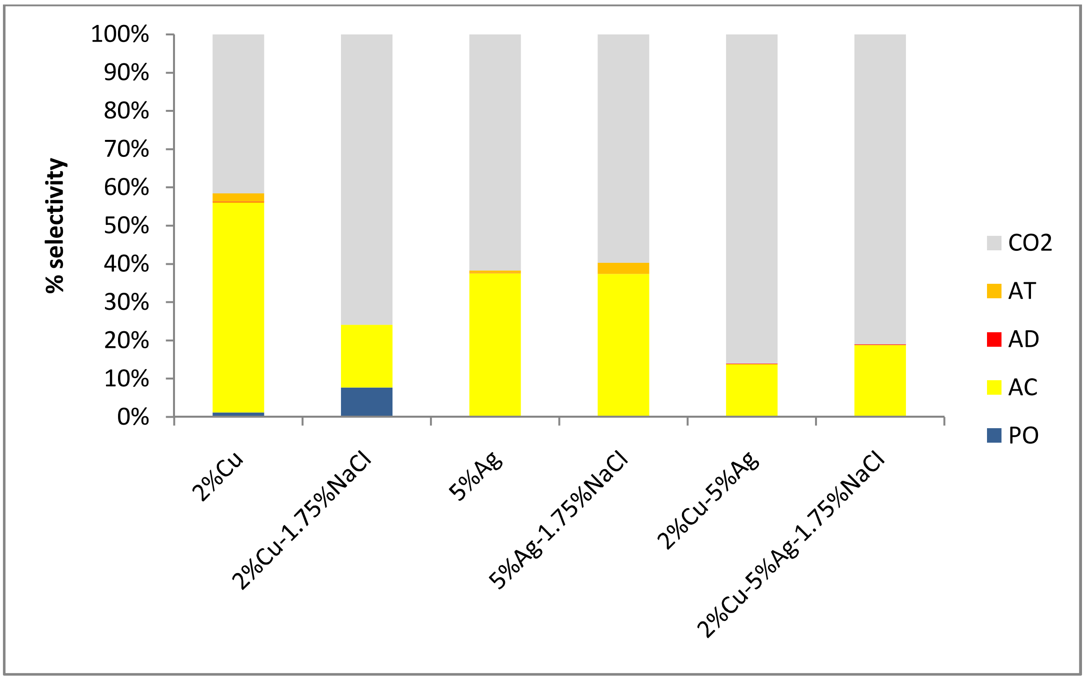


Figure 4.16: Selectivity of the products (carbon dioxide (CO_2), acetone (AT), acetaldehyde(AT), acrolein(AC), propylene oxide(PO)) of Cu&Ag based catalysts

4.1.6. Supported Mn and Cu Catalysts

Firstly, binary combinations of Mn and Cu metals prepared with different metallic weight ratios and the activity of these c-SiO_2 supported bimetallic systems were investigated. As seen in the Figure 4.17, 2%wt Mn-5%wt Cu/c-SiO_2 catalyst gave the highest PO selectivity and propylene conversion among these catalysts with different metal ratios. Then, the study continues with the investigation of NaCl effect on the catalytic performance of 2%wt Mn- 5%wt Cu/c-SiO_2 catalyst.

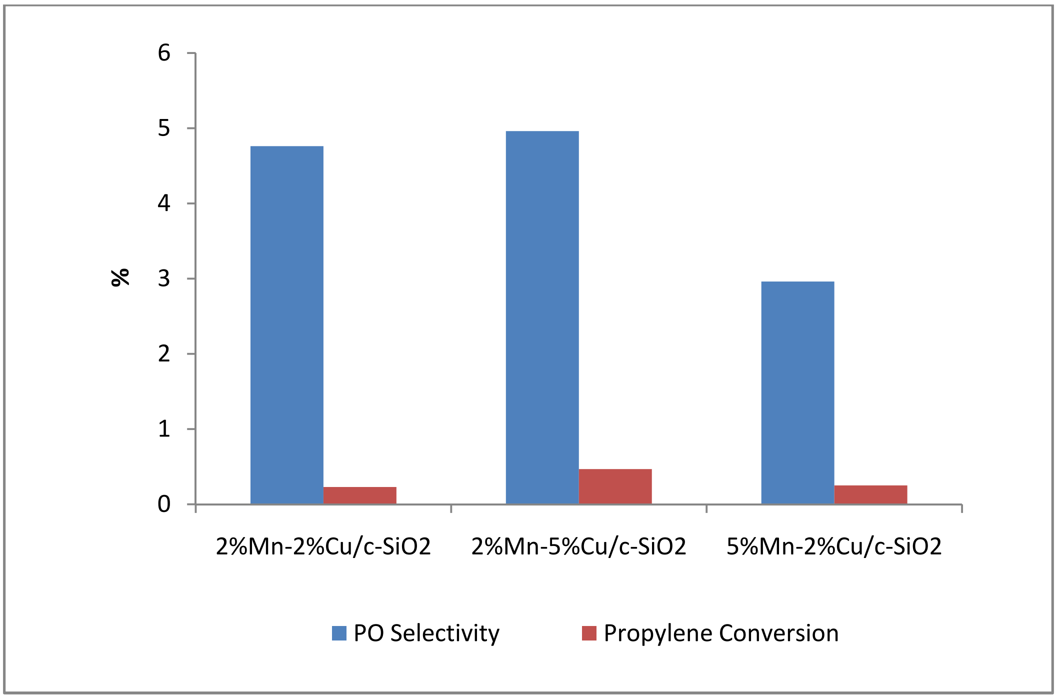


Figure 4.17: PO selectivity and propylene conversion of bimetallic Mn-Cu/c-SiO_2 systems prepared with different metallic weight ratios

The catalytic performances of monometallic 2%wt Mn/c-SiO_2 and5%wt Cu/c-SiO_2 catalysts with their binary combination (2%wt Mn-5%wt Cu/c-SiO_2) and the effect of NaCl on this bimetallic system were evaluated according to test results shown in Figure 4.18 and Figure 4.19.

As seen in the figures, it was clearly seen that mainly combustion reaction took place for Mn/c-SiO_2 catalyst and 96.7% selectivity of CO_2 was observed. CO_2 formation was also at high level for Cu/c-SiO_2 catalyst, but AC and AT was also produced as a second and third product with high selectivities, which are 37% and 9% respectively. Accordingly, monometallic Mn/c-SiO_2 and Cu/c-SiO_2 catalyst were determined inactive for PO formation. However, when activity test result of their binary combination was investigated, it was observed clearly that Mn-Cu/c-

SiO_2bimetallic system promoted PO formation (4.96% PO selectivity at 3.18% propylene conversion). More interestingly, adding NaCl had a great curative effect on the performance of the Mn-Cu/c-SiO_2 system. While propylene conversion decreased from 3.18% to 1.64%, NaCl addition led to an improvement toward PO selectivity by a factor of ~3 times and 15.54% PO selectivity was obtained.

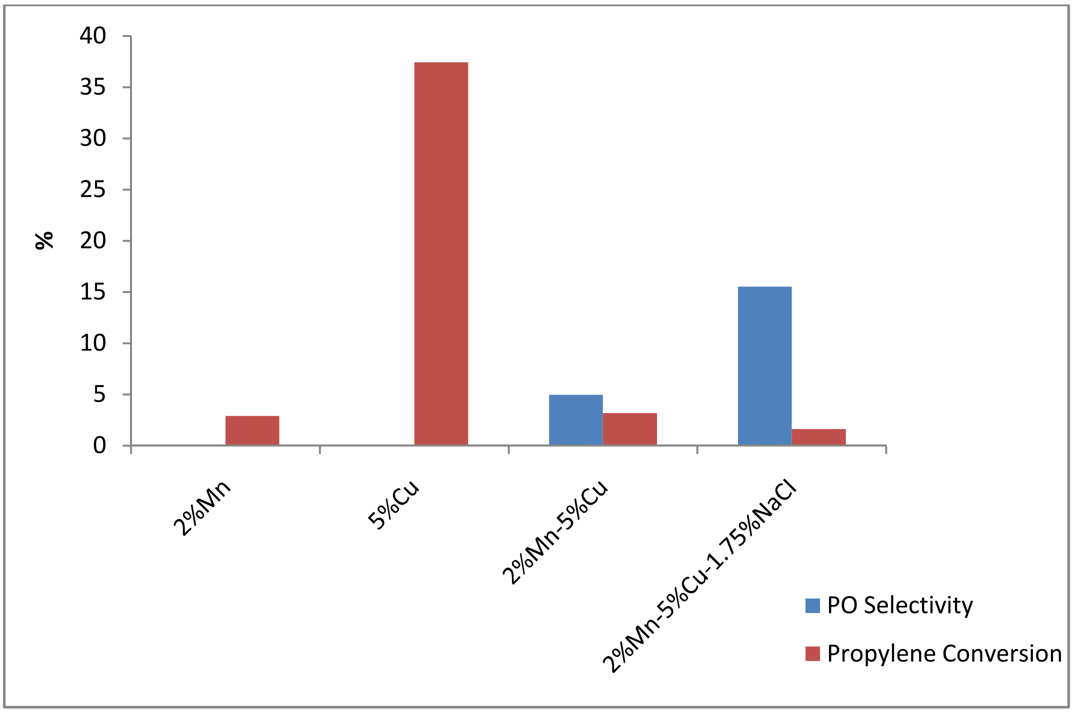


Figure 4.18: PO selectivity and propylene conversion of Mn&Cu based catalysts at 300˚C

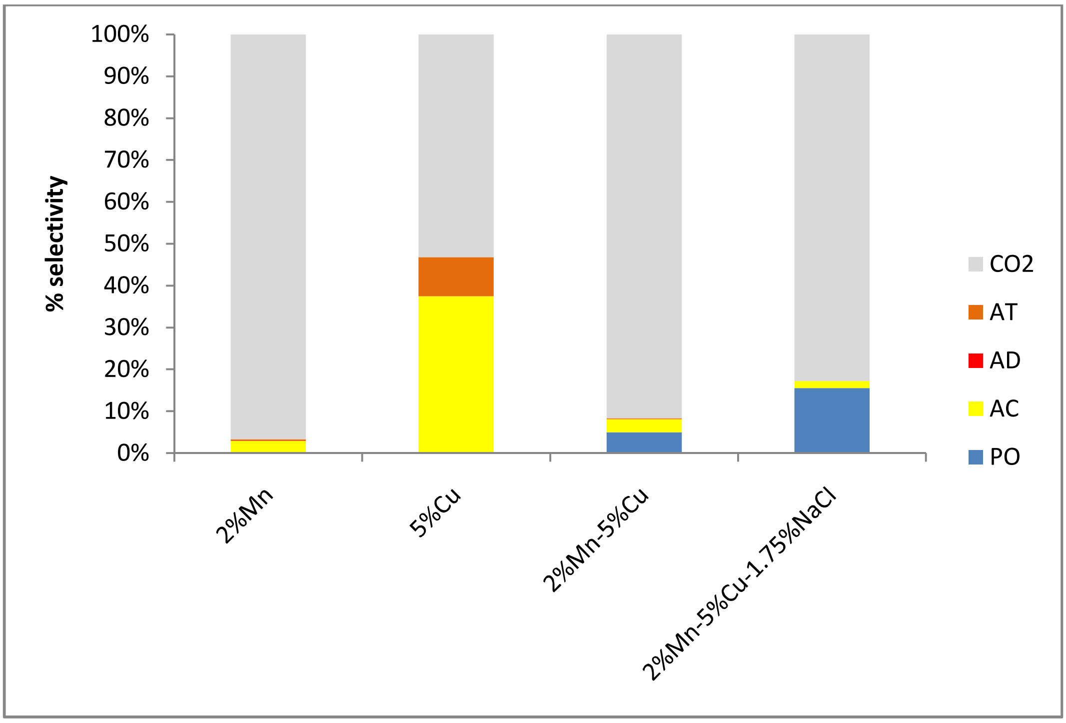


Figure 4.19: Selectivity of the products (carbon dioxide(CO_2), acetone (AT), acetaldehyde(AT), acrolein(AC), propylene oxide(PO)) of Mn&Cu based catalysts

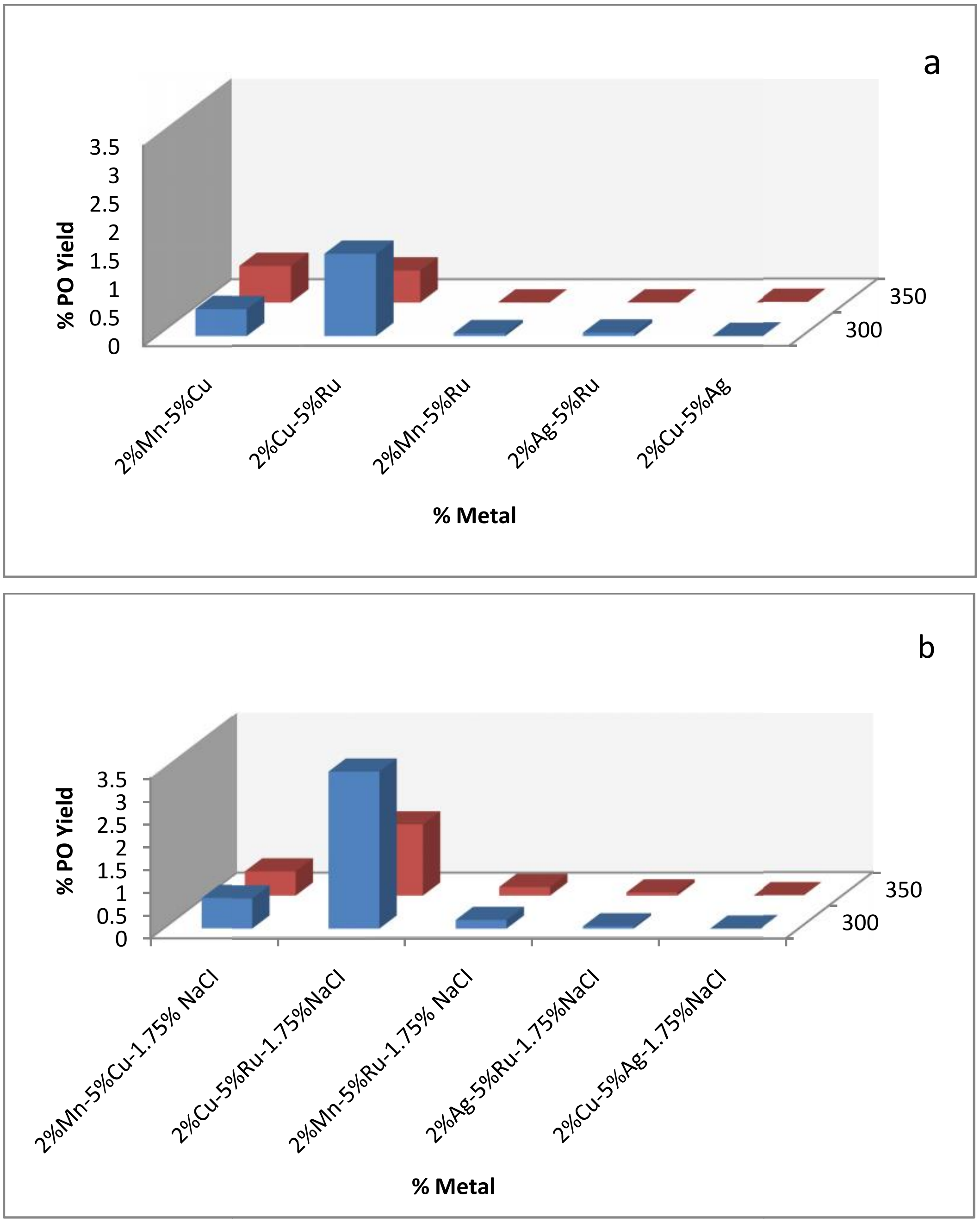


Figure 4.20: a) Comparison results of % PO yield between bimetallic catalysts supported on c-SiO_2 and b) the effect of NaCl on the % PO yield of these bimetallic systems

Comparison results of %PO yield (at 300˚C and 350˚C) between all investigated c-SiO_2 supported bimetallic systems prepared with the same metal ratio (2%wt X-5%wt Y where x,y=Ru, Cu, Ag, Mn) were summarized in Figure 4.20-a. From the figure, it was clearly seen that the maximum PO yield was obtained for 2%wtCu-5%wt Ru/c-SiO_2 catalyst. Other Ru containing bimetallic systems prepared with Ag or Mn were determined as inefficient for epoxidation of propylene reaction to PO. When results of PO yield of these catalysts were compared after NaCl modification (shown in Figure 4.20-b), again Cu-Ru bimetallic catalyst was determined as the most improved catalyst with 3.44% PO yield at 300˚C. As shown in the Figure 4.20 (a)-(b), all the catalytic systems were screened at 300˚C and 350˚C.It was observed that increasingtemperature from 300˚C to 350˚C caused a decline in activity so 350˚C was determined as very high for the reaction temperature.

In addition, the effect of reaction temperatures on the catalytic performance was also investigated at interval temperatures 250 to 350˚C. The influence of reaction temperatures on the catalytic activity of the most effective catalyst (2%wt Cu- 5%wt Ru-1.75%wt NaCl/c-SiO_2) was summarized in Figure 4.21. As seen in the figure, while propylene conversion continuously increased with reaction temperature, PO selectivity conversely declined except an increase at 300˚C. It was also concluded that the maximum PO yield of 3.44% was obtained at 300˚C.

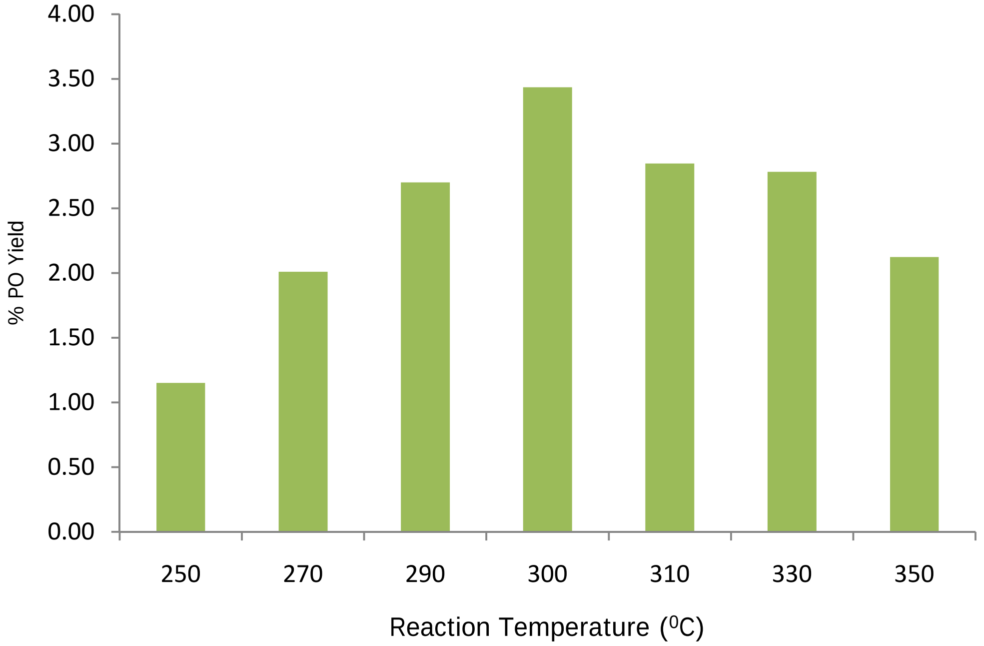
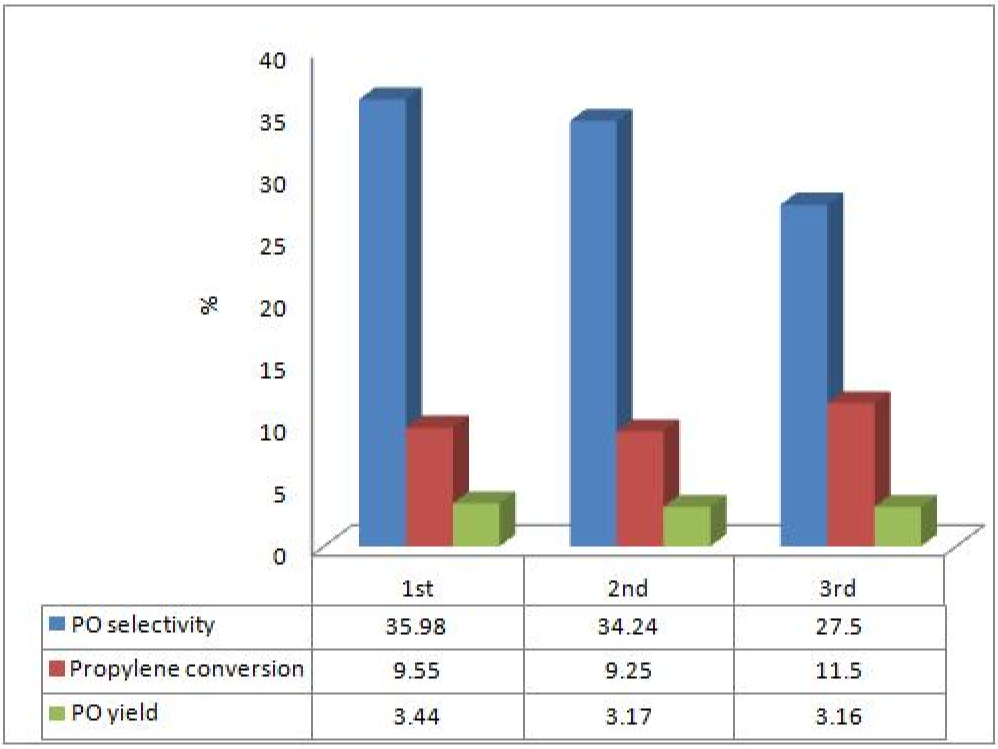


Figure 4.21: The effect of reaction temperature on the catalytic performance of the2%Cu-5%Ru-1.75NaCl/c-SiO_2

Catalyst reproducibility is also important for catalytic science. So the most successful catalyst (2%wt Cu- 5%wt Ru-1.75%wt NaCl/c-SiO2) was re-tested two times after the first screening test. In Figure 4.22, little difference in PO selectivity and propylene conversion was observed, however the comparison of PO yields showed that nearly same PO productivity was obtained. This difference could be explained by the air sensitivity of catalysts.



	1st	2nd	3rd
🟦 PO selectivity	35.98	34.24	27.5
🟥 Propylene conversion	9.55	9.25	11.5
🟩 PO yield	3.44	3.17	3.16

Figure 4.22: The reproducibility of 2%Cu-5%Ru-1.75%NaCl/c-SiO_2 catalyst

4.2. Characterization Results

4.2.1. BET Analysis

Commercial silica support (c-SiO_2) with and without metals showed type II isotherm, and both silica (SiO_2) and silica synthesized with template (t-SiO_2) supports with and without metals showed type IV isotherm according to BDDT. The shape of the hysteresis loops varies from one support to another according to IUPAC classification as shown in Figure 4.23.

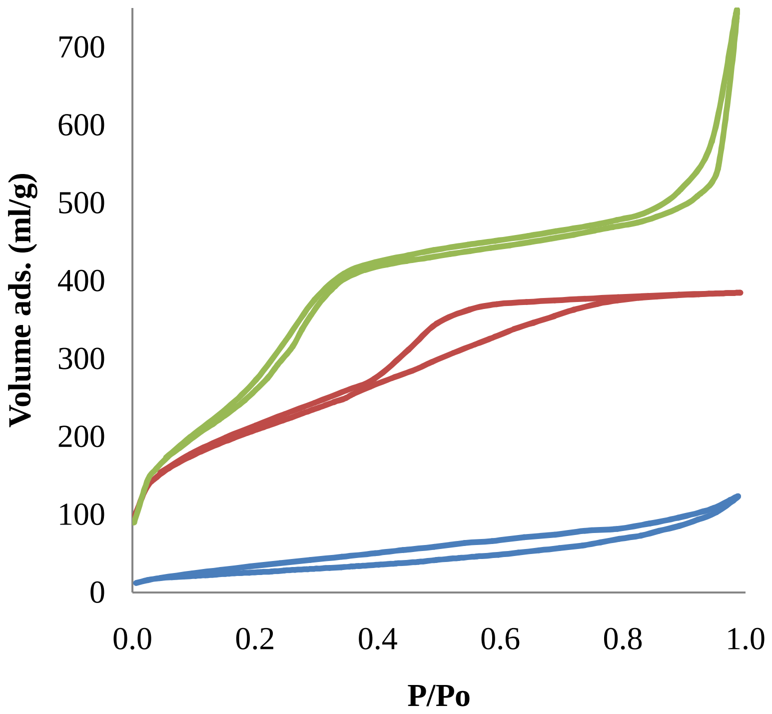


Figure4.23: N_2 isotherm of support materials

The hysteresis loop of commercial silica (c-SiO_2) is close to H3 type in IUPAC classification and is usually given by the aggregates of platy particles or adsorbents containing slit-shaped pores. The broad hysteresis loop belongs to low surface area silica (SiO_2) shows desorption branch being much steeper than the adsorption branch; thus indicates the filling and emptying of the mesopores by capillary condensation. The nearly reversible isotherm of silica synthesized with template (t-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. An addition of metals into the support caused a decrease in both pore size and surface area of material because of plugging of the pores with metal particle as shown in Table 4.2. In addition there are no changes in hysteresis loop shape after loading of metals.

In Table 4.2, surface areas of the 2/Cu-5%Ru catalysts supported on t-SiO_2, $SiO_2$and c-SiO_2 were shown as 799 m^2/g, 595 m^2/g and 82 m^2/g, respectively. That means pore size of the catalyst supported on t-SiO_2 smaller than SiO_2 and c-SiO_2, conversely. Smaller pore size means that it becomes hard to escape of PO from the catalyst and further reactions takes place that decrease the PO yield. Activity test results showed that 2%Cu-5%Ru catalyst supported on c-SiO_2 have highest PO yield when compared to 2%Cu-5%Ru catalysts supported on SiO_2 and t-SiO_2. That was consistent with the results obtained by BET analysis where PO yield is conversely proportional to pore size.

Table 4.2: Surface area and isomer type of the supports and catalysts

Catalyst	**Surface area (m^2/g)**	**Isomer type**
c-SiO_2	97	Type 2
5%Ru-2%Cu/c-SiO_2	82	Type 2
t-SiO_2	936	Type 4
5%Ru-2%Cu/t-SiO_2	799	Type 4
SiO_2	718	Type 4
5%Ru-2%Cu/SiO_2	595	Type 4

4.2.2. XRD Analysis

The effect of support material was also investigated with XRD analysis. For this purpose XRD patterns of 2%Cu-5%Ru-1.75%NaCl catalyst supported over SiO_2, c-SiO_2 and t-SiO_2 were shown in Figure 4.24. The peak observed in the XRD pattern are belongs to RuO_2 and Cu_2O. There is no significant effect of support material on the metal particle size according to Scherrer equation.

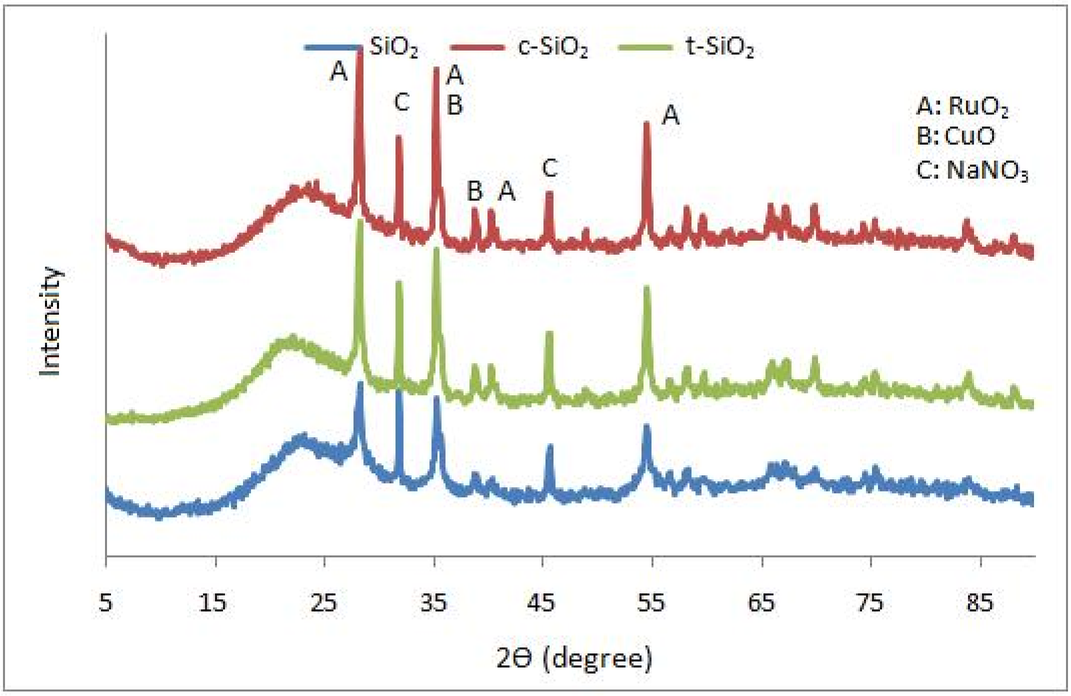


Figure 4.24: XRD patterns of Ru-Cu-NaCl catalyst supported over SiO_2, c-SiO_2andt-SiO_2

The diffraction peaks at around 28, 35, 40, 55˚ were attributed to RuO_2 and diffraction peak around 35 and 38˚ were attributed to CuO. However the first CuO peak around 35˚ is overlap with RuO_2 peak.

To better understand the effect of NaCl over each metals (Ru and Cu), they were promoted with NaCl separately and investigated with XRD analysis shown in Figure

4.25. Addition of the NaCl did not affect CuO and Ru_2O peak positions and area under the peaks.

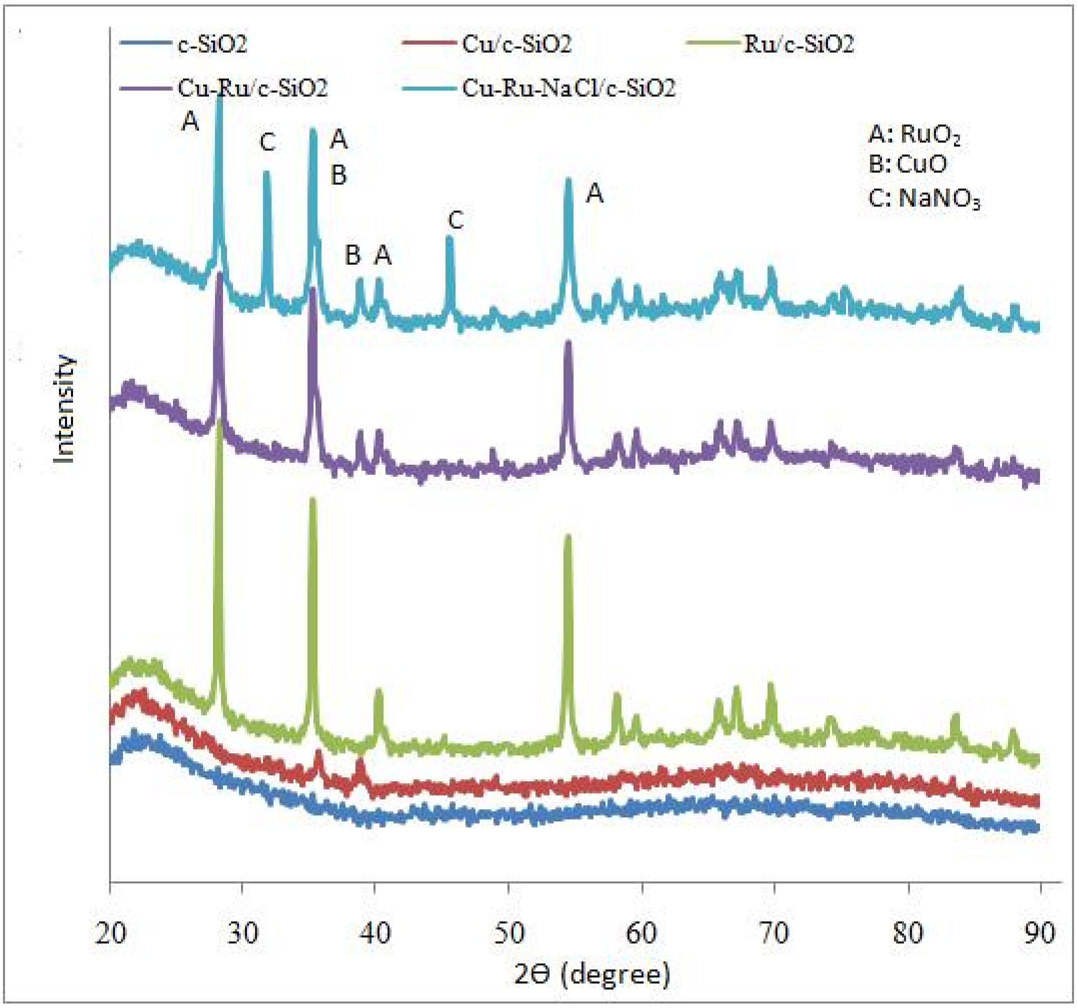


Figure 4.25: XRD patterns of Cu&Ru based catalysts supported over c-SiO_2

In other theoretical study performed in our group, the performance of chlorinated Cu_2O(001) and Ru_2O(110) surface were compared for epoxidation reaction with nonchlorinated surfaces. An addition of Cl on the surface slightly increased the activation barrier of allylic hydrogen stripping and the closer chlorine to the reaction site further increase activation barrier. Comparison between chlorinated and nonchlorinated RuO_2(110) surface showed that chlorine addition did not improve PO formation but decreased activation barrier of unwanted allylic hydrogen stripping reaction and caused combustion reaction (Kurnaz, 2011).

4.2.3. XPS analysis of Cu,Ru Doped c-SiO_2 Samples

Below is the list of the samples analyzed in the XPS measurements:

2%Cu/c-SiO_2 (5)
5%Ru/c-SiO_2 (6)
2%Cu5%Ru/c-SiO_2 (9)
2%Cu5%Ru1.75NaCl/c-SiO_2 (4)
7%Cu5%Ru1.75NaCl/c-SiO_2
7%Cu5%Ru/c-SiO_2

The XP spectra of Si2p, O1s, C1s, Ru3p, Cu2p, and Na1s were collected during the XPS analysis. All of the spectra were calibrated using the Si2p signal of silica support material located at a binding energy (BE) of 103.3 eV. The following typical flood gun (FG) settings were used during the XPS data acquisition for charge-compensation purposes: Electron Energy = 5 eV, Emission Current = 70 µA (denoted as “5x70” in Figure 4.27). The 7%Cu5%Ru/c-SiO_2 sample spectra were acquired using “6x70” and “4x80” FG parameters.

The Ru3d (i.e. the main XPS signal of Ru) signal overlaps with the intense C1s signal complicating the analysis of the Ru3d region, particularly for low Ru loadings, which in turn hinders the accurate determination of Ru oxidation states. Thus, instead of the Ru3d region, Ru3p region of the XP spectra were monitored and analyzed (Figure 4.26) in the XPS experiments. For the currently analyzed samples, the $Ru3p_{3/2}$ peak is observed at a typical BE of ~463 eV which is attributed to the metallic state of Ru; the higher BE shoulder at ~465 eV can be attributed to RuO_2 species.

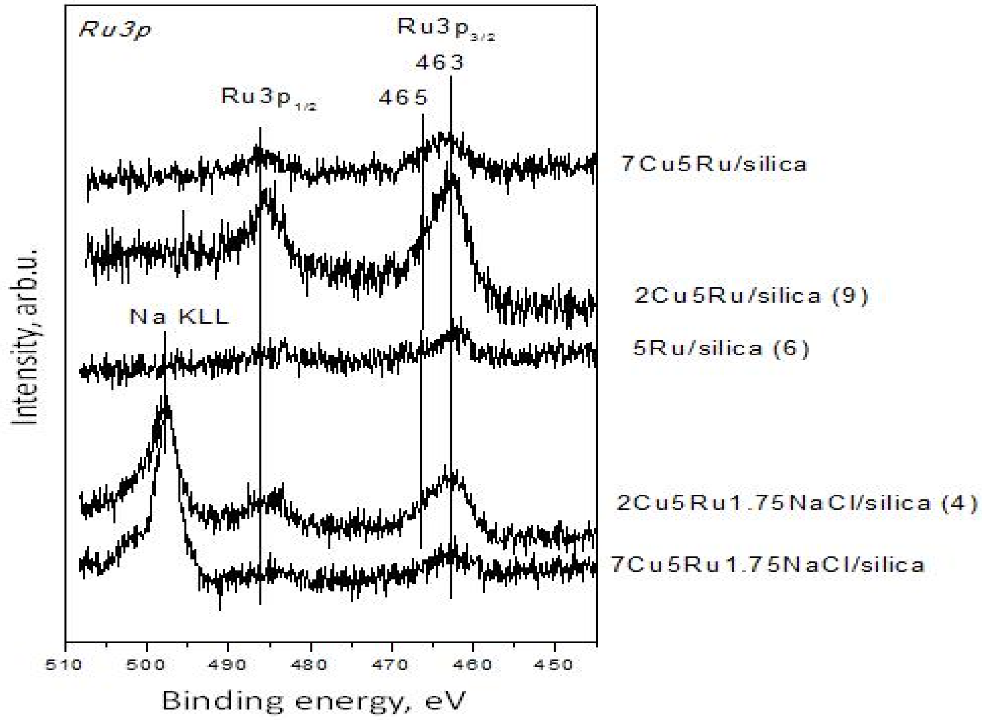


Figure 4.26: Ru3pXP spectra of the analyzed samples (the flood gun parameterswere 5 eV×70 μA)

The Cu2p XP spectra of NaCl-promoted samples (2%Cu5%Ru1.75NaCl/c-SiO_2 (4) and 7%Cu5%Ru1.75NaCl/c-SiO_2) in Figure 4.27, yield a $Cu2p_{3/2}$ peak at 933 eV which is consistent with the presence of CuO species. On the other hand, Cu2p XP spectra of the NaCl-free samples reveal a strong differential charging behavior, yielding a significant $Cu2p_{3/2}$ BE shift of c.a. +5 eV. This detrimentally large differential charging behavior, which is extremely sensitive to the flood gun charge compensation parameters used during the XPS data acquisition, is observed only in the absence of NaCl and is most likely due to the poor electrical conductivity at the

Cu/c-SiO_2 or Cu/Ru/c-SiO_2 interfaces. As a result of this drastic differential charging behavior, Cu 2p BE values of the NaCl-free samples are shifted out of the regular Cu 2p BE window, in spite of the wide variety of alternative charge compensation parameters used in the current XPS data acquisition attempts. For instance, Figure 4.27 presents XPS data for the 7%Cu5%Ru/c-SiO_2 sample with two different charge compensation parameters (i.e. “4x80” and “6x70”). It is visible in these spectra that decreasing the electron beam energy of the flood gun to 4 eV (i.e. “4x80” case) results in a Cu2$p_{3/2}$ peak shift to lower BE values (i.e. to 935 eV), where a differential charging of c.a. +2 eV is still visible for this measurement. On the other hand, XPS analysis of the same sample with a charge compensation using an electron beam energy of 6 eV (i.e. “6x70” case) does not provide any significant charge compensation for the Cu sites and Cu states seem to be still shifted to higher BE values that are outside the regular BE window. These results clearly demonstrate the extent of the drastic differential charging on the NaCl-free samples and the strong dependence of the Cu2p XPS signal of these samples to the charge compensation parameters.

Interestingly, the presence of the NaCl promoter drastically facilitates the charge compensation efficiency during the XPS analysis, shifting the Cu 2p BE back to the regular Cu 2p energy window. It is likely that on these samples, NaCl functions as an electronic promoter enabling the charge transfer at the Cu/c-SiO_2 and/or Cu/Ru/c-SiO_2 interface and preventing the charge build up on the surface during the XPS analysis.

XPS results presented in Figures 4.26 and 4.27 are also summarized in Table 4.3.

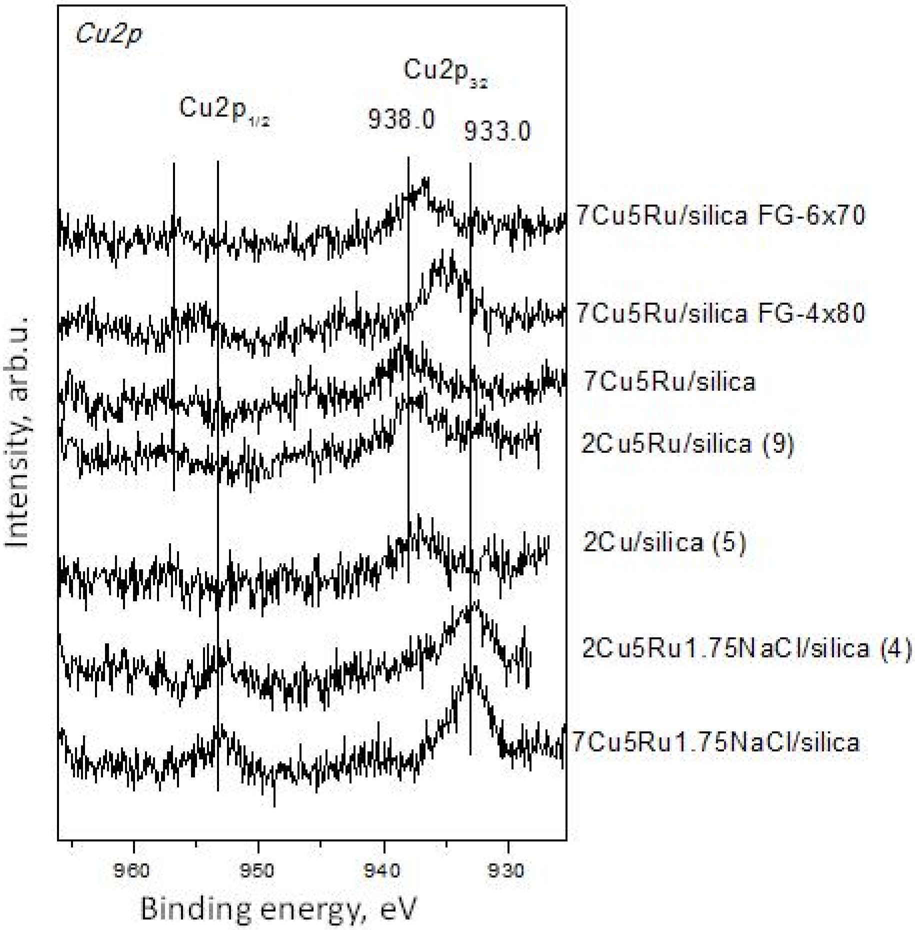


Figure 4.27: Cu2pXP spectra of the analyzed samples (unless mentioned otherwise, flood gun parameters used during the XPS analysis were $E_{electron}$= 5 eV and $I_{emission}$= 70 µA)

Table4.3: Binding energies (eV) of the main components

	Ru3p$_{3/2}$	Cu2p$_{3/2}$	O1s (FWHM)	
2%Cu/c-SiO$_2$ (5) 5x70	-	937.6	533.4 (2.75)	532.1 (2.14) 533.7 (2.14)
5%Ru/c-SiO$_2$ (6) 5x70	462.0	-	532.7 (1.86)	
2%Cu5%Ru/c-SiO$_2$(9) 5x70	463.0	937.4	533.6 (2.92)	532.4 (2.16) 533.9 (2.16)
2%Cu5%Ru1.75NaCl/ c-SiO$_2$(4) 5x70	462.9	932.9	532.8 (2.03)	
7%Cu5%Ru1.75NaCl/ c-SiO$_2$ 5x70	463.0	932.9	532.7 (2.14)	
7%Cu5%Ru/c-SiO$_2$ 5x70	463.3	938.2		532.4 (2.21) 534.2 (2.21)
7%Cu5%Ru/c-SiO$_2$ 4x80	462.8	935.0		532.8 (2.19) 534.1 (2.19)
7%Cu5%Ru/c-SiO$_2$ 6x70	464.0	937.0		531.3 (2.29) 537.6 (2.31)

Relative elemental atomic ratios on the surface of the investigated samples were also calculated using the corresponding atomic sensitivity factors (ASF) and the XPS data. These findings are presented in Table 4.4. It is worth mentioning that ASF(Na1s)/ASF(Cl2p) = 5. Thus, due to the significantly low sensitivity of the XPS technique towards Cl as well as the relatively small loading of Cl used in the catalyst preparation, Cl2p signal was below the detection limit.

Table 4.4: Relative surface atomic ratios of the elements investigated in the XPS analysis.

	Ru/Si	Cu/Si	O/Si	Na/Si
2%Cu/c-SiO_2 (5) 5x70	-	0.0005	1.8	-
5%Ru/c-SiO_2 (6) 5x70	0.001	-	1.9	-
2%Cu5%Ru/c-SiO_2 (9) 5x70	0.007	0.001	1.9	-
2%Cu5%Ru1.75NaCl/c-SiO_2 (4) 5x70	0.003	0.001	1.8	0.005
7%Cu5%Ru1.75NaCl/c-SiO_2 5x70	0.001	0.002	1.8	0.010
7%Cu5%Ru/c-SiO_2 5x70	0.003	0.001	2.0	-

A combined analysis of the Ru3p and Cu2p XP spectra of the investigated samples reveal important aspects regarding the structural properties of these materials and shed light on the influence of the NaCl catalytic promoter. Ru sites do not seem to reveal any indication of severe differential charging and can easily be charge-compensated. In other words, there seems to be no significant charge build-up on the Ru sites or on the Ru/c-SiO_2 interface during the XPS analysis. In contrast to these observations, Cu 2p signal for NaCl-free samples disclose a severe differential charging behavior indicating a remarkable amount of charge build-up on the Cu sites or at the Cu/c-SiO_2 interface. These two strikingly different differential charging behaviors of Ru and Cu sites on the same bimetallic catalyst surface suggest that in the absence of NaCl, Ru and Cu sites probably do not reside in close proximity with respect to each other, neither they exist in the form of a bimetallic alloy. In other words, for the NaCl-free samples, Ru and Cu sites are likely to be dispersed as separate phases on the catalyst surface.

Unlike the behavior described above, on the NaCl-promoted samples, a completely different trend is observed where both Ru and Cu sites seem to be readily charge-compensated. This observation suggests that NaCl functions as an electronic promoter preventing the charge build-up at the Cu/c-SiO_2, Ru/c-SiO_2 and Cu/Ru/c-SiO_2 interfaces. Furthermore, for the NaCl-containing samples, there is no direct indication of Cu and Ru sites existing as separate domains on the catalyst surface.

Thus, XPS experiments suggest that NaCl catalytic promoter has a strong interaction particularly with the Cu sites on the Cu/Ru/c-SiO_2 catalyst surface, altering the electronic structure of Cu sites. On the other hand, the electronic structure of the Ru sites seems to be altered in a minor fashion upon NaCl promotion.

4.2.4. FTIR Analysis of Cu, Ru Doped Silica Samples via CO Adsorption

Figure 4.29 represents the FTIR spectra obtained after CO(g) adsorption and saturation on (a) 2%Cu/c-SiO_2, (b) 5%Ru/c-SiO_2, (c) 2%Cu5%Ru/c-SiO_2 and (d) 2%Cu5%Ru1.75NaCl/c-SiO_2 samples at 323 K. Prior to CO adsorption, samples were reduced in 10 torr of H_2(g) at 473 K during 15 min. For the *2%Cu/silica* related spectrum, the only relevant vibrational feature is the weak signal at 2124 cm^{-1} that can be attributed to Cu^0-CO and/or Cu^+-CO species. CO coordinated on SiO_2 support has not been observed.

The presence of Ru on SiO_2 support (b, c, d) leads to appearance of some additional vibrational bands. The band at 2124 cm^{-1} (spectrum (b)) indicates that CO chemisorbed over reduced Ru^0 sites. The band at 2067 cm^{-1} has been previously assigned to $Ru(CO)_3$ species on metallic Ru centers in the literature. The broad feature at about 1987 cm^{-1}has been assigned to CO adsorbed on coordinatively unsaturated (cus) Ru sites (i.e. Ru defect sites) and/or to almost isolated Ru^0–CO species. The origin of the bands at 2175 cm^{-1} is not clear, however, it is possible to assign them to Ru^{n+}–CO where $n > 2$. The additional type of CO adsorbed species has been also observed on Ru containing samples: the IR feature at 1783 cm^{-1} was attributed to bridging carbonyls of the Ru_2^0–CO type.

A comparison of the spectra (a), (b) and (c) in Figure 4.28 suggests that going from monometallic (i.e. 2%Cu/c-SiO_2 and 5%Ru/c-SiO_2) to bimetallic catalyst preparation increases not only the total CO adsorption on the overall catalyst surface but it also increases the CO uptake of the individual Ru and Cu sites. This observation points to the fact that Cu-Ru bimetallic catalyst reveals a synergistic behavior leading to a better dispersion of the Cu and Ru active sites on the silica support material.

Finally, comparison of the spectra (c) and (d) also provide an important insight regarding the influence of the NaCl promoter on the 2%Cu5%Ru/c-SiO_2 structure. It is apparent that the presence of NaCl decreases the CO adsorption signals in the FTIR data. This can be attributed to a strong interaction of NaCl with the active sites on the catalyst surface, in line with the current XPS results discussed above. It is possible that NaCl sites may lead to sintering of the Cu, Ru and/or Cu/Ru sites and thus result in an attenuation of the CO adsorption efficiency. Alternatively, NaCl can partially cover or block the Cu, Ru and/or Cu/Ru sites preventing the CO adsorption to a certain extent.

In overall, CO adsorption experiments via FTIR clearly demonstrate that bimetallic systems reveal a synergistic behavior by exposing more active sites on the silica support material with respect to their monometallic counterparts. Furthermore, NaCl promoter directly interacts with the active sites and modifies their adsorption properties towards CO.

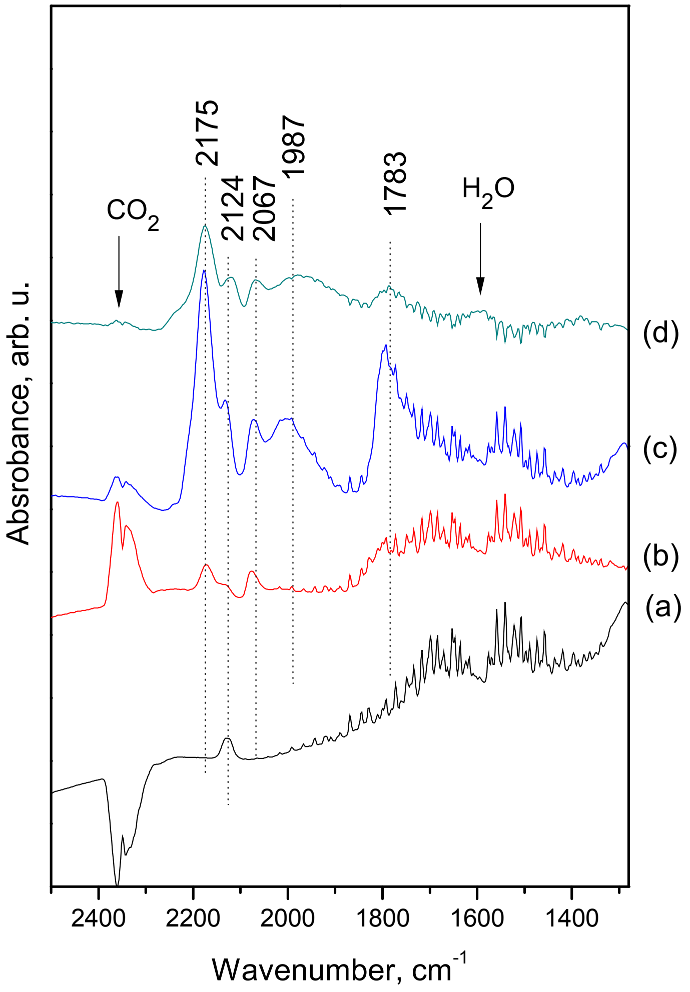


Figure 4.28: FTIR Spectra of CO adsorption on a) 2%Cu/c-SiO$_2$, b) 5%Ru/c-SiO$_2$,c)2%Cu5%Ru/c-SiO$_2$ d) 2%Cu5%Ru1.75NaCl/c-SiO$_2$

CHAPTER 5

CONCLUSIONS

A wide range of silica supported mono- and multimetallic heterogeneous catalysts were synthesized by high-throughput sol–gel and impregnation methods then, examinedby high-throughput screening methods for the direct synthesis of PO from propylene and oxygen at atmospheric pressure. The main goals of this study were to examine the effects of metal loading, metal-metal interaction, support type, reaction temperature and promoter effect. Previous studies' results have been taken into account so as to decide on the new catalysts candidates during the study.

The study got started with the investigation of the effect of different alkali salts ($NaNO_3$, $LiNO_3$, KNO_3, NaCl, LiCl and KAc) on the catalytic performances of Cu catalysts with different metal loadings. The outcomes indicated that the most efficient promoter is sodium nitrate salt than chloride and acetate salts for catalysts supported into t-SiO_2. Though, the expected catalytic performance could not be achieved from monometallic Cu catalysts promoted with various alkaline metal precursors.

In the next stage of the study, Cu-Ru catalysts modified with diverse promoters were investigated to measure the effect of distinct supports and modifiers based on the study that reached highest activity over a new class of silica-supported multimetallic RuO_2-CuO_x-NaCl catalysts held by Seubsai and coworkers.

The efficiency of bimetallic Cu-Ru catalysts supported on SiO_2, was approved to be higher than that of monometallic Cu and Ru catalysts in both UCLA and METU test units.Bimetallic Cu-Ru catalysts with different amount of metals were investigated and2%Cu-5%Ru/SiO_2 catalyst was obtained as the highest efficient one among several others. Following the determination of the most efficient metal ratio, to examine the metal-support interaction with the best performance, bimetallic catalyst was supported on the different silica materials (c-SiO_2,t-SiO_2 and SiO_2) by impregnation method. Despite of the high PO selectivity obtained for the t-SiO_2 supported catalyst, the optimum result was obtained for commercial silica (c-SiO_2) supported catalyst. SiO_2 supported catalysts usually ended with combustion reaction.

Next, the different promoters' effect on the performance of the catalyst was investigated for c-SiO_2 supported catalysts. To this end, alkaline promoters ($NaNO_3$, LiCl, KNO_3, NaCl and KAc) usually reported in the literature was added into the metal catalysts by co-impregnation method. According to the results, NaCl raised the PO yield of Ru-Cu catalyst more than other promoters. To better understand the effect of NaCl over each metal, they were promoted separately and the results showed that NaCl addition influenced Cu/c-SiO_2 catalyst positively but Ru/c-SiO_2performance deteriorated with promoter. Compared to un-promoted monometallic Cu/c-SiO_2 and Ru/c-SiO_2 catalysts, propylene consumption and PO selectivity had a visible increase in Cu-Ru/c-SiO_2 bimetallic system. NaCl promoter addition to the Cu-Ru/SiO_2 bimetallic system, made the yield reach its maximum.

XP spectra of the investigated samples provided important ideasabout the structural properties of these materials and enlightened the influence of the NaCl catalytic promoter. These Ru sites did not reveal any indication of severe differential charging and can easily be charge-compensated. In contrast to these observations, Cu 2p signal for NaCl-free samples disclose a severe differential charging behavior indicating a remarkable amount of charge build-up on the Cu sites or at the Cu/c-SiO_2 interface. These two strikingly different differential charging behaviors of Ru and Cu sites on the same bimetallic catalyst surface suggested that in the absence of NaCl, Ru and Cu sites probably do not reside in close proximity with respect to each other, neither they exist in the form of a bimetallic alloy. However, a totally different trend was faced after the NaCl addition to the samples that both Ru and Cu sites show charge-compensation. This indicates that NaCl functions as an electronic promoter preventing the charge build-up at the Cu/c-SiO_2, Ru/c-SiO_2 and Cu/Ru/c-SiO_2 interfaces. Additionally, no observation were made to say Cu and Ru sites existing as separate domains on the catalyst surface, for the NaCl-promoted catalysts. Thus, XPS experiments propose that NaCl catalytic promoter has an important interaction particularly with the Cu sites on the Cu/Ru/c-SiO_2 catalyst surface, changing the electronic structure of Cu sites. However, the electronic structure of the Ru sites seems to be altered in a minor fashion upon NaCl promotion.

In addition, CO adsorption experiments via FTIR clearly demonstrated that bimetallic systems reveal a synergistic behavior by exposing more active sites on the silica support material in regard to their monometallic counterparts. Furthermore, NaCl promoter directly interacts with the active sites and modifies their adsorption properties towards CO.

Following the observation of c-SiO_2 supported Ru-Cu-NaCl multimetallic system's effectiveness for direct epoxidation of propylene,bimetalliccatalytic systems containing Ag, Ru, Mn and Cu metals were investigated. The inquiry for the effect of NaCl on these bimetallic systems is included to this investigation.At the end Ag containing bimetallic systems and the effect of NaCl on these systems were defined as inefficient for epoxidation of propylene reaction to PO.Ru-Mn wasalso determined as inefficient while Mn-Cu/c-SiO_2 bimetallic system was promoting PO formationsurprisingly. NaCI had also an impressive curative effect on the performance of the Mn-Cu/c-SiO_2 system.

After the comparison of investigations on all c-SiO_2 supported bimetallic systems, the maximum PO yield was obtained for Cu-Ru/c-SiO_2 catalyst obviously. Also, according to the comparison of results for PO yield of these catalysts after NaCI modification, Cu-Ru bimetallic catalyst was defined as the most improved catalyst. Besides, during this study the reactions are completed at a large temperature range between 250 to 350˚C in order to investigate the effect of reaction temperatures. As a result, 300˚C was determined as the ideal reaction temperature.

To conclude, considering all the studies for development of most active and selective novel catalyst for direct epoxidation of propylene to propylene oxide, Cu-Ru-NaCI trimetallic system was determined as the most effective catalyst so far. However obtained PO selectivity and propylene conversion are still not sufficient for industrial application. To increase the success of the catalyst, more activity tests can be performed with different reaction conditions such as feed gas composition, metal ratio, reaction temperature, and gas flow rate. The effect of CI added feed gas on the activity can also be studied in further studies. This study showed the effectiveness of high throughput catalyst preparation and screening methods for exploring a large number of catalytic systems and discovering novel catalysts.

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APPENDICIES

APPENDIX A.REACTION PRODUCTS

Products formed during epoxidation of propylene by molecular oxygen:

$[CH_2CHCH_3]+{}^{1}\!/_{2}O_2 \rightarrow [C_3H_6O]$	Propylene oxide (PO)
$[CH_2CHCH_3]+{}^{1}\!/_{2}O_2 \rightarrow [CH_3CH_2CHO]$	Propionaldehyde (PaL)
$[CH_2CHCH_3]+{}^{1}\!/_{2}O_2 \rightarrow [CH_2CHCHO]$	Acrolein (AC)
$[CH_2CHCH_3]+{}^{1}\!/_{2}O_2 \rightarrow [CH_3COCH_3]$	Acetone (AT)
$[CH_2CHCH_3]+O_2 \rightarrow [CH_3CHO]+[CH_2O]$	Acetaldehyde (AD)
$[CH_2CHCH_3]+{}^{9}\!/_{2}O_2 \rightarrow 3[CO_2]+3[H_2O]$	Carbondioxide (CO_2)
$[CH_2CHCH_3]+3O_2 \rightarrow 3[CO]+3[H_2O]$	Carbonmonoxide (CO)

APPENDIX B. INVESTIGATED CATALYSTS

Table B.1: Investigated catalysts in the study

Catalyst No	Catalyst Name	Catalyst No	Catalyst Name
1	2%Cu-%0.8 KNO_3 /SiO_2	**22**	3%Cu-1.5%$LiNO_3$ /t-SiO_2
2	2%Cu-%0.8 KNO_3/c-SiO_2	**23**	3%Cu-2.25% $LiNO_3$/t-SiO_2
3	2%Cu-%0.8$NaNO_3$ /SiO_2	**24**	5%Cu-2.5% $LiNO_3$ /t-SiO_2
4	2%Cu-%0.8$NaNO_3$ /c-SiO_2	**25**	5%Cu-3.75% $LiNO_3$ /t-SiO_2
5	2%Cu-%0.25NaCl/SiO_2	**26**	5%Cu-5% $LiNO_3$/t-SiO_2
6	2%Cu-%0.8NaCl/SiO_2	**27**	3%Cu-1.5%KNO_3 /t-SiO_2
7	2%Cu-%0.8LiCl/SiO_2	**28**	3%Cu-2.25%KNO_3/t-SiO_2
8	2%Cu-%0.8LiCl/c-SiO_2	**29**	5%Cu-2.5%KNO_3/t-SiO_2
9	3%Cu/c-SiO_2	**30**	5%Cu-3.75%KNO_3/t-SiO_2
10	5%Cu/SiO_2	**31**	5%Cu-5%KNO_3/t-SiO_2
11	5%Cu/c-SiO_2	**32**	7%Cu-3.5%KNO_3/t-SiO_2
12	7%Cu/SiO_2	**33**	7%Cu-5.25%KNO_3/t-SiO_2
13	7%Cu/c-SiO_2	**34**	7%Cu-7%KNO_3/t-SiO_2
14	3%Cu-1.5%$NaNO_3$ /t-SiO_2	**35**	3%Cu-1.5%NaCl/t-SiO_2
15	3%Cu-2.25% $NaNO_3$ /t-SiO_2	**36**	3%Cu-2.25%NaCl/SiO_2
16	5%Cu-2.5% $NaNO_3$ /t-SiO_2	**37**	5%Cu-2.5% NaCl /t-SiO_2
17	5%Cu-3.75% $NaNO_3$ /t-SiO_2	**38**	5%Cu-3.75% NaCl /t-SiO_2
18	5%Cu-5% $NaNO_3$ /t-SiO_2	**39**	5%Cu-5% NaCl /t-SiO_2
19	7%Cu-3.5% NaNO3 /t-SiO_2	**40**	7%Cu-3.5% NaCl /t-SiO_2
20	7%Cu-5.25% NaNO3/t-SiO_2	**41**	7%Cu-5.25% NaCl /t-SiO_2
21	7%Cu-7% NaNO3 /t-SiO_2	**42**	7%Cu-7% NaCl /t-SiO_2

Table B.1 cont'd

Catalyst No	Catalyst Name	Catalyst No	Catalyst Name
43	3%Cu-1.5%LiCl/t-SiO_2	**64**	1%Cu/SiO_2
44	3%Cu-2.25% LiCl /t-SiO_2	**65**	0.5%Cu-0.1%NaCl/SiO_2
45	5%Cu-2.5% LiCl /t-SiO_2	**66**	0.5%Cu-0.1%KNO_3/SiO_2
46	5%Cu-3.75% LiCl/t-SiO_2	**67**	1%Ru/SiO_2
47	5%Cu-5% LiCl /t-SiO_2	**68**	0.5%Cu-0.5%Ru/SiO_2
48	7%Cu-3.5% LiCl /t-SiO_2	**69**	1%Cu-1%Ru/SiO_2
49	7%Cu-5.25% LiCl/t-SiO_2	**70**	2%Cu-0.5%Ru/SiO_2
50	7%Cu-7% LiCl /t-SiO_2	**71**	1%Cu-2%Ru/SiO_2
51	2%Cu-5%Ru/SiO_2	**72**	3%Ru-0.5%Cu/SiO_2
52	2%Cu-5%Ru/c-SiO_2	**73**	3%Ru-1%Cu/SiO_2
53	2%Cu-5%Ru/t-SiO_2	**74**	0.5%Cu-3%Ru1.5%$NaNO_3$/SiO_2
54	2%Cu-5%Ru-1.75%$NaNO_3$/c-SiO_2	**75**	0.5%Cu-3%Ru-1.5%KNO_3/SiO_2
55	2%Cu-5%Ru-1.75% LiCl/c-SiO_2	**76**	0.5%Cu-4%Ru/SiO_2
56	2%Cu-5%Ru-1.75%KNO_3/c-SiO_2	**77**	0.5%Cu-4%Ru-2%KNO_3 /SiO_2
57	2%Cu-5%Ru-1.75%NaCl/c-SiO_2	**78**	0.5%Cu-4%Ru-2% $NaNO_3$ /SiO_2
58	3%Cu-5%Ru-2%KNO_3/c-SiO_2	**79**	1%Cu-4%Ru/SiO_2
59	4%Cu-5%Ru-2.25%KNO_3/c-SiO_2	**80**	2%Cu-%0.8 KAc /SiO_2
60	5%Cu-5%Ru-2.5%KNO_3/c-SiO_2	**81**	3%Cu-1.5%KAc/t-SiO_2
61	2%Cu/SiO_2	**82**	3%Cu-2.25% KAc /t-SiO_2
62	2%Ru/SiO_2	**83**	5%Cu-2.5% KAc /t-SiO_2
63	2%Cu-2%Ru/SiO_2	**84**	5%Cu-3.75% KAc/t-SiO_2

Table B.1 cont'd

Catalyst No	Catalyst Name	Catalyst No	Catalyst Name
85	5%Cu-5% KAc /t-SiO_2	**100**	5%Ag-1.75%NaCl /c-SiO_2
86	7%Cu-3.5% KAc /t-SiO_2	**101**	2%Ag-5%Ru-/c-SiO_2
87	7%Cu-5.25% KAc/t-SiO_2	**102**	2%Ag-5%Ru-1.75% NaCl /c-SiO_2
88	7%Cu-7% KAc /t-SiO_2	**103**	2%Cu-5%Ag-/c-SiO_2
89	2%Cu-5%Ru-1.75%KAc/c-SiO_2	**104**	2%Cu-5%Ag-1.75% NaCl /c-SiO_2
90	2%Cu/SiO_2	**105**	2%Mn/c-SiO_2
91	5%Cu/SiO_2	**106**	5%Mn/c-SiO_2
92	5%Ru/SiO_2	**109**	2%Mn-2%Cu-/c-SiO_2
93	2%Cu-5%Ru-1.75%NaCl/SiO_2	**110**	2%Mn-2%Cu-1.75%NaCl /c-SiO_2
94	2%Cu-5%Ru-1.75%NaCl/t-SiO_2	**111**	2%Mn-5%Ru-/c-SiO_2
95	2%Cu-1.75%NaCl/c-SiO_2	**112**	2%Mn-5%Ru-1.75% NaCl /c-SiO_2
96	5%Ru-1.75%NaCl /c-SiO_2	**113**	2%Mn-5%Cu-1.75% NaCl /c-SiO_2
97	2%Ag/c-SiO_2	**114**	5%Mn-2%Cu-1.75% NaCl /c-SiO_2
98	2%Ag-1.75%NaCl/c-SiO_2	**115**	2%Mn-5%Cu/c-SiO_2
99	5%Ag/c-SiO_2	**116**	5%Mn-2%Cu/c-SiO_2

APPENDIX C.ACTIVITY TESTING RESULTS OF INVESTIGATED CATALYSTS

Table C.1: Activity testing results of investigated catalysts (T=300°C)

Catalyst No	T=300°C (1atm, C_3H_6/O_2=0.5)						
	% Selectivity					%Propylene Conversion	% PO Yield
	PO	AC	AT	AD	CO_2		
1	5.43	14.34	1.16	0.26	78.81	1.04	0.06
2	3.15	16.78	0.00	0.70	79.37	0.38	0.01
3	8.14	25.42	0.00	0.68	65.76	0.40	0.03
4	0.00	14.15	0.00	0.00	85.85	0.14	0.00
5	17.01	29.55	0.00	0.60	52.84	0.45	0.08
6	12.64	22.99	2.30	0.00	62.07	0.35	0.04
7	1.19	14.00	3.57	0.00	81.23	1.35	0.02
8	2.16	3.64	0.00	0.00	94.20	2.54	0.05
9	0.00	14.13	0.00	0.15	85.71	0.75	0.00
10	3.17	45.45	1.69	0.56	49.12	1.62	0.05
11	0.00	15.50	1.37	0.30	82.83	0.75	0.00
12	2.57	42.15	1.37	0.51	53.40	1.99	0.05
13	0.00	13.27	0.77	0.17	85.80	1.34	0.00
14	6.07	13.41	0.21	0.28	80.03	3.21	0.19
15	17.52	2.16	0.81	0.54	78.98	1.47	0.26

Table C.1 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
16	14.55	23.13	0.72	0.48	61.13	1.66	0.24
17	15.96	24.66	0.58	0.58	58.22	1.36	0.22
18	17.78	28.65	0.99	0.66	51.92	1.20	0.21
19	16.05	29.96	0.71	0.48	52.79	1.11	0.18
20	21.77	26.55	0.53	0.35	50.80	0.74	0.16
21	16.94	27.53	0.71	0.47	54.35	1.12	0.19
22	16.61	33.22	0.00	0.69	49.48	0.38	0.06
23	10.51	27.71	0.00	0.64	61.15	0.41	0.04
24	12.16	25.00	0.00	0.45	62.39	0.58	0.07
25	3.35	11.00	0.00	0.32	85.33	0.83	0.03
26	15.89	13.91	0.00	0.66	69.54	0.40	0.06
27	16.67	36.11	0.00	0.46	46.76	0.57	0.10
28	10.62	35.40	0.00	0.00	53.98	0.45	0.05
29	14.38	42.15	0.00	0.33	43.14	0.80	0.11
30	12.25	34.80	0.00	0.33	52.61	0.81	0.10
31	9.88	34.13	0.00	0.00	55.99	0.44	0.04
32	12.81	39.67	0.83	0.55	46.14	0.96	0.12
33	9.93	32.20	0.60	0.40	56.87	1.32	0.13

Table C.1 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
34	7.26	22.69	0.00	0.30	69.74	0.87	0.06
35	5.12	10.73	2.20	0.00	81.95	1.33	0.07
36	5.64	10.03	2.82	0.10	81.40	1.03	0.06
37	6.74	11.59	2.96	0.09	78.62	1.20	0.08
38	4.98	9.37	1.76	0.10	83.80	1.11	0.06
39	1.46	7.28	0.00	0.10	91.17	1.11	0.02
40	6.69	12.04	2.67	0.15	78.45	0.86	0.06
41	10.61	16.98	1.42	0.24	70.75	0.54	0.06
42	12.50	35.42	0.00	0.00	52.08	0.18	0.02
43	0.95	13.92	7.91	0.00	77.22	1.21	0.01
44	0.00	9.36	17.56	0.00	73.08	0.98	0.00
45	0.00	7.71	11.14	0.00	81.14	1.34	0.00
46	0.47	4.19	0.93	0.00	94.41	1.42	0.01
47	2.42	6.67	1.21	0.00	89.70	0.54	0.01
48	0.67	4.88	16.64	0.00	77.81	1.49	0.01
49	2.22	14.78	54.68	0.00	28.33	0.45	0.01
50	1.01	3.03	0.76	0.00	95.21	1.31	0.01
51	3.52	0.76	0.09	0.01	95.63	22.63	0.80

Table C.1 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
52	7.08	0.83	0.06	0.01	92.01	19.85	1.41
53	11.93	5.76	0.31	0.07	81.94	3.74	0.45
54	11.97	2.27	0.65	0.00	85.11	1.19	0.14
55	0.00	9.57	26.65	0.00	63.78	0.56	0.00
56	19.26	7.59	1.75	0.00	71.40	0.66	0.13
57	35.98	0.52	0.00	0.00	63.50	9.55	3.44
58	19.12	3.72	2.65	0.00	74.51	0.72	0.14
59	13.80	2.40	1.20	0.00	82.60	1.28	0.18
60	13.26	2.77	1.23	0.00	82.73	1.25	0.17
61	4.44	56.30	1.85	0.74	36.67	0.99	0.04
62	1.63	6.23	0.81	0.09	91.24	2.71	0.04
63	5.12	5.69	0.49	0.05	88.65	4.52	0.23
64	5.54	45.81	2.52	0.00	46.14	0.73	0.04
65	10.45	46.27	2.99	1.00	39.30	0.25	0.03
66	12.55	51.46	0.00	0.84	35.15	0.29	0.04
67	1.02	6.47	1.02	0.11	91.37	2.32	0.02
68	4.51	5.72	0.61	0.09	89.08	5.07	0.23
69	6.87	2.58	0.29	0.03	90.24	7.16	0.49

Table C.1 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
70	5.05	1.70	0.26	0.02	92.97	12.03	0.61
71	5.27	2.59	0.31	0.03	91.79	7.64	0.40
72	4.57	1.71	0.27	0.00	93.45	11.57	0.53
73	6.87	1.60	0.20	0.02	91.31	10.04	0.69
74	1.78	2.84	0.36	0.00	95.03	2.88	0.05
75	0.42	0.99	0.99	0.00	97.60	2.41	0.01
76	4.14	2.03	0.32	0.36	93.15	9.57	0.40
77	1.19	2.18	0.00	0.00	96.63	1.72	0.02
78	0.00	2.69	0.00	0.00	97.31	0.42	0.00
79	4.85	1.21	0.20	0.02	93.71	12.97	0.63
80	2.08	25.00	0.00	0.00	72.92	0.28	0.01
81	8.08	41.21	0.36	0.30	50.06	2.27	0.18
82	9.79	41.26	0.93	0.47	47.55	0.82	0.08
83	10.79	41.69	1.17	0.39	45.97	0.64	0.07
84	15.12	34.56	0.96	0.48	48.88	0.82	0.12
85	9.51	31.22	0.73	0.33	58.21	0.96	0.09
86	9.24	39.67	0.68	0.45	49.96	0.89	0.08
87	8.62	34.02	0.44	0.44	56.48	1.03	0.09
88	9.74	24.07	0.55	0.24	65.40	1.43	0.14

Table C.1 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
89	8.11	33.39	0.72	0.00	57.79	0.97	0.08
90	1.20	54.91	2.20	0.13	41.55	0.83	0.01
91	0.00	37.45	9.36	0.00	53.19	0.50	0.00
92	0.59	3.54	0.84	0.03	95.00	9.03	0.05
93	4.87	0.52	0.40	0.00	94.21	12.37	0.60
94	6.18	2.40	0.91	0.00	90.51	3.17	0.20
95	7.72	16.40	0.00	0.00	75.88	0.31	0.02
96	0.00	1.53	0.00	0.00	98.47	5.41	0.00
97	0.00	10.00	0.00	0.00	90.00	1.15	0.00
98	2.72	5.45	0.00	0.00	91.83	0.81	0.02
99	0.00	37.61	0.55	0.12	61.72	1.35	0.00
100	0.00	37.40	2.88	0.00	59.73	0.58	0.00
101	0.20	0.89	0.17	0.01	98.73	27.58	0.06
102	0.26	0.37	0.11	0.00	99.25	18.03	0.05
103	0.00	13.79	0.00	0.16	86.04	0.70	0.00
104	0.00	18.79	0.00	0.22	80.98	0.48	0.00
105	0.00	2.92	0.32	0.05	96.70	2.38	0.00
106	0.00	1.65	0.00	0.04	98.31	3.33	0.00
107	2.46	3.51	0.00	0.00	94.04	1.07	0.03

Table C.1 cont’d

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
108	1.73	1.15	0.00	0.00	97.12	2.03	0.03
109	4.76	4.91	0.22	0.05	90.06	4.92	0.23
110	7.13	3.87	0.61	0.00	88.39	1.74	0.12
111	2.71	3.10	0.97	0.00	93.22	1.92	0.05
112	2.82	0.35	0.00	0.00	96.84	6.73	0.19
113	15.54	1.64	0.00	0.00	82.82	4.24	0.66
114	7.51	1.44	0.00	0.00	91.05	2.52	0.19
115	4.96	3.18	0.16	0.05	91.65	9.46	0.47
116	2.96	2.83	0.31	0.06	93.85	8.51	0.25

Table C.2: Activity testing results of investigated catalysts (T=350°C)

Catalyst No	T=350°C (1 atm, C_3H_6/O_2=0.5)						
	% Selectivity					%.Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
1	3.40	15.48	0.34	0.23	80.54	2.34	0.08
2	1.30	23.04	0.00	0.00	75.65	0.92	0.01
3	5.39	25.59	0.00	0.45	68.57	1.18	0.06
4	0.00	18.21	0.00	0.32	81.47	0.42	0.00
5	10.81	23.89	0.85	0.38	64.08	1.40	0.15
6	8.28	12.61	0.00	0.12	78.99	1.11	0.09
7	2.01	14.69	0.36	0.08	82.86	3.36	0.07
8	0.00	2.13	1.58	0.00	96.28	6.19	0.00
9	0.00	10.76	0.57	0.09	88.58	2.39	0.00
10	1.58	38.35	1.15	0.44	58.48	5.58	0.09
11	0.00	7.94	0.58	0.08	91.41	2.94	0.00
12	1.34	35.87	0.94	0.40	61.45	6.83	0.09
13	0.00	7.72	0.32	0.05	91.91	4.21	0.00
14	4.35	11.87	0.22	0.23	83.34	7.86	0.34
15	10.14	15.10	0.44	0.39	73.94	5.34	0.54
16	10.45	17.23	0.46	0.36	71.50	5.11	0.53
17	10.82	19.12	0.37	0.44	69.26	4.18	0.45

Table C.2 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
18	12.12	22.80	0.73	0.55	63.80	3.76	0.46
19	11.20	22.62	0.55	0.44	65.18	3.51	0.39
20	15.68	21.88	0.33	0.33	61.79	2.38	0.37
21	10.22	26.28	1.22	0.81	61.48	1.60	0.16
22	10.23	26.30	1.22	0.81	61.44	1.60	0.16
23	8.05	7.22	1.11	0.74	82.89	1.40	0.11
24	8.35	22.59	1.14	0.63	67.28	2.05	0.17
25	3.84	14.85	0.00	0.35	80.96	2.26	0.09
26	6.48	21.61	0.72	0.48	70.71	1.10	0.07
27	12.73	34.49	0.93	0.46	51.39	1.71	0.22
28	7.26	26.82	0.00	0.19	65.74	1.42	0.10
29	10.92	34.48	0.62	0.42	53.56	2.54	0.28
30	9.91	29.90	0.52	0.23	59.44	2.28	0.23
31	7.35	26.18	0.00	0.20	66.27	1.34	0.10
32	8.96	33.83	0.62	0.41	56.18	3.18	0.28
33	10.33	3.77	0.72	0.38	84.80	2.76	0.28
34	6.67	20.73	0.36	0.24	72.00	2.19	0.15
35	2.18	8.24	0.85	0.03	88.70	3.43	0.07

Table C.2 cont’d

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
36	3.20	6.84	0.66	0.07	89.22	2.95	0.09
37	2.97	7.41	0.99	0.07	88.57	3.29	0.10
38	2.29	6.41	0.34	0.08	90.88	2.84	0.07
39	0.35	7.30	0.00	0.04	92.30	2.76	0.01
40	3.74	6.14	0.60	0.05	89.47	2.44	0.09
41	3.78	8.31	0.00	0.08	87.83	1.45	0.05
42	0.00	37.50	0.00	0.00	62.50	0.43	0.00
43	1.09	17.75	0.97	0.04	80.15	3.01	0.03
44	0.89	18.54	1.25	0.00	79.32	2.05	0.02
45	0.68	14.69	1.81	0.00	82.82	3.24	0.02
46	1.25	3.86	6.66	0.00	88.22	3.43	0.04
47	0.00	10.19	0.00	0.00	89.81	1.43	0.00
48	1.13	5.41	6.31	0.00	87.16	2.94	0.03
49	1.17	3.82	6.90	0.00	88.12	3.12	0.04
50	0.22	3.87	0.33	0.00	95.58	2.99	0.01
51	0.57	0.54	0.04	0.01	98.85	41.99	0.24
52	3.56	2.22	0.10	0.02	94.11	15.77	0.56
53	4.68	3.74	0.00	0.00	91.58	2.44	0.11

Table C.2 cont’d

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
54	4.75	3.64	0.00	0.00	91.61	2.40	0.11
55	0.00	10.59	16.85	0.00	72.55	0.79	0.00
56	5.17	6.20	0.69	0.00	87.94	1.10	0.06
57	17.83	1.91	0.00	0.00	80.26	8.75	1.56
58	5.92	0.74	0.00	0.00	93.34	1.54	0.09
59	3.45	2.87	0.29	0.00	93.39	2.64	0.09
60	3.35	2.62	0.29	0.00	93.73	2.60	0.09
61	2.57	50.19	1.80	0.51	44.93	2.82	0.07
62	0.16	3.43	0.42	0.04	95.96	27.05	0.04
63	2.19	2.57	0.15	0.03	95.05	14.21	0.31
64	2.95	28.42	2.02	0.00	66.61	2.33	0.07
65	4.33	38.53	2.16	0.58	54.40	0.84	0.04
66	6.43	38.59	2.25	0.64	52.09	1.13	0.07
67	4.57	23.25	0.31	0.28	71.59	3.78	0.17
68	0.13	1.30	0.10	0.02	98.45	24.23	0.03
69	2.42	1.64	0.11	0.02	95.80	22.56	0.55
70	0.81	0.93	0.06	0.01	98.19	38.56	0.31
71	1.36	1.51	0.09	0.01	97.03	26.30	0.36

Table C.2 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
72	0.50	0.96	0.07	0.01	98.46	36.83	0.19
73	1.69	1.31	0.07	0.01	96.92	30.42	0.51
74	0.47	1.70	0.00	0.00	97.83	7.57	0.04
75	0.75	0.28	0.00	0.00	98.97	6.44	0.05
76	0.74	0.98	0.08	0.01	98.19	32.71	0.24
77	0.21	1.63	0.00	0.00	98.16	5.03	0.01
78	0.00	0.62	0.00	0.00	99.38	1.20	0.00
79	1.22	0.92	0.07	0.01	97.78	32.77	0.40
80	2.69	20.97	0.81	0.00	75.54	1.12	0.03
81	4.86	26.30	0.71	0.28	67.84	9.59	0.47
82	5.27	33.03	1.25	0.33	60.12	2.89	0.15
83	7.50	33.39	0.93	0.34	57.84	2.76	0.21
84	10.10	25.87	0.63	0.33	63.08	3.62	0.37
85	6.54	23.77	0.46	0.26	68.97	3.60	0.24
86	5.97	32.80	0.39	0.35	60.49	3.71	0.22
87	5.85	26.91	0.41	0.28	66.55	3.88	0.23
88	6.61	18.63	0.30	0.20	74.26	4.96	0.33
89	3.02	6.14	0.94	0.00	89.90	3.45	0.10

Table C.2 cont'd

Catalyst No	% Selectivity					%Propylene Conversion	%PO Yield
	PO	AC	AT	AD	CO_2		
90	0.40	38.65	7.17	0.13	53.64	4.26	0.02
91	0.00	16.09	5.02	0.12	78.78	3.65	0.00
92	0.05	15.42	2.30	0.12	82.12	36.54	0.02
93	3.33	0.76	0.08	0.00	95.82	22.76	0.76
94	2.50	1.77	0.26	0.00	95.47	8.85	0.22
95	0.91	10.71	0.46	0.00	87.93	1.54	0.01
96	0.09	1.04	0.12	0.00	98.74	12.87	0.01
97	0.18	0.32	0.05	0.00	99.45	24.77	0.04
98	0.00	10.13	0.00	0.08	89.79	2.84	0.00
99	0.00	21.55	0.84	0.11	77.50	5.53	0.00
100	0.00	26.23	2.43	0.08	71.26	2.47	0.00
101	0.00	0.36	0.11	0.00	99.53	55.16	0.00
102	0.22	0.22	0.22	0.00	99.33	30.29	0.07
103	0.00	7.14	0.48	0.08	92.31	3.11	0.00
104	0.00	11.80	0.00	0.13	88.07	1.79	0.00
105	0.00	1.35	0.14	0.02	98.49	8.19	0.00
106	0.00	0.63	0.00	0.00	99.37	12.53	0.00
107	2.38	1.41	0.00	0.00	96.21	3.56	0.08

Table C.2 cont’d

Catalyst No	% Selectivity					%Propylene Conversion	% PO Yield
	PO	AC	AT	AD	CO_2		
108	1.74	1.48	0.00	0.00	96.79	4.46	0.08
109	2.43	2.26	0.21	0.03	95.09	29.65	0.72
110	3.27	4.32	0.35	0.00	92.05	3.15	0.10
111	0.00	0.81	0.19	0.01	98.98	51.05	0.00
112	1.53	0.28	0.09	0.00	98.10	12.61	0.19
113	7.20	2.94	0.00	0.00	89.86	7.34	0.53
114	3.93	2.11	0.00	0.00	93.96	3.92	0.15
115	2.00	1.97	0.15	0.02	95.86	32.20	0.64
116	1.47	1.13	0.14	0.02	97.24	37.60	0.55