

SYNTHESIS AND CHARACTERIZATION OF OSMIUM(0)  
NANOCLUSTERS AND THEIR CATALYTIC USE IN  
AEROBIC ALCOHOL OXIDATION

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

BY

SERDAR AKBAYRAK

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR  
THE DEGREE OF MASTER OF SCIENCE  
IN  
CHEMISTRY

FEBRUARY 2011

Approval of the thesis:

**SYNTHESIS AND CHARACTERIZATION OF OSMIUM(0)  
NANOCLUSTERS AND THEIR CATALYTIC USE IN  
AEROBIC ALCOHOL OXIDATION**

submitted by **SERDAR AKBAYRAK** in partial fulfillment of the requirements for  
the degree of **Master of Science in Chemistry Department, Middle East  
Technical University** by,

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

Prof. Dr. İlker Özkan  
Head of Department, **Chemistry**

Prof. Dr. Saim Özkar  
Supervisor, **Chemistry Dept., METU**

**Examining Committee Members:**

Prof. Dr. Gülsün GÖKAĞAÇ  
Chemistry Dept., METU

Prof. Dr. Saim ÖZKAR  
Chemistry Dept., METU

Prof. Dr. Deniz ÜNER  
Chemical Engineering Dept., METU

Assoc. Prof. Dr. Ayşen YILMAZ  
Chemistry Dept., METU

Assoc. Prof. Dr. Emren ESENTÜRK  
Chemistry Dept., METU

**Date:** 10/02/2011

**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: Serdar AKBAYRAK

Signature

## ABSTRACT

### **SYNTHESIS AND CHARACTERIZATION OF OSMIUM(0) NANOCLUSTERS AND THEIR CATALYTIC USE IN AEROBIC ALCOHOL OXIDATION**

Akbayrak, Serdar

M.Sc., Department of Chemistry

Supervisor: Prof. Dr. Saim Özkar

February 2011, 48 pages

Transition metal nanoclusters are more active and selective catalysts than their bulk counterparts as the fraction of surface atoms increases with the decreasing particle size. When stabilized in organic or aqueous solutions, they can catalyze many reactions. The catalytic activity of metal nanoclusters depends on the particle size and size distribution. Particle size can be controlled by encapsulating the nanoclusters in the cavities of highly ordered porous materials such as zeolites. In this project, osmium(0) nanoclusters were formed within the void spaces of zeolite. Thus, nanoclusters of certain size were prepared as supported catalyst. Osmium(III) cations were introduced into the cavities of zeolite by ion exchange and were reduced partially or completely to form intrazeolite osmium(0) nanoclusters. The intrazeolite osmium(0) nanoclusters were characterized by HRTEM, TEM, EDX, XPS, XRD, ICP-OES spectroscopic methods and N<sub>2</sub> adsorption-desorption technique. Intrazeolite osmium(0) nanoclusters were employed as catalyst in the aerobic oxidation of alcohols in organic solution.

**Keywords:** Osmium(0) nanoclusters, Heterogenous catalyst, Alcohol oxidation.

## ÖZ

# İNTRAZEOLİT OSMİYUM(0) NANOKÜMELERİN SENTEZİ, TANIMLANMASI VE ALKOLLERİN AEROBİK OKSİDASYONUNDA KULLANILMASI

Akbayrak, Serdar

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. Saim Özkar

Şubat 2011, 48 sayfa

Geçiş metal nanokümleri parçacık boyutlarının küçük ve yüzey alanlarının geniş olması sebebiyle etkinliği ve seçiciliği külçe metallerine göre daha yüksek olan katalizörlerdir. Gerek organik fazda ve gerekse sulu çözeltilerde kararlı hale getirilen metal nanokümleri bir çok tepkimeyi etkin bir şekilde katalizlemektedir. Metal nanokümlerinin katalitik etkinliği, tane boyutu ve boyut dağılımı ile yakından ilgilidir. Tane boyutunu kontrol altına almanın bir yolu nanokümleri zeolit gibi düzenli gözenekli yapıya sahip malzemeler içerisinde üretmektir. Bu projede, osmiyum(0) nanokümleri zeolitin düzenli gözeneklerinde oluşturulmuş ve katı yüzeyde taşınabilen boyutları belirli katalizörler üretilmiştir. Zeolit gözeneklerine iyon değişimi ile yerleştirilen osmiyum(III) iyonu indirgenerek intrazeolit osmiyum(0) nanokümleri oluşturulmuştur. İntrazeolit osmiyum(0) nanokümleri HRTEM, TEM, EDX, XPS, XRD, ICP-OES spektroskopik yöntemleri ve N<sub>2</sub> adsorpsiyon-desorpsiyon metodu ile tanımlanmıştır. Üretilen intrazeolit osmiyum(0) nanokümleri organik fazda alkollerin aerobik oksidasyonunda katalizör olarak kullanılmıştır.

**Anahtar Kelimeler:** Osmiyum(0) nanokümelere, Heterojen katalizör, Alkol oksidasyonu.

**To My Family**

## ACKNOWLEDGEMENTS

I would like to thank to my supervisor Prof. Dr. Saim Özkar for his great support, valuable advices and guidance throughout in this study. I am very grateful to him for his kindly sharing my problems.

I would like to thank Dr. Mehmet Zahmakıran for his encouragement and valuable ideas during my study.

I would like to express my special thanks to Nazlı İpek for her understanding and endless support.

I would like to thank Dr. Önder Metin, Melek Dinç, Tuğçe Ayvalı, Ebru Ünel, Salim Çalışkan, Huriye Erdoğan, Zafer Öztürk, Tuğba Orhan and Derya Çelik for their friendship.

I would like to give my special thanks to Salih Ertan for his precious friendship.

I also express my thanks to Sinop University for their support during my studies.

I say a big “thank you” to my family for everything.

## TABLE OF CONTENTS

ABSTRACT .....	iv
ÖZ .....	vi
ACKNOWLEDGEMENTS .....	ix
CHAPTERS .....	1
1.INTRODUCTION .....	1
2.THE USE OF TRANSITION METAL NANOCCLUSERS AS CATALYSTS... 3	
2.1. Catalysis .....	3
2.2. The Applications of Transition Metal Nanoclusters in Catalysis..... 5	
2.3. Preparation and Stabilization of Transition Metal Nanoclusters..... 6	
2.3.1. Electrostatic Stabilization/DLVO Theory .....	7
2.3.2. Steric Stabilization .....	8
2.4. The Composition and the Structure of Zeolites..... 9	
2.5. Oxidation of Alcohols .....	14
3.EXPERIMENTAL .....	16
3.1. Materials .....	16
3.2. Characterization of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y .....	17
3.3. Preparation of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y .....	18
3.4. Catalytic Aerobic Oxidation of Alcohols Under 1 atm O <sub>2</sub> Using Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y..... 19	
3.5. Catalytic Aerobic Oxidation of Alcohols Under Air Using Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y..... 19	
3.6. Effect of Osmium Loading on the Catalytic Activity of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y in the Aerobic Oxidation of Benzyl alcohol..... 20	
3.7. Leaching Test of Osmium(0) Nanoclusters in the Aerobic Oxidation of Benzyl alcohol Under 1 atm O <sub>2</sub> ..... 21	

3.8. Reusability and Isolability Tests of Osmium(0) Nanoclusters in the Aerobic Oxidation of Benzyl alcohol.....	21
3.9. Catalytic Lifetime of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y .....	22
4.RESULTS AND DISCUSSIONS .....	23
4.1. Preparation and Characterization of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y .....	23
4.2. The Catalytic Activity Tests .....	33
4.2.1. The Catalytic Activity of Osmium Free Zeolite-Y and Osmium(III)-Zeolite-Y in the Aerobic Oxidation of Alcohol .....	33
4.2.2. The Catalytic Activity Tests of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y .....	33
4.2.3. Catalytic Lifetime, Reusability and Isolability of Osmium(0) Nanoclusters Stabilized in Zeolite Framework .....	41
5.CONCLUSION .....	42
REFERENCES.....	43

## LIST OF FIGURES

### FIGURES

<b>Figure 1.</b> Schematic representation of electrostatic interaction between two particles [44].	7
<b>Figure 2.</b> Schematic representation of steric stabilization [52].	8
<b>Figure 3.</b> Schematic representation of some subunits and cages/cavities in several framework types.	10
<b>Figure 4.</b> Schematic representation of the SOD framework type [57].	11
<b>Figure 5.</b> Schematic representation of the LTA framework type [57].	12
<b>Figure 6.</b> Building units of FAU: double six rings consisting of six TO <sub>4</sub> units each (T=Si and Al) and sodalites, respectively [56].	12
<b>Figure 7.</b> Experimental apparatus.	20
<b>Figure 8.</b> Powder XRD patterns of zeolite-Y, Os <sup>3+</sup> -exchanged zeolite-Y with an osmium content of 2.1 % wt and Os(0)-Y.	24
<b>Figure 9.</b> Scanning Electron Microscopy (SEM) image of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt.	25
<b>Figure 10.</b> SEM image of Os(0)-Y with osmium loading of 2.1 % wt.	26
<b>Figure 11.</b> SEM image of Os <sup>3+</sup> -exchanged zeolite-Y with osmium loading of 2.1 % wt. (scale bar equals to 5.0 μm)	26
<b>Figure 12.</b> SEM image of zeolite-Y (Na <sub>56</sub> Y). (scale bar equals to 5.0 μm)	27
<b>Figure 13.</b> TEM image of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt. (scale bar equals to 5 nm)	28
<b>Figure 14.</b> HRTEM image of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt (scale bar equals to 1 nm).	28
<b>Figure 15.</b> TEM-EDX spectrum of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt.	29
<b>Figure 16.</b> X-ray photoelectron spectrum of Os(0)-Y in the region of 1200-0 eV.	30
<b>Figure 17.</b> The nitrogen adsorption-desorption isotherms of (a) zeolite-Y and (b) Os(0)-Y with osmium loading of 2.1 % wt.	31
<b>Figure 18.</b> Os(0)-Y catalyzed aerobic oxidation of alcohols to carbonyl compounds at 80 °C under 1 atm O <sub>2</sub> or air.	33

## LIST OF TABLES

### TABLES

<b>Table 1.</b> Aerobic oxidation of alcohols catalyzed by Os(0)-Y catalyst under air. All these reactions were performed by using 1 mmol substrate and 400 mg Os(0)-Y (0.044 mmol Os) in 5 mL toluene at 80°C and the conversion of substrates was determined by GC analysis. ....	35
<b>Table 2.</b> Aerobic oxidation of alcohols catalyzed by Os(0)-Y catalyst by using 1 mmol substrate and 400 mg Os(0)-Y in 5 mL toluene at 80°C under 1 atm O <sub>2</sub> .....	36
<b>Table 3.</b> Activities of various well known catalysts used in the oxidation of benzyl alcohol in terms of TOF values in toluene. ....	37
<b>Table 4.</b> Activities of various well known catalysts used in the oxidation of 1-phenylethanol in terms of TOF values in toluene. ....	38
<b>Table 5.</b> Activities of various well known catalysts used in the oxidation of diphenylmethanol in terms of TOF values in toluene.....	39
<b>Table 6.</b> Activities of various well known catalysts used in the oxidation of 2-(Hydroxymethyl) thiophene in terms of TOF values in toluene. ....	40

## LIST OF ABBREVIATIONS

DLVO : Derjugin-Landau-Verwey-Overbeek

TOF : Turnover Frequency

TTON : Total Turnover Number

OMS : Octahedral Molecular Sieve

FAU : Faujasite

## CHAPTER 1

### INTRODUCTION

At the present time there is a considerable interest in the synthesis and the use of transition metal nanoclusters because of their novel and attractive physical/chemical properties [1]. The use of transition metal nanoclusters in catalysis leads to the significant development in the synthesis of fine chemicals from the economical and environmental concerns [2]. Various methods have been developed for the preparation of transition metal nanoclusters stabilized by the employment of anions, ligands, solvents and polymers [3]. However, in their catalytic application one of the most important problems is the aggregation of these nanoclusters which causes a decrease in catalytic activity and lifetime. Therefore, the utilization of microporous and mesoporous materials as host for the preparation of metal and metal oxide nanoparticles appears to be an efficient way of preventing aggregation [4]. Zeolite-Y, faujasite type zeolite, is considered to be a suitable host material providing highly ordered large cavities with an inner diameter of 1.3 nm [5]. Zeolites can be used for the assembly of metal and metal oxide nanoclusters as the pore size restriction could limit the growth of particles [6]. Moreover, metal and metal oxide nanoparticles encapsulated within the cavities of zeolites or between the zeolite-supported layers (i.e., zeolite films, powders or membranes supported on the surface of solid materials) [7], may provide the control of kinetics for the catalytic reactions. The preparation of zeolite confined metal(0) nanoclusters is commonly achieved by a procedure comprising of the introduction of metal cations into the zeolite by ion exchange followed by their reduction with H<sub>2</sub> at temperatures higher than 300 °C. Unfortunately, this well-known high temperature treatment may cause alteration in

the zeolite framework due to the formation of unstable acid form and may lead to the migration of a large portion of the guest metal atoms out of cavities of the zeolite [8].

Recent studies have demonstrated the capability of zeolite matrix in stabilizing the ruthenium(0) [9], and rhodium(0) [10] nanoclusters formed in-situ during the hydrolysis of sodium borohydride and ammonia-borane, respectively, at room temperature. In this study, osmium(0) nanoclusters were stabilized by the framework of zeolite-Y and characterized by ICP-OES, XRD, XPS, SEM, TEM, HRTEM, TEM/EDX, and N<sub>2</sub>-adsorption/desorption technique. The results reveal the formation of well-dispersed osmium(0) nanoclusters within the zeolite matrix by keeping the morphology and crystallinity of the host intact.

This study also includes the catalytic application of Os(0)-zeolite-Y nanoclusters in the aerobic oxidation of alcohols to carbonyl compounds which is one of the most important and challenging transformations in the synthesis of fine chemicals and intermediates [11] and traditionally has been carried out with stoichiometric amount of oxidants [12]. Unfortunately, most of these oxidants are toxic, hazardous or are required in large excess and some of these processes generate equal amount of metal waste [13]. Therefore, the development of green, effective, selective, and reusable catalysts for the oxidation of alcohols to carbonyl compounds by only molecular O<sub>2</sub> as oxidant is of great importance from both economic and environmental standpoints of view. Osmium(0) nanoclusters stabilized by the framework of zeolite-Y provide high catalytic activity in the oxidation of alcohols to carbonyl compounds with molecular oxygen.

## CHAPTER 2

### THE USE OF TRANSITION METAL NANOCLUSTERS AS CATALYSTS

#### 2.1. Catalysis

Catalysis plays a crucial role in the field of chemistry. A great deal of chemical products has been in contact with catalysts. Catalysis is the key to the efficiency of chemical conversion. Due to the environmental concern, limited energy and raw materials; the need of catalysis is very high. To control environmental pollution and to reduce chemical waste problems, catalytic processes have become an indispensable research area for the scientists and these processes have been developed to decrease the amount of industrial waste. Therefore, catalysis is an important tool for minimization of the waste and sustainable processes [14].

As a simple definition, a catalyst is something that makes a reaction go faster, without being consumed in the process. Since a catalyst is not consumed, it can be seen in many consecutive cycles during a reaction. This decreases the amount of required catalysts in the process. To simplify the concept of catalysts, catalysis can be explained in three different categories, namely, homogeneous catalysis, heterogeneous catalysis and biocatalysis. In homogeneous catalysis, the catalyst is in the same phase as the reactants and the products. Generally, the catalyst and the substrate are reacted in a solvent. In heterogeneous catalysis, the catalyst and the reactants are in different phases. Heterogeneous catalysts are frequently referred as a system in which catalyst is solid. Catalyst is easily separated in the heterogeneous systems. This makes the heterogeneous catalysis more advantageous. Biocatalysis is a different case between homogenous and heterogeneous catalysis. Biocatalysts, for example enzymes, are the fastest catalysts with respect to homogeneous and heterogeneous ones [14].

A general approach for a reaction using a catalyst is that reactants diffuse the catalyst pore, adsorb on its surface, after finding the active site perform a reaction there. The interactions on the surface of a catalyst have a great influence on the stability, activity and selectivity of a catalyst. A catalyst having a good stability will change very slowly under the conditions of use. In fact, this is only a theory that a catalyst remains unchanged.

The main properties of a catalyst are its activity, stability, efficiency and selectivity. Activity of a catalyst can be expressed with turnover number (TON), the number of moles of substrate that a mole of catalyst can convert before becoming inactivated. Total turnover number (TTON), the number of moles of product per mole of catalyst, indicates the life time of a catalyst. Catalytic efficiency is also important definition for a catalyst. It is described as turn over frequency (TOF), the number of moles of product per mole of active site of catalyst per unit time. Selectivity can be thought as the percentage of desired products in a reaction [15]. It plays a crucial role in industry to reduce the chemical waste [16].

Shape and mechanical strength, mass and heat transfer are the key factors in catalysis. The mechanical strength of a catalyst indicates the resistance of a catalyst to crushing. The shape and mechanical strength of a catalyst determine the packing and flow of the reactants and products in the reactor.

Mass and heat transfer during a reaction are also notable factors. If it is assumed that the reaction is homogeneous and stirred well, the substrates will have equal chance of getting the catalytic intermediates but if the reaction is heterogeneous, this situation is different. After a molecule reaches the catalyst particles, there is no guarantee that it will react further. In heterogeneous catalysis containing porous materials, the reactants must first diffuse into the pores. After adsorption, they may need to travel on the surface in order to reach the active site of the catalyst. The entrance of reactants and the exit of products in the reaction medium give rise to heat and mass transfer [14].

Regenerability and reproducibility are also crucial factors for a catalyst. It is expected that the catalyst is found intact at the end of the reaction. When the activity and selectivity of a catalyst is insufficient, it can be regenerated with a treatment to develop these properties. For examples, the poisons on the catalyst can be removed by applying suitable gases or some burning process. The quality of successive charges reflects the reproducibility of a catalyst. To develop the catalyst from the laboratory to the industry is an indispensable concern. The preparation of a catalyst should be feasible in industrial applications under acceptable economic conditions.

## **2.2. The Applications of Transition Metal Nanoclusters in Catalysis**

Nanoclusters have generally less than 10 nm diameter and they are nearly monodispersed particles [17]. The properties of nanoclusters are between bulk and single particle species [18,19]. There is a considerable interest in the synthesis and the use of transition metal nanoclusters because of their novel and attractive physical/chemical properties [20].

Transition metal nanoclusters have a great popularity in the most of scientific researches [21]. Their use in different areas makes the study of transition metal nanoclusters attractive. By the application of these clusters in catalysis [22], quantum computers [23], photochemistry [24], optics [25], nanoelectronics [26], chemical sensors [27], light-emitting diodes [28], ferrofluids for cell separations [29], the transition metal nanoclusters become noteworthy topic in the most of the researches [30].

Transition metal nanoclusters have high surface area providing numerous potentially active sites. Therefore, they have large application in chemical reactions as catalysts, which makes significant development in the synthesis of fine chemicals from the economical and environmental standpoints of view [20]. As catalysts, transition metals are used in a great many reactions; namely, oxidation of alcohols [20], hydrogenation [31], Suzuki [32], hydrosilations [33], hydrogenolysis [34], catalytic reforming [35], Heck couplings [36].

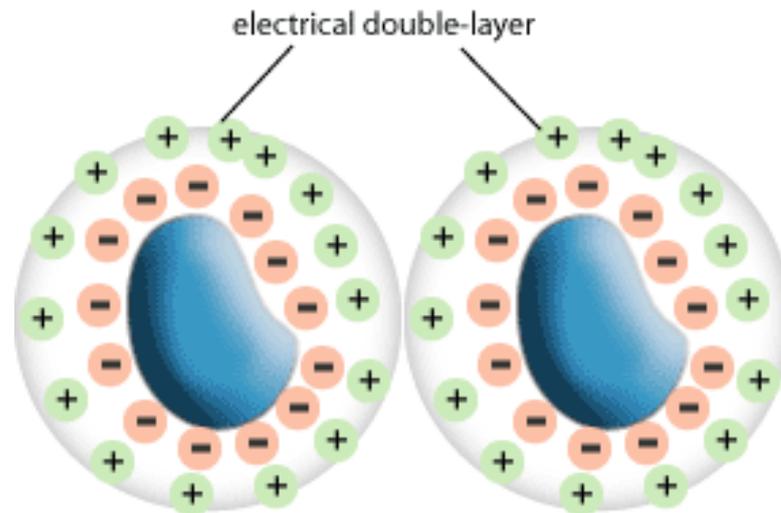
### **2.3. Preparation and Stabilization of Transition Metal Nanoclusters**

Transition metal nanoclusters are prepared by using one of two approaches: top-down and bottom up. Top-down method is known as a physical method in which bulk metal is grounded mechanically or metal structures are thermally decomposed into nanoclusters [37]. In that approach, the distribution of particles is larger than 10 nm and the particles cannot be prepared reproducibly, which causes the irreproducible catalytic activity [16]. The latter approach is the most frequently used method for the preparation of metal nanocluster. In the bottom-up approach transition metal nanoclusters can be prepared by the reduction treatment in which metal salts are reduced using hydrogen [38], alcohols [39], or chemical hydrides [20]. In addition, metal nanoclusters can also be prepared by thermolysis [40], photolysis [41].

Transition metal nanoclusters are stabilized not to go in bulk metal. To keep the particles separated from each other and to control the degree of particle size, it is a crucial step to use a stabilizer for the preparation of long termed transition metal nanoclusters. Generally, two approaches exist to stabilize these nanoclusters; namely, electrostatic stabilization (also known as DLVO type) and steric stabilization [30].

### 2.3.1. Electrostatic Stabilization/DLVO Theory

This theory was developed by Derjaguin, Landau, Verwey and Overbeek in 1940's. It describes the stabilization of colloids. According to the electrostatic stabilization theory, adsorption of ions to the metal surface [42] creating an electrical double layer [43] makes a Coulombic repulsion force between individual particles. The aggregation of particles is prevented by this electrostatic repulsion [30].

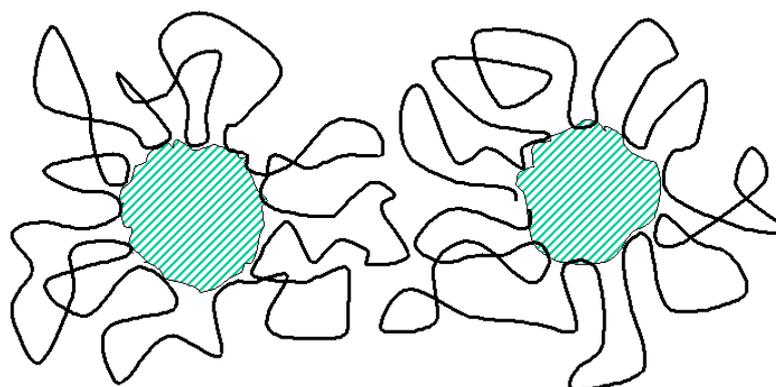


**Figure 1.** Schematic representation of electrostatic interaction between two particles [44].

As illustrated in Figure 1, a cloud of oppositely charged ions develops around the charged particles and a repulsive force between these particles provides an electrical barrier preventing from aggregation when they approach each other.

### 2.3.2. Steric Stabilization

It is achieved by attaching macromolecules to the surface of particles or surrounding these particles by a protecting group. The adsorbed layers on the particles make steric stabilization by preventing from the contact of these particles to each other [45] as shown in Figure 2. Poly(vinylpyrrolidone) [46], poly(styrene) [47], poly (methyl methacrylate) [48], poly(methylhydrosiloxane) [49] are well known polymers to stabilize the metal nanoclusters. In addition to those polymers, some dendrimers such as poly(amidoamine) and poly(propylene imine) [ 50 ], microgels [51], are the examples for steric stabilization [30].



**Figure 2.** Schematic representation of steric stabilization [52].

Zeolites can also be used to stabilize the metal nanoclusters. In this study, zeolite-Y was used for the stabilization of metal(0) nanoclusters.

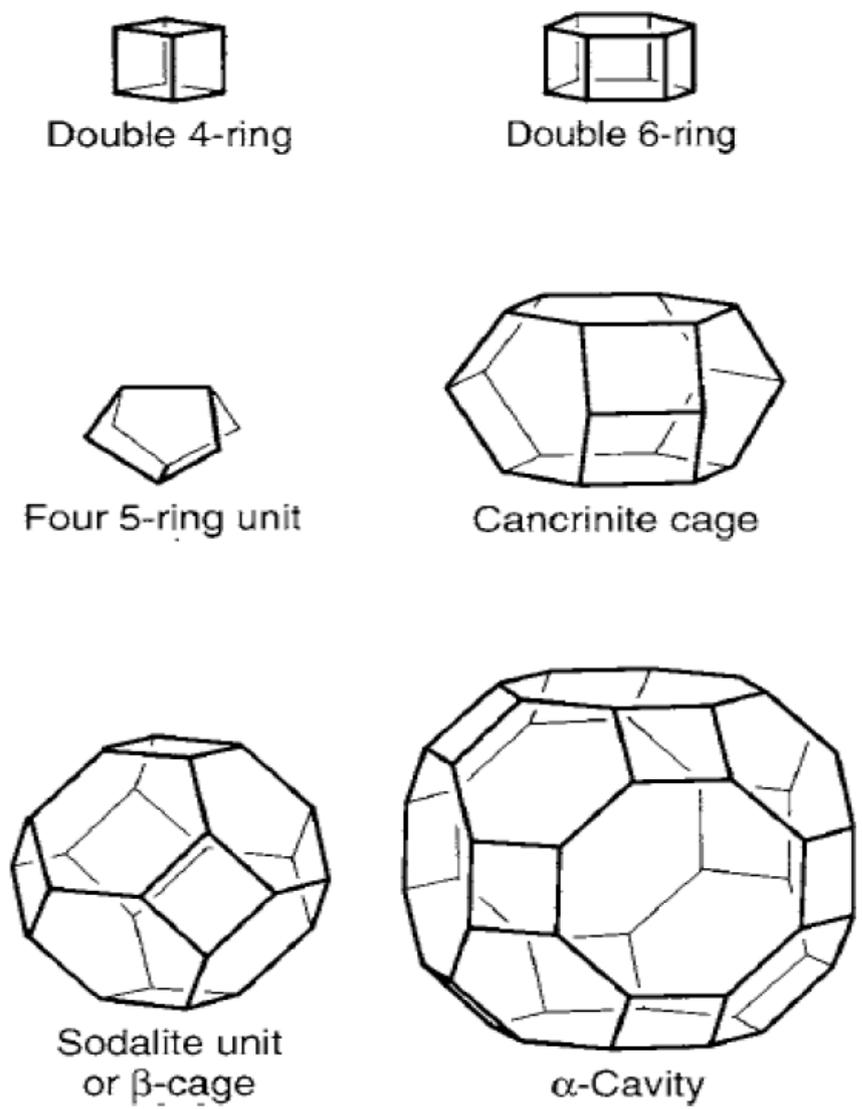
## 2.4. The Composition and the Structure of Zeolites

Zeolites are crystalline aluminosilicates of group IA and group IIA elements, such as sodium, potassium, magnesium and calcium [53]. Zeolites can be represented by  $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot w \cdot H_2O$ . Where n is the valence of cation M, w is the number of water molecules per unit cell, x and y are the total number of tetrahedral per unit cell.

Zeolites are three dimensional crystalline inorganic polymers. They are formed by four connected framework of  $AlO_4$  and  $SiO_4$  tetrahedra linked each other by the sharing of oxygen ions. Each  $AlO_4$  tetrahedron in the framework gives a net charge that is balanced by an extra-framework cation. The framework of zeolites contains intracrystalline channels or interconnected voids which are occupied by the cations and water molecules [54]. The cations are mobile and undergo ion exchange. The water in the zeolite can be removed from the voids by heating.

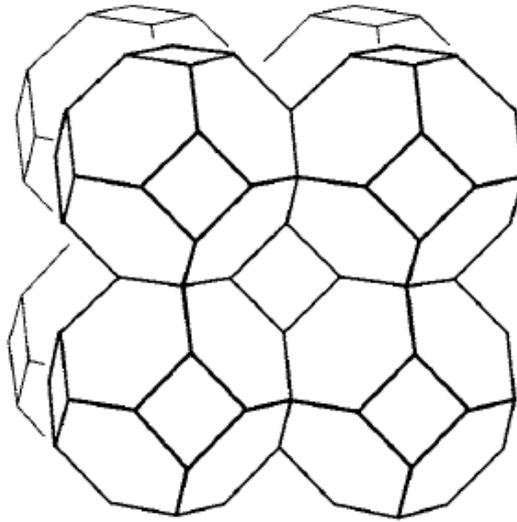
Zeolites have useful properties for the catalytic applications. They have microporous character with uniform pore dimensions and they allow certain hydrocarbons to enter the crystals while they can reject the others due to their molecular size. In addition, they can be used in ion exchange reactions. They can be easily modified by using their ion exchange properties. For example; metal particle introductions, exchange of charge compensating cations and replacement of silisium and aluminum in the zeolite framework are useful properties of zeolites. Zeolites also have high thermal stability [55].

The structures of zeolites are composed of subunits and cages as represented in Figure 3. The properties of these subunits and cages affect the ion exchange selectivity and the number of cation sites of zeolites. In addition, the catalytic behavior of zeolites is also affected by the dimensionality of the channel system that changes by the types of subunits and cages. Therefore, the structural analysis of zeolites is crucial.



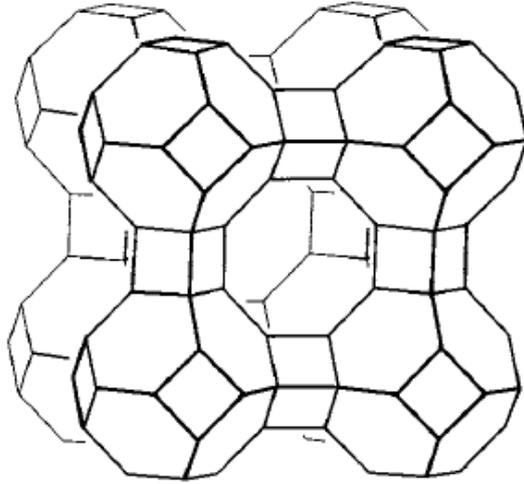
**Figure 3.** Schematic representation of some subunits and cages/cavities in several framework types.

According to the data of the Structure Commission of the International Zeolite Association, there are 194 framework types for zeolites [56]. However, only a few of them describe zeolites or zeolite-like materials used in industrial applications. For example, sodalite (SOD), zeolite A (LTA) and faujasite (FAU) are the selected of these aluminosilicates which are represented in Figures 4, 5 and 6, respectively.



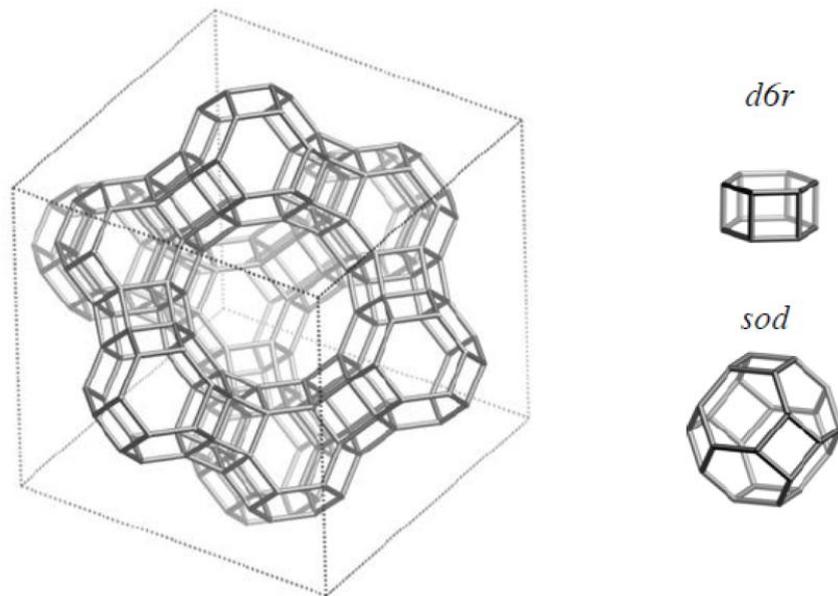
**Figure 4.** Schematic representation of the SOD framework type [57].

Sodalites have only six ring windows as illustrated in Figure 4 and they have very limited sorption capacity [57].



**Figure 5.** Schematic representation of the LTA framework type [57].

LTA framework type is composed of sodalite cages in the primitive cubic arrangement represented in Figure 5.



**Figure 6.** Building units of FAU: double six rings consisting of six TO<sub>4</sub> units each (T=Si and Al) and sodalites, respectively [56].

In the Faujasite framework, sodalite cages are joined to one another via double 6-rings as represented in Figure 6. This creates the so-called supercage with four, tetrahedrally oriented, 12-ring pore openings, and a 3-dimensional channel system which makes easy to transfer the molecules during the reaction. The diameters of these supercages ( $\alpha$ -cages) and sodalite cages ( $\beta$ -cages) in Faujasite framework type are 1.3 and 0.7 nm, respectively and they are large enough to admit the large molecules [16].

It is crucial to know that information on the framework type and its chemical composition and also nature of the species within the channels can clarify the observed properties of zeolites. For example, an aluminosilicate framework has a negative charge whereas an aluminophosphate is neutral, a large cation can block or reduce the effective size of a pore opening, a small cation might distort a pore opening, or a sorbed species can influence the catalytic, optical, magnetic, or electronic properties of a zeolite [57].

In this study, zeolite-Y ( $\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{140} \cdot 250\text{H}_2\text{O}$ ) with FAU framework was used in alcohol oxidation reactions considering the useful properties of FAU as a host material.

## 2.5. Oxidation of Alcohols

Oxidation of alcohols is attractive reaction to prepare fine chemicals. Alcohols can be oxidized to the corresponding aldehydes or ketones. Those reactions are one of the most desirable chemical transformations in organic synthesis as these products are important precursors and intermediates for many drugs, vitamins and fragrances in the perfume industry [58,59]. Notably, benzaldehyde, produced by the oxidation of benzyl alcohol, has a key position in the industry. It is used as an intermediate for the perfume and flavouring compounds. Benzaldehyde is also used in the preparation of dyes and plastics [60]. Benzophenone, a product of oxidation of diphenylmethanol reaction, is another important compound used in organic chemistry. It has a wide application in photochemistry as a photosensitizer. Benzophenone is also used in printing industry [61].

The world wide annual production of carbonyl compounds many of which is produced from alcohol oxidation shows an increase [62]. For example, in the 1980s, an estimated 18 million kilograms were produced annually in Japan, Europe, and North America, a level that can be assumed to continue [63]. However, the application of stoichiometric inorganic and organic oxidants such as chromium reagents [64], activated dimethyl sulfoxide reagents [65], permanganates [66] is not suitable due to the environmental and economical concerns. Most of these oxidants are toxic, hazardous or are required in large excess and some of these processes generate equal amounts of metal waste [67]. Therefore, the development of green, effective, selective, and reusable catalysts for the oxidation of alcohols to carbonyl compounds by molecular O<sub>2</sub> as oxidant is of great importance [20]. Due to the advantages of using air or dioxygen as stiochiometric oxidant, it is clearly seen that there are many searches to develop new catalysts for the aerobic oxidation of alcohols to their corresponding aldehydes and ketones using oxygen [68].

In this study, the effect of catalyst composition and preparation conditions on the catalytic activity were investigated in the liquid phase oxidation of various alcohols, namely, benzyl alcohol, heptanol, thiophenemethanol, diphenylcarbinol. The activity of the osmium(0) nanoclusters was given in terms of turnover frequencies.

## CHAPTER 3

### EXPERIMENTAL

#### 3.1. Materials

Osmium(III) chloride trihydrate ( $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ ), sodium borohydride ( $\text{NaBH}_4$ , 98%), and toluene were purchased from Aldrich. Benzyl alcohol (purity > 99.9 %), 1-phenyl ethanol (purity > 99.9 %), 3-5 dimethyl benzyl alcohol (purity > 99.9 %), 1-cyclohexen-ol (purity > 99.9 %), 2-thiophenylmethanol (purity > 99.9 %), 2-pyridinylmethanol (purity > 99.9 %), 1-heptanol (purity > 99.9 %), 2-heptanol (purity > 99.9 %), diphenyl carbinol (purity > 99.9 %) were purchased from Sigma and were used without further purification.

“Zeolite ( $\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{140} \cdot 250\text{H}_2\text{O}$ ) was purchased from Zeolyst Inc. Deionized water was distilled by water purification system (Milli-Q system). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C” [20].

### **3.2. Characterization of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y**

“The osmium content of the samples were determined by ICP-OES (inductively coupled plasma optical emission spectroscopy) using Leeman, Direct Reading Echelle after each sample was completely dissolved in a mixture of HNO<sub>3</sub>/HCl (1/3 ratio).

Powder X-ray diffraction (XRD) patterns of the samples were recorded with a MAC Science MXP 3TZ diffractometer using Cu K $\alpha$  radiation (wavelength 1.5406 Å, 40 kV, 55 mA). Scanning electron microscope (SEM) images were measured using a JEOL JSM-5310LV at 15 kV and 33 Pa in a low-vacuum mode without metal coating by sticking the powder samples on SEM sample holder.

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) analyses were performed on a JEM-2010F microscope (JEOL) operating at 200 kV. A small amount of powder sample was placed on the copper grid of the transmission electron microscope. Samples were examined at magnification between 100 and 400K. The elemental analyses of the powder samples were recorded during the TEM analyses with an energy dispersive X-ray (EDX) analyzer (KEVEX Delta series) mounted on the Hitachi S-800 modulated to JEM-2010F microscope.

The XPS analyses of the samples were performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al K $\alpha$  radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). The nitrogen adsorption-desorption experiments were carried out at 77 K using a NOVA 3000 series instrument (Quantachrome Instruments). The powder samples were out gassed under vacuum at 573 K for 3 h before the adsorption of nitrogen” [20].

### 3.3. Preparation of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y

Zeolite-Y was slurried with 0.1 M NaCl to remove sodium defect sites, washed until free of chloride and calcined in dry oxygen at 500 °C for 12 h.

Osmium(III) cations were introduced into the zeolite-Y by ion exchange of 1.0 g zeolite-Y in 100 mL aqueous solution of 77 mg  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  for 72 h at room temperature. The opaque-brown supernatant solution became colorless after 72 h, indicating the complete ion exchange.

The sample was then filtered by suction filtration (under 0.1 torr vacuum) using Whatman-1 (90 mm) filter paper, washed three times with 20 mL of deionized water and the remnant was dried under  $10^{-3}$  torr static vacuum at room temperature.

Osmium content of the  $\text{Os}^{3+}$  exchanged-zeolite-Y sample was found to be 2.1 wt % by ICP-OES analysis corresponding to 64 % of osmium used for the ion exchange.

Then, 0.4 g  $\text{Os}^{3+}$  exchanged zeolite-Y was added into 100 mL of 0.015 mol  $\text{NaBH}_4$  solution at room temperature.

When the hydrogen generation from the reaction solution ended (~3 h), the solid powders were isolated again by suction filtration, washed three times with 20 mL of deionized water to remove metaborate and chloride anions and dried under vacuum ( $10^{-3}$  torr, approximately 10% weight loss corresponding to removal of 40 % water absorbed in zeolite) at ambient temperature.

The samples of Os(0)-Y were bottled as black powders.

### **3.4. Catalytic Aerobic Oxidation of Alcohols Under 1 atm O<sub>2</sub> Using Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y**

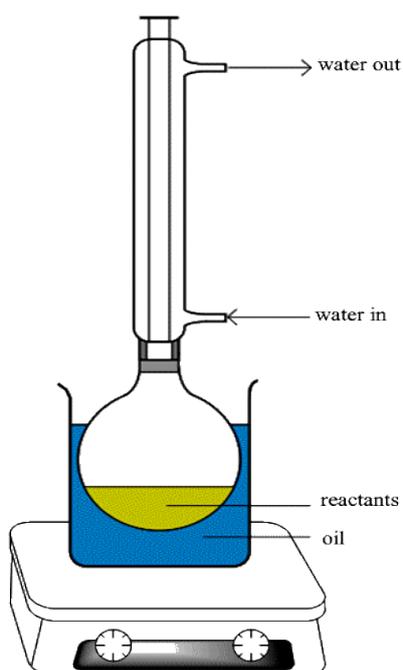
In a typical experiment, 0.4 g of Os(0)-Y (2.1 wt % Os, corresponding to 0.044 mmol Os) was put into a 250 mL reaction vessel (Parr Ins. Model 4560). The reactor was evacuated to 200 Torr and filled with pure O<sub>2</sub> (99.5 %) to 760 Torr, and this cycle was repeated 8 times.

“Then the reactor was heated to  $80 \pm 1$  °C and at this temperature under O<sub>2</sub> purging 1 mmol alcohol in 5 mL toluene was added via tap of reactor by using a 10 mL gas-tight syringe, then the pressure of 760 Torr was established and the reaction was started (t = 0 min.) by stirring the mixture at 900 rpm under 760 Torr O<sub>2</sub>.”

The progresses of the reaction were followed by GC analysis of the samples drawn from the reaction solution using dodecane as internal standard. All of the GC analyses were performed on a TRB-WAX column (30 m x 0.25 mm x 0.25 μm) with a Shimadzu GC-2010 equipped with a FID detector.

### **3.5. Catalytic Aerobic Oxidation of Alcohols Under Air Using Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y**

The oxidation reactions were carried out in a vessel (with a reflux condenser) containing 1 mmol alcohol, 5 mL toluene and 0.4 g Os(0)-Y (2.1 wt %) and a stir bar. The aerobic oxidation of alcohol was conducted in an 80 °C oil bath in air under ambient pressure. Figure 7 shows the basic experimental set up.



**Figure 7.** Experimental apparatus

### **3.6. Effect of Osmium Loading on the Catalytic Activity of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y in the Aerobic Oxidation of Benzyl alcohol**

In a series of experiments the catalytic activity of zeolite framework stabilized osmium(0) nanoclusters ( $O_s = 0.044$  mmol in all) with various osmium loadings 0.9, 2.1, 3.1, 6.8 % wt  $O_s$  were tested in the aerobic oxidation of benzyl alcohol.

The experiments were performed in the same way as described in the section “Catalytic aerobic oxidation of alcohols under air using osmium(0) nanoclusters stabilized by the framework of zeolite-Y”.

The best catalytic activity was achieved by 2.1 % wt osmium loaded sample. For all the tests reported hereafter, the osmium loading used was  $\cong 2.1$  wt % unless

otherwise stated. In that loading the majority of osmium(0) nanoclusters locate most probably in the supercage ( $\alpha$ -cage), where the substrate can more readily access to osmium(0) nanoclusters compared to  $\beta$ -cage of Zeolite-Y.

### **3.7. Leaching Test of Osmium(0) Nanoclusters in the Aerobic Oxidation of Benzyl alcohol Under 1 atm O<sub>2</sub>**

After the complete catalytic oxidation of benzyl alcohol using Os(0)-Y had been achieved, the hot solution was filtered by suction filtration, the filtrate was put into the reactor, benzyl alcohol was added and the reactor was pressurized to 1 atm with pure O<sub>2</sub>. The reaction was followed by GC analysis. No oxidation of benzyl alcohol was observed after 6 hours. Additionally, no osmium metal was detected in the filtrate by ICP which had a detection limit of 24 ppb for Os.

### **3.8. Reusability and Isolability Tests of Osmium(0) Nanoclusters in the Aerobic Oxidation of Benzyl alcohol**

The isolability and reusability of Os(0)-Y, two crucial measures in heterogeneous catalysis, were tested in the aerobic oxidation of benzyl alcohol. The oxidation reaction were carried out in a vessel (with a reflux condenser) containing 1 mmol alcohol, 5 mL toluene and 0.4 g Os(0)-Y (2.1 wt %) and a stir bar at 80 °C in air under ambient pressure.

After the complete oxidation of benzyl alcohol, Os(0)-Y were isolated as dark brown powders by suction filtration, washed with acetone, and dried under vacuum at room temperature. The dried sample of Os(0)-Y can be bottled and stored under ambient conditions. Furthermore, when redispersed in toluene, Os(0)-Y are yet active catalyst in the oxidation of benzyl alcohol.

### **3.9. Catalytic Lifetime of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y**

The catalytic lifetime test was started with 5 mmol benzyl alcohol and 0.4 g Os(0)-Y (2.1 wt %) in 5 mL toluene at 80 °C. The reaction was followed by GC analysis. Total turnover number of osmium(0) nanoclusters was determined for the lifetime test.

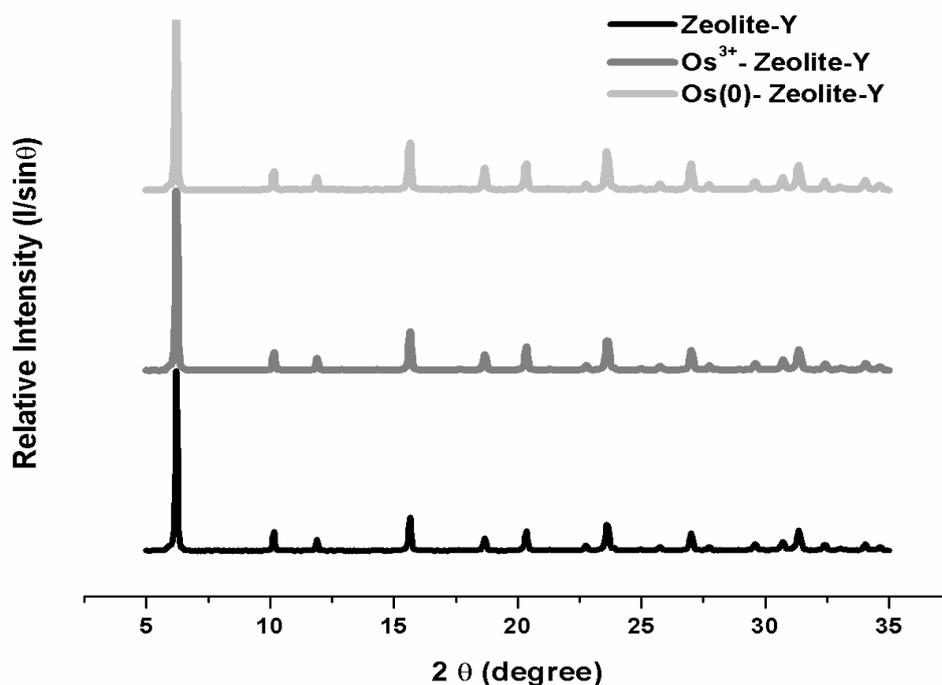
## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1. Preparation and Characterization of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y

Preparation of osmium(0) nanoclusters contains two basic procedures. Firstly, zeolite-Y was added to the aqueous solution of osmium(III) trichloride and stirred for 3 days at room temperature for the ion exchange. At the end of the ion exchange, suspension was filtered, washed with deionized water and dried under vacuum. After the first step, some of the extra framework of  $\text{Na}^+$  cations were replaced by  $\text{Os}^{3+}$  cations and  $\text{Os}^{3+}$  cations in the zeolite-Y framework were obtained. Secondly,  $\text{Os}^{3+}$  cations in the framework of zeolite-Y were reduced using sodium borohydride in aqueous solution at room temperature. After filtering, washing and drying the suspension, Os(0) nanoclusters stabilized by zeolite-Y framework was obtained as powder materials and was used for catalytic reactions.

$\text{Os}^{3+}$  exchanged zeolite-Y and Os(0)-Y were characterized by XRD to get information whether this procedure caused a change in the crystallinity of zeolite-Y. For this reason, XRD patterns of  $\text{Os}^{3+}$ -zeolite-Y and Os(0)-zeolite-Y were taken and compared with that of zeolite-Y which are given all together in Figure 8.



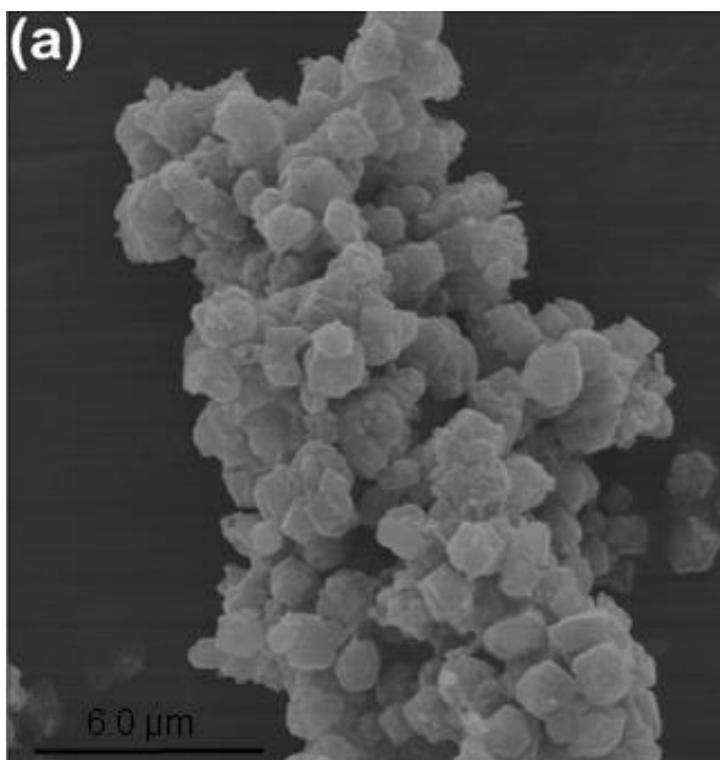
**Figure 8.** Powder XRD patterns of zeolite-Y, Os<sup>3+</sup>-exchanged zeolite-Y with an osmium content of 2.1 % wt and Os(0)-Y.

“As seen from the comparison of XRD patterns of zeolite-Y and Os<sup>3+</sup> exchanged zeolite-Y (Fig. 8), there is no noticeable change in both the intensities and positions of the Bragg peaks, indicating that neither the crystallinity nor the lattice of zeolite-Y is altered by the ion exchange as expected. From the Os(0)-zeolite-Y pattern, one can conclude that the reduction of osmium(III) ion forming the osmium(0) nanoclusters within the supercages causes no observable alteration in the framework lattice and no loss in the crystallinity of zeolite-Y [20].”

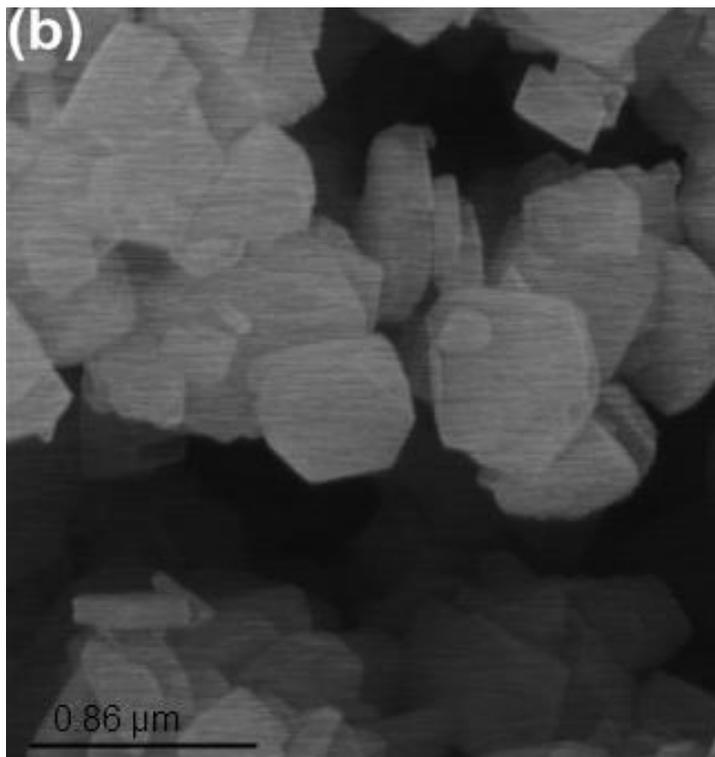
To determine the amount of metal loading and also to prove the incorporation osmium(III) cations in zeolite frameworks, ICP-OES was used. According to the ICP-OES result, there were 2.1 wt % osmium in the host material.

To investigate the morphology and composition of Os(0)-Y, SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-Ray Analysis), TEM (Transmission Electron Microscopy), HRTEM (High Resolution Transmission Electron Microscopy) analyses were done.

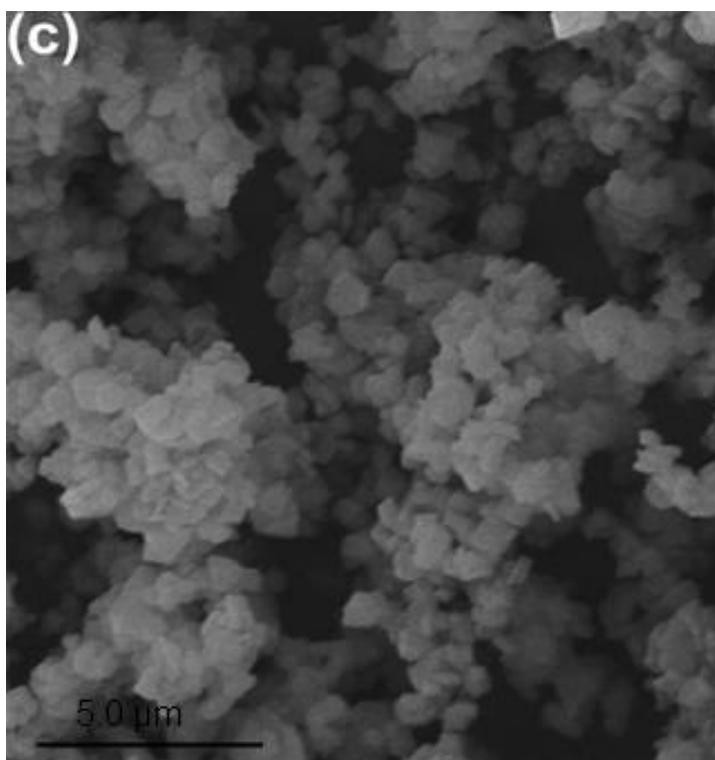
Figure 9, 10, 11 and 12 show SEM images of Os(0)-Y, Os<sup>3+</sup>-Y with an osmium loading of 2.1 % wt and that of zeolite-Y taken in different magnifications.



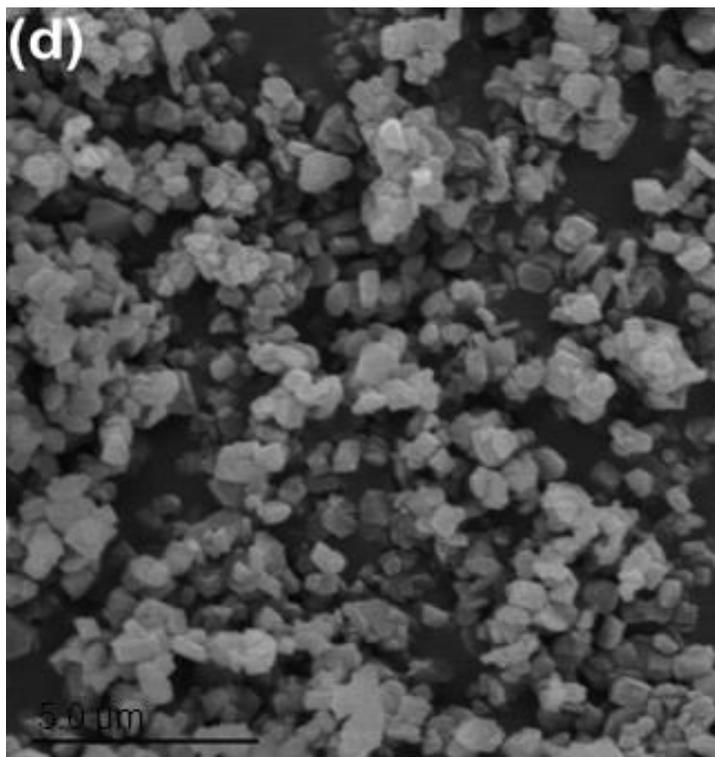
**Figure 9.** Scanning Electron Microscopy (SEM) image of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt.



**Figure 10.** SEM image of Os(0)-Y with osmium loading of 2.1 % wt.



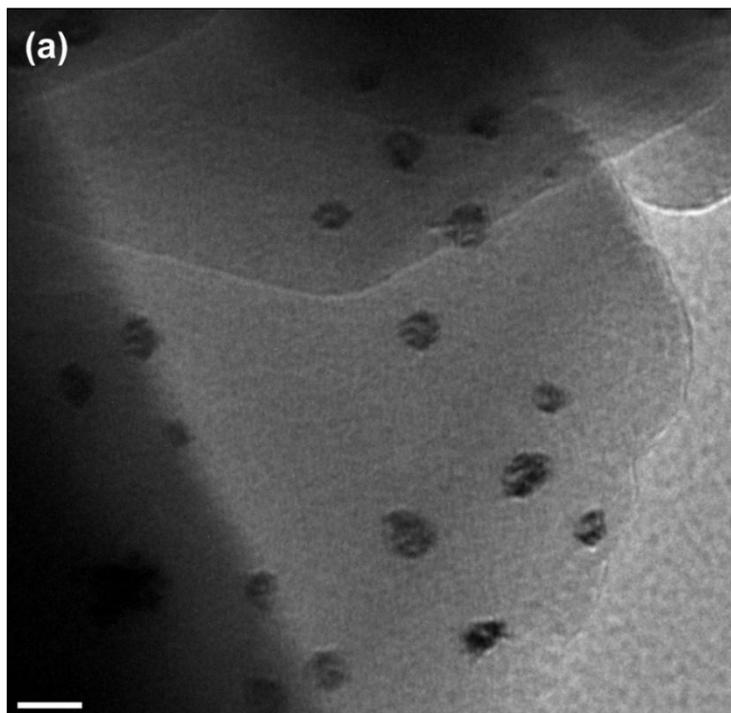
**Figure 11.** SEM image of Os<sup>3+</sup>-exchanged zeolite-Y with osmium loading of 2.1 % wt. (scale bar equals to 5.0 μm)



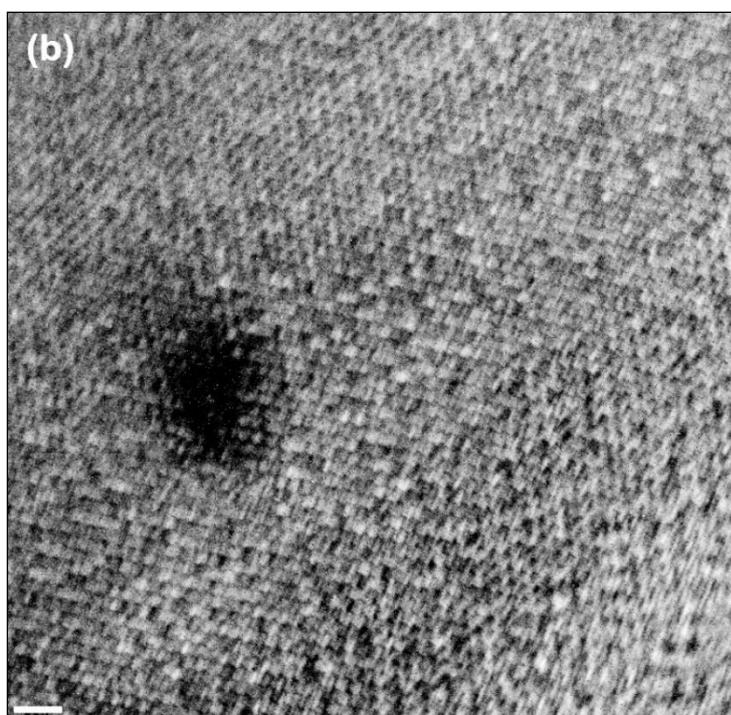
**Figure 12.** SEM image of zeolite-Y ( $\text{Na}_{56}\text{Y}$ ). (scale bar equals to 5.0  $\mu\text{m}$ )

Scanning Electron Microscopy (SEM) images in Figures 9, 10, 11 and 12 indicate that there exist only crystals of zeolite-Y and there is no bulk osmium formed in observable size outside the zeolite crystals. In addition, it can be understood that the method used for the preparation of Os(0)-Y does not cause any observable defects in the structure of zeolite-Y, a fact which is also supported by the XRD results.

In Figures 13, 14 and 15, transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), TEM-EDX images of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt. are shown, respectively.

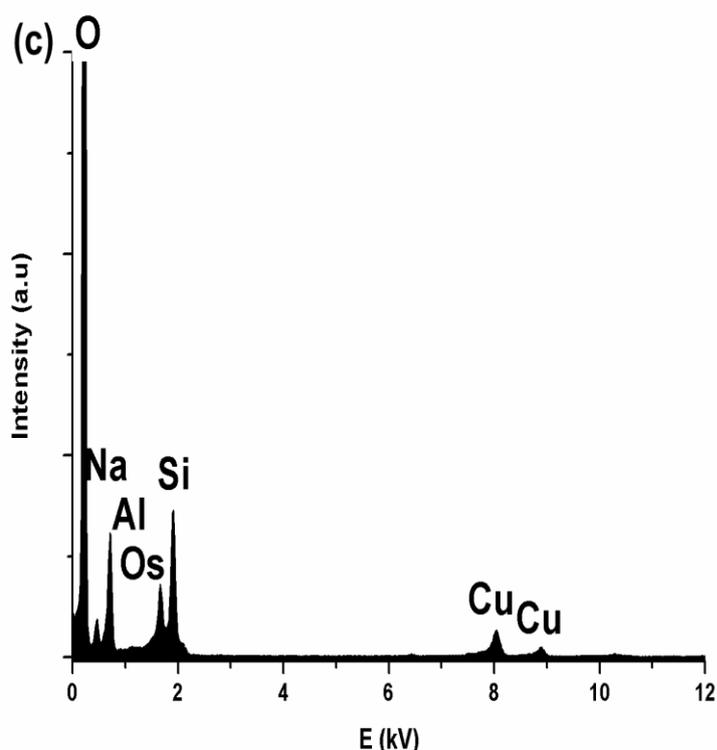


**Figure 13.** TEM image of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt. (scale bar equals to 5 nm)



**Figure 14.** HRTEM image of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt (scale bar equals to 1 nm).

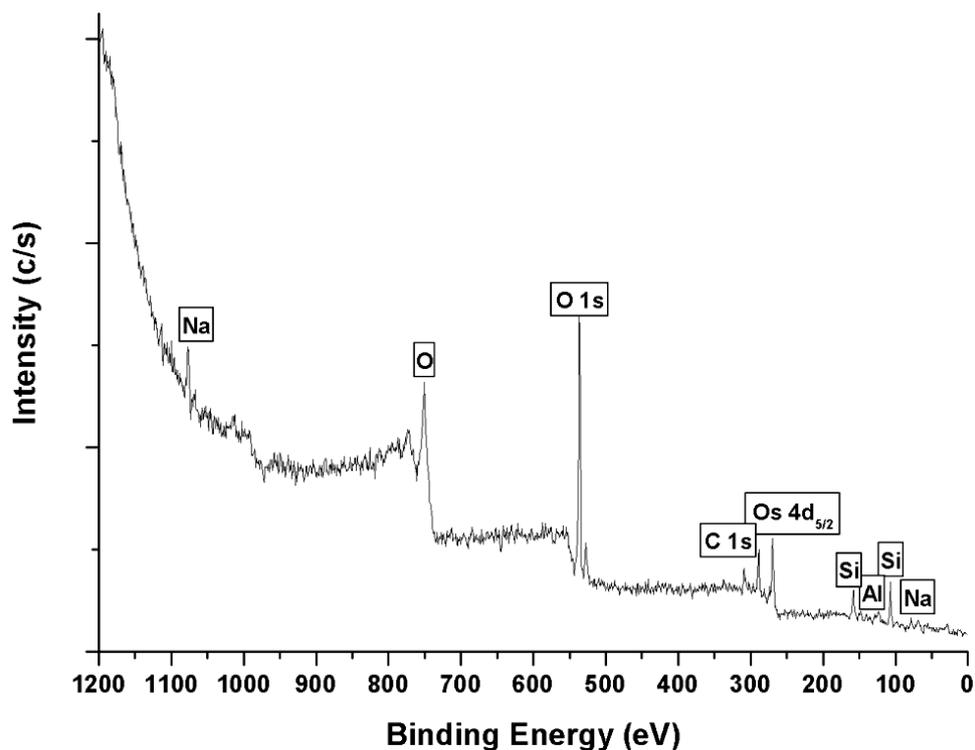
From the TEM image in Figure 13, it is seen that there are a few osmium(0) nanoclusters on the external surface of zeolite and these nanoclusters appear to be stable and do not agglomerate to the bulk metal. In addition to the nanoclusters on the external surface of zeolite, the high resolution-TEM image of the Os(0)-Y sample in Fig. 14 shows the distribution of osmium species within the cavities of zeolite-Y.



**Figure 15.** TEM-EDX spectrum of osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt.

TEM-EDX spectrum of Os(0)-Y given in Fig. 15 shows that osmium is the only element detected in addition to the zeolite framework elements (Si, Al, O, Na) and Cu from the grid.

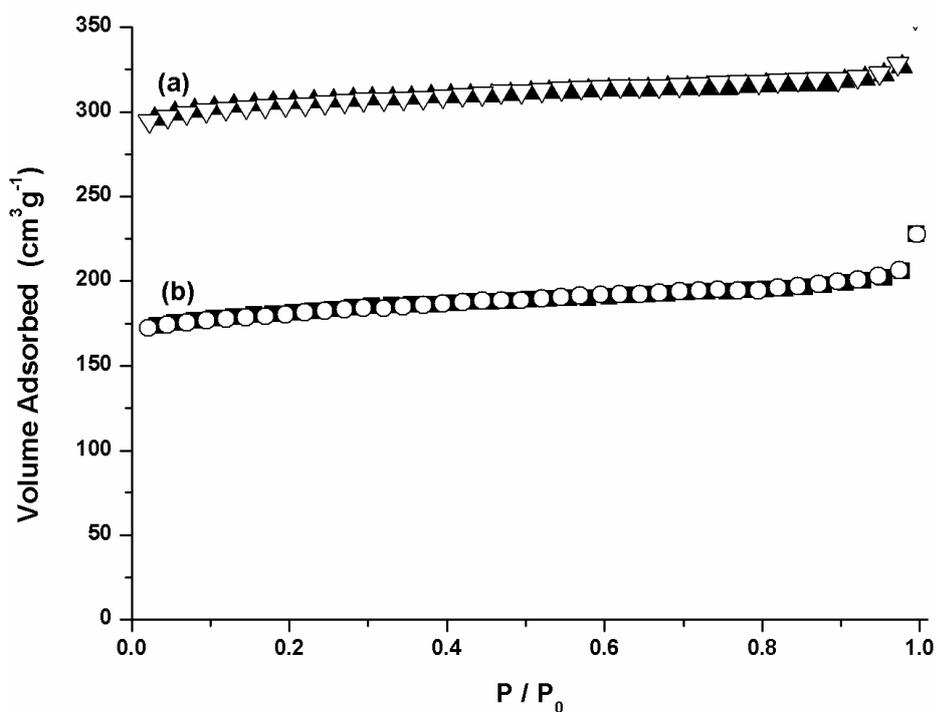
X-ray photoelectron spectroscopy provides further insight into oxidation state of osmium in zeolite framework and elemental composition. A survey XPS scan of Os(0)-Y depicted in Figure 16 shows a prominent peak at 274 eV, readily assigned to Os(0) 4d<sub>5/2</sub> [69] and also indicates that osmium is the only element detected in addition to the zeolite framework elements, which supports the finding by the TEM-EDX.



**Figure 16.** X-ray photoelectron spectrum of Os(0)-Y in the region of 1200-0 eV.

In the figure 16, X-ray photoelectron spectroscopy analysis shows that there are other elements, which come from zeolite framework, except from osmium(0). It is worth noting that the sample for the XPS spectrum was prepared by the reduction of osmium(III) cations in zeolite-Y.

In addition to the qualitative analysis of osmium(0) nanoclusters, nitrogen adsorption - desorption isotherms of zeolite-Y and osmium(0) nanoclusters stabilized in zeolite-Y framework with osmium loading of 2.1 % wt are given in Figure 17 indicating quantitative information.



**Figure 17.** The nitrogen adsorption-desorption isotherms of (a) zeolite-Y and (b) Os(0)-Y with osmium loading of 2.1 % wt.

From Figure 17, it is clearly understood that zeolite-Y and Os(0)-Y show Type I shape which is a characteristic of microporous materials [70]. The micropore volume and area were determined for zeolite-Y and Os(0)-Y by t-plot method [71].

According to the nitrogen adsorption-desorption analysis the micropore volume of zeolite-Y and Os(0)-Y were found as 0.333 and 0.172 cm<sup>3</sup>/g respectively. The micropore areas of those were also calculated. The micropore area of zeolite-Y and Os(0)-Y were 753 and 398 m<sup>2</sup>/g respectively.

The remarkable decrease in the micropore volume and micropore area can be attributed to the encapsulation of osmium species in the cavities of zeolite-Y. Furthermore, no hysteresis loop was observed in the N<sub>2</sub> adsorption-desorption isotherm of Os(0)-Y indicating that the procedure followed in the preparation of Os(0)-Y does not cause any alteration in the microporous structure of zeolite-Y.

## 4.2. The Catalytic Activity Tests

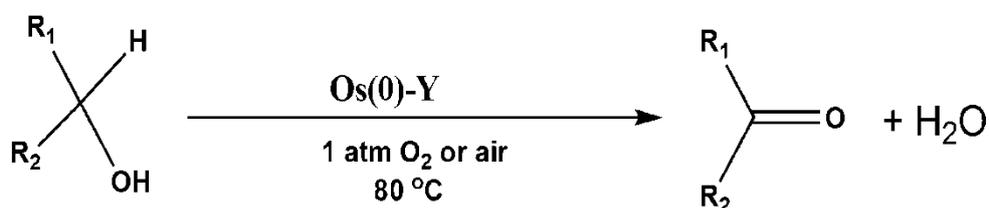
### 4.2.1. The Catalytic Activity of Osmium Free Zeolite-Y and Osmium(III)-Zeolite-Y in the Aerobic Oxidation of Alcohol

Before starting the catalytic test of osmium(0) nanoclusters stabilized in the zeolite framework, osmium free zeolite-Y and osmium(III)-zeolite-Y were tested in the oxidation of benzyl alcohol.

The control experiments showed that the host material zeolite-Y is inactive in the aerobic oxidation of benzyl alcohol under the same conditions (as described in the experimental section) whereas osmium(III)-exchanged zeolite-Y provides only a TOF value of  $0.4 \text{ h}^{-1}$

### 4.2.2. The Catalytic Activity Tests of Osmium(0) Nanoclusters Stabilized by the Framework of Zeolite-Y

Osmium(0) nanoclusters stabilized by the framework of zeolite-Y were tested as catalyst in the aerobic oxidation of various alcohols at  $80 \text{ }^\circ\text{C}$  under 1 atm  $\text{O}_2$  pressure or air. (Fig.18)



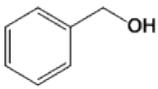
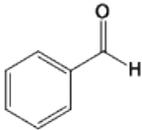
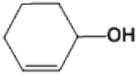
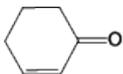
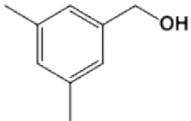
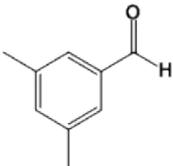
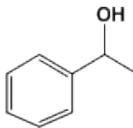
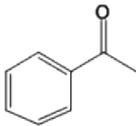
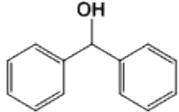
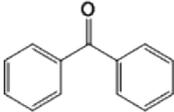
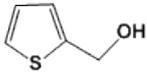
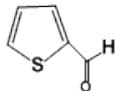
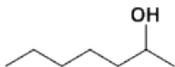
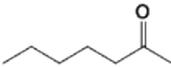
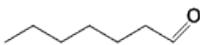
**Figure 18.** Os(0)-Y catalyzed aerobic oxidation of alcohols to carbonyl compounds at  $80 \text{ }^\circ\text{C}$  under 1 atm  $\text{O}_2$  or air.

Table 1 lists the substrates and the products of the oxidation reactions under air and indicates the conversion and the turnover frequency of these reactions. Benzyl alcohol (Entry 1), 1-cyclohexen-ol (Entry 2), 3,5-dimethyl methanol (Entry 3), 1-phenylethanol (Entry 4), diphenylmethanol (Entry 5), 2-(hydroxymethyl) thiophene (Entry 6), 2-heptanol (Entry 7) and 1-heptanol (Entry 8) were used as substrates in the oxidation reactions under air and all these reactions were performed by using 1 mmol substrate and 400 mg Os(0)-Y (0.044 mmol Os) in 5 mL toluene at 80°C.

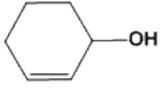
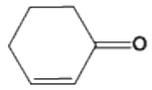
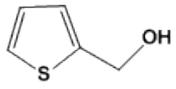
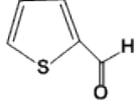
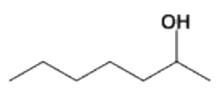
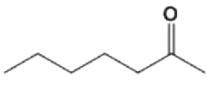
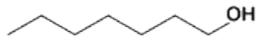
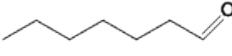
As it is seen from Table 1, Os(0)-Y show high catalytic activity and selectivity in the aerobic oxidation of alcohols to carbonyl compounds. Most of the benzylic and allylic alcohols (entries 1-8) were converted to the corresponding carbonyl compounds in >99% selectivity. Benzyl alcohol (Entry 1), 3,5-dimethyl methanol (Entry 3), 1-phenyl ethanol (Entry 4), diphenylmethanol (Entry 5), 2-(hydroxymethyl)thiophene (Entry 6) were totally converted to corresponding aldehydes or ketones by osmium(0) nanoclusters stabilized in zeolite-Y framework under air. The turnover frequencies of these reactions are 14, 8, 12, 23, 6 h<sup>-1</sup> respectively. However, 1-cyclohexen-ol (Entry 2), 2-heptanol (Entry 7), 1-heptanol (Entry 8) were not totally converted under air even if the long reaction times. The turnover frequencies of these reactions are 3, 4, 2 h<sup>-1</sup> respectively.

In addition, the activity of osmium(0) nanoclusters stabilized by zeolite-Y was also tested using pure oxygen under 1 atm pressure for the oxidation of alcohols. It is concluded from Table 2 that higher conversions of alcohols to the corresponding aldehydes and ketones in 1 atm O<sub>2</sub> were achieved. Os(0)-zeolite-Y can convert all 1-cyclohexen-ol (Entry 1), 2-(hydroxymethyl)thiophene (Entry 2), 2-heptanol (Entry 3) to the corresponding ketones. For these alcohols, the turnover frequencies are 16, 22 and 9 h<sup>-1</sup>, respectively whereas the turnover frequencies under air were 3, 6 and 4 h<sup>-1</sup>, respectively. Os(0)-zeolite-Y can also oxidize 75 percent of 1-heptanol with a TOF value of 5 h<sup>-1</sup>.(Entry 4)

**Table 1.** Aerobic oxidation of alcohols catalyzed by Os(0)-Y catalyst under air. All these reactions were performed by using 1 mmol substrate and 400 mg Os(0)-Y (0.044 mmol Os) in 5 mL toluene at 80°C and the conversion of substrates was determined by GC analysis.

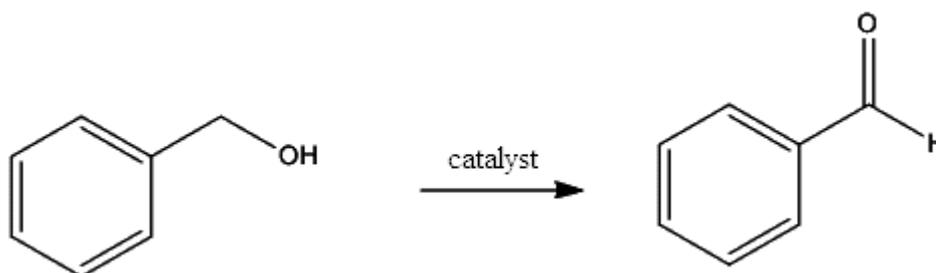
Entry	Substrate	Product	t(h)	TOF (h <sup>-1</sup> )	Conversion (%)
1			3	14	100
2			24	3	51
3			6	8	100
4			3	12	100
5			1	23	100
6			12	6	100
7			18	4	90
8			24	2	47

**Table 2.** Aerobic oxidation of alcohols catalyzed by Os(0)-Y catalyst by using 1 mmol substrate and 400 mg Os(0)-Y in 5 mL toluene at 80°C under 1 atm O<sub>2</sub>.

Entry	Substrate	Product	t (h)	TOF (h <sup>-1</sup> )	Conversion (%)
1			3	16	100
2			1	22	99
3			10	9	100
4			24	5	75

Zeolite framework stabilized osmium(0) nanoclusters show substantially higher activity in the oxidation of benzylalcohol, 1-phenylethanol, diphenylmethanol and 2-(hydroxymethyl)thiophene. The activity of Os(0)-Y can be compared with some well known catalyst in the literature for these reactions as listed in Tables 3, 4, 5 and 6.

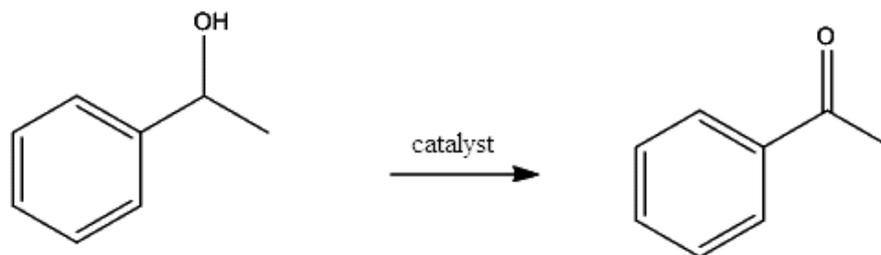
### Oxidation of Benzyl Alcohol to Benzaldehyde



**Table 3.** Activities of various well known catalysts used in the oxidation of benzyl alcohol in terms of TOF values in toluene.

catalyst	T(°C)	TOF (h <sup>-1</sup> )	ref
NR <sub>3</sub> <sup>+</sup> RuO <sub>4</sub> <sup>-</sup> /MCM-41	80	170	72
RuO <sub>4</sub> <sup>-</sup> /polymer	75	20	73
<b>Os(0)-Y</b>	80	14	20
Pr <sub>4</sub> N <sup>+</sup> RuO <sub>4</sub> <sup>-</sup> /ormosil(SiO <sub>2</sub> )	75	13	74
Ru-Co-Al- hydrotalcite	60	9.3	75
10% RuO <sub>2</sub> /FAU zeolite	80	8.5	76
[RuCl <sub>2</sub> (p-cymene)] <sub>2</sub> /C	110	4.7	77
Na <sub>5</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> /C	100	4.5	78
Ru <sub>0.35</sub> MnFe <sub>1.5</sub> Cu <sub>0.15</sub> O <sub>x</sub>	22	3.4	79
Ru <sup>+3</sup> - hydroxyapatite	80	2	80
RuO <sub>2</sub> .xH <sub>2</sub> O	80	1.4	76
Ru-Mg-Al-hydrotalcite	60	1.1	81
H-K-OMS-2	110	0.5	82

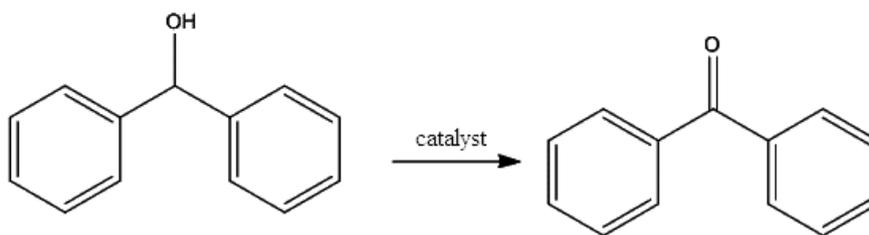
## Oxidation of 1-Phenylethanol to Acetophenone



**Table 4.** Activities of various well known catalysts used in the oxidation of 1-phenylethanol in terms of TOF values in toluene.

catalyst	T( $^{\circ}\text{C}$ )	TOF ( $\text{h}^{-1}$ )	ref
<b>Os(0)-Y</b>	80	12	20
Ru-Co-Al- hydrotalcite	60	6.2	75
$\text{Na}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{C}$	100	4.5	78
$\text{Ru}_{0.35}\text{MnFe}_{1.5}\text{Cu}_{0.15}\text{O}_x$	22	3.5	79
$\text{Pr}_4\text{N}^+\text{RuO}_4^-/\text{ormosil}(\text{SiO}_2)$	75	3	74
$\text{Ru}^{+3}$ - hydroxyapatite	80	3	80
H-K-OMS-2	110	0.5	82
Ru-Mg-Al-hydrotalcite	60	0.5	75

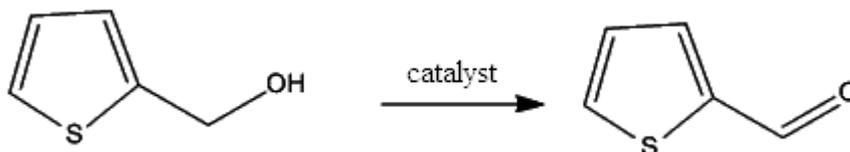
## Oxidation of Diphenylmethanol to Benzophenone



**Table 5.** Activities of various well known catalysts used in the oxidation of diphenylmethanol in terms of TOF values in toluene.

catalyst	T( <sup>o</sup> C)	TOF (h <sup>-1</sup> )	ref
<b>Os(0)-Y</b>	80	23	20
Ru-Co-Al- hydrotalcite	60	9.3	75
Ru <sup>+3</sup> - hydroxyapatite	80	3	80
Ru <sub>0,35</sub> MnFe <sub>1,5</sub> Cu <sub>0,15</sub> O <sub>x</sub>	22	4	79
Ru-Mg-Al-hydrotalcite	60	1.2	81
H-K-OMS-2	110	0.5	82

### Oxidation of 2-(Hydroxymethyl)thiophene



**Table 6.** Activities of various well known catalysts used in the oxidation of 2-(Hydroxymethyl) thiophene in terms of TOF values in toluene.

catalyst	T(°C)	TOF (h <sup>-1</sup> )	ref
Ru-Co-Al- hydrotalcite	60	14	75
<b>Os(0)-Y</b>	80	6.0	20
Ru <sub>0.35</sub> MnFe <sub>1.5</sub> Cu <sub>0.15</sub> O <sub>x</sub>	22	3.1	79
Ru <sup>+3</sup> - hydroxyapatite	80	3	80
H-K-OMS-2	110	0.5	82

Osmium(0) nanoclusters stabilized in the framework of zeolite-Y has remarkable catalytic activities in the oxidation of benzyl alcohol, 1-phenylethanol, diphenylmethanol and 2-(hydroxymethyl) thiophene as indicated in Tables 3, 4, 5 and 6, respectively. As it is seen in Tables 3, 4 and 5, Os(0)-Y has the highest catalytic activity in the oxidation of benzyl alcohol, 1-phenylethanol, diphenylmethanol as compared with Ru-Co-Al-hydrotalcite, Ru<sup>3+</sup>HAP, Ru<sub>0.35</sub>MnFe<sub>1.5</sub>Cu<sub>0.15</sub>O<sub>x</sub>, Ru-Mg-Al- hydrotalcite and H-K-OMS-2. Os(0)-Y with a TOF value of 6 h<sup>-1</sup> is also one of the active catalysts used in the oxidation of 2-(hydroxymethyl) thiophene in the literature.(Table 6)

### **4.2.3. Catalytic Lifetime, Reusability and Isolability of Osmium(0) Nanoclusters Stabilized in Zeolite Framework**

The catalytic lifetime of osmium(0) nanoclusters-zeolite-Y was determined by measuring the total turnover number (TTON). Os(0)-Y provided a TTON of 71 mol benzaldehyde/ mol Os under the reaction conditions indicated in section 3.9.

The isolability and reusability are two crucial measures in heterogeneous catalysis. Therefore, Os(0)-Y were tested in the aerobic oxidation of benzyl alcohol. For this reusability test, the reaction conditions were totally the same as the ones indicated in section 3.9. After the complete oxidation of benzyl alcohol, Os(0)-Y were isolated as dark brown powders by suction filtration, washed with acetone, and dried under vacuum at room temperature. The dried sample of Os(0)-Y can be bottled and stored under ambient conditions. Furthermore, when redispersed in toluene, Os(0)-Y were yet active catalyst in the oxidation of benzyl alcohol. They retained 25 % of their initial catalytic activity with the complete conversion of benzyl alcohol to benzaldehyde even at third run. Taking all the results together one can conclude that Os(0)-Y are isolable, bottleable, redispersible, and repeatedly usable as an active catalyst in the aerobic oxidation of alcohols.

In addition to those tests, a control experiment was performed to show that the oxidation of benzyl alcohol is completely stopped by the removal of Os(0)-Y from the reaction solution.

## CHAPTER 5

### CONCLUSIONS

In conclusion, the main findings of this work as well as the implications or predictions can be summarized as follows.

Osmium(0) nanoclusters stabilized by the framework of zeolite-Y, Os(0)-Y, were prepared, for the first time, by using an easy two step procedure which consist of the ion-exchange of Os<sup>3+</sup> ions with the extra framework Na<sup>+</sup> ions in zeolite-Y, and the reduction of the Os<sup>3+</sup> ions in the cavities of zeolite-Y with sodium borohydride in aqueous solution at room temperature.

Os(0)-Y was characterized by using ICP-OES, XRD, XPS, TEM, HRTEM, TEM/EDX, SEM, and N<sub>2</sub> adsorption-desorption techniques. The results of these techniques reveal the formation of well-dispersed osmium(0) nanoclusters within the zeolite framework without causing alteration in the framework lattice, mesopores formation, or loss in the crystallinity of the host material.

Os(0)-Y provide high catalytic activity and selectivity in the aerobic oxidation of both activated and unactivated alcohols, which may have a carbon-carbon double bond or a heteroatom, such as sulfur, under mild conditions by using 1 atm O<sub>2</sub> or air without using any oxidizing agents and additives.

Additionally, Os(0)-Y are highly stable in terms of crystallinity, and morphology, which makes them bottleable and reusable.

The high catalytic activity, easy preparation, isolability, bottleability, and reusability of Os(0)-Y raise the prospect of using this type of materials for the aerobic oxidation of alcohols in industrial applications as well as in small scale organic synthesis.

## REFERENCES

- [1] (a) Schmid, G., *Chem.Rev.*, **1992**, 92, 1709. (b) Schmid, G., *Clusters and Colloids From Theory to Applications*, Wiley-VCH, Weinheim, **1994**.
- [2] (a) Roucoux A., Philippot, K., *The Handbook of Homogeneous Hydrogenation*, J.G. de Vries C. J. Elsevier, Wiley-VCH, **2007**. (b) Roucoux, A., Nowicki, A., Philippot, K., *Nanoparticles and Catalysis*, Wiley-VCH, **2007**.
- [3] Roucoux, A., Schulz, J., Patin, H., *Chem. Rev.*, **2002**, 102, 3757.
- [4] (a) Tzou, M. S., Teo, B. K., Sachtler, W. M. H., *J. Catal.*, **1988**, 113, 220. (b) Homeyer, S. T., W. M. H. Sachtler, *J. Catal.*, **1989**, 117, 91. (c) Zhang, Z., Zhang, Y. D., Hines, W. A., Budnick, J. I., Sachtler, W. M. H., *J. Am. Chem. Soc.*, **1992**, 114, 4843. (d) Tang, Q., Zhang, Q., Wang, P., Wang, Y., Wan, H., *Chem.Mater.*, **2004**, 16, 967. (e) Seidel, A., Loos J., Boddenberg, B., *J. Mater. Chem.*, **1999**, 9, 2495.
- [5] Breck, D. W., *Zeolite Molecular Sieves*, Wiley, New York, **1984**.
- [6] (a) Sun, Y., Sun, T., Seff, K., *Chem. Rev.*, **1994**, 94, 857. (b) Ryoo, R., June-Cho, S., Pak, C., Guk-Kim, J., Ki-Ihm, S., Yong-Lee, J., *J. Am. Chem. Soc.*, **1992**, 114, 76. (c) Doolittle, J. W., Dutta, P. K., *Langmuir*, **2006**, 22, 4825. (d) Gucci, L., Kiricsi, I., *Appl. Catal., A*, **1999**, 186, 375. (e) Gucci, L., Beck, A., Horvath, D., *Top. Catal.*, **2002**, 19, 157. (f) Tang, Q., Zhang, Q., Wang, P., Wang, Y., Wan, H., *Microporous Mesoporous Mater.*, **2005**, 86, 38. (g) Ozin, G. A., Prokopowicz R. A., Özkar, S., *J. Am. Chem. Soc.*, **1992**, 114, 8953. (h) Moller, K., Bein, T., Özkar S., Ozin, G. A., *J. Phys. Chem.*, **1991**, 95, 5276.
- [7] Tosheva, L., Valtchev, V. P., *Chem. Mater.*, **2005**, 17, 2494.
- [8] (a) Ryoo, R., Jung, S. M., Cho S. J., Shul, Y. G., *J. Phys. Chem.*, **1992**, 96, 9922. (b) Apple, T., Shoemaker, R., *J. Phys. Chem.*, **1987**, 91, 4024.
- [9] (a) Zahmakıran, M., Özkar, S., *Langmuir*, **2008**, 24, 7065. (b) Zahmakıran, M., Özkar, S., *Langmuir*, **2009**, 25, 2667. (c) Zahmakıran, M., Tonbul, Y., Özkar, S., *J. Am. Chem. Soc.*, **2010**, 132, 6541.
- [10] Zahmakıran, M., Özkar, S., *Appl. Catal., B*, **2009**, 89, 104.
- [11] (a) Zhou, P. L., Gates, B. C., *J. Chem. Soc., Chem. Commun.*, **1989**, 347. (b) Enderle, B., Labouriau, A., Ott, K. C., Gates, B. C., *J. Phys. Chem.B*, **2002**, 106, 2109. (c) Maloney, S. D., Zhou, P. L., Kelley, M. J., Gates, B. C., *J. Phys. Chem.*, **1991**, 95, 5409.
- [12] (a) Lamb, H. H., Wolfer, M., Gates, B. C., *J. Chem. Soc., Chem. Commun.*, **1990**, 1296. (b) Bhirud, V. A., Iddir, H., Browning, N. G., Gates, B. C., *J.*

- Phys. Chem. B*, **2005**, 109, 12738. (c) Bhirud, V. A., Panjabi, G., Salvi, S. N., Phillips, B. L., Gates, B. C., *Langmuir*, **2004**, 20, 6173. (d) Kulkarni, A., Mehraeen, S., Reed, B. W., Okamoto, N. L., Browning N. D., Gates, B. C., *J. Phys. Chem. C*, **2009**, 113, 13377.
- [13] (a) Goellner, J. F., Neyman, K. M., Mayer, M., Nortemann, F., Gates B. C., Roch, N., *Langmuir*, **2000**, 16, 2736. (b) Allard, L. F., Panjabi, G. A., Salvi, S. N., Gates, B. C., *Nano Lett.*, **2002**, 2, 381.
- [14] G.,Rothenber, *Catalysis: Concepts and Green Applications*; Wiley –WCH., Weinheim, **2008**.
- [15] Van Santen, R.A.,Neurock, M.; *Molecular Heterogeneous Catalysis*; Wiley – WCH., Weinheim, **2006**.
- [16] Zahmakıran, M.; Ph-D Theses: *The Preparation and Characterization of Zeolite Framework Stabilized Ruthenium(0) Nanoclusters; A Superb Catalyst for The Hydrolysis of Sodium Borohydride and The Hydrogenation of Aromatics Under Mild Conditions*, **2010**.
- [17] Finke. R.G., Aiken III, J.D., *Journal of Molecular Catalysis A: Chemical*, **1999**, 145,1.
- [18] Schmid, G., *Clusters and Colloids: From Theory to Applications*, VCH Publishers, New York, **1994**.
- [19] De Jongh, L.J., *Physics and Chemistry of Metal Cluster Compounds*, Kluwer Publishers, Dordrecht, **1994**.
- [20] Zahmakıran, M., Akbayrak,S., Kodaira,T. Özkar, S., *Dalton Trans.*, **2010**, 39, 7521–7527.
- [21] (a) Schmid G., L. Chi, *Adv. Mater.*,**1998**,10 515. (b) Schmid, M., Baumle, M., Geerkens, I. Heim, Osemann, C., Sawitowski, T., *Chem. Soc. Rev.* **1999**, 28,179. (c) Aiken III, J.D., Finke, R.G., *J. Mol. Cat. A*, **1999**, 145, 1.(d) Roucoux, A., Schulz, J., Patin, H., *Chem. Rev.*, **2002**, 102, 3757. (e) Cushing, B.L., Kolesnichenko, V.L., Connor, C.J., *Chem. Rev.* **2004**, 104, 3893.
- [22] (a) Lin, Y., Finke, R.G., *J. Am. Chem. Soc.* **1994**, 116, 8335. (b) Aiken III, J.D., Finke, R.G., *Chem. Mater.* **1999**, 11, 1035. (c) Somorjai, G.A., Borodko, Y.G., *Catal. Lett.* **2001**, 76,1.
- [23] Glanz, J., *Science*, **1995**, 269, 1363.
- [24] Henglein, A., *Chem. Rev.* **1989**, 89, 1861.
- [25] Caseri, W., *Macromol. Rapid Commun.*, **2000**, 21, 705.

- [26] Schmid, G., Simon, U., *Chem. Commun.* **2005**, 6, 697.
- [27] Elghanian, R., Storhoff, J.J., Mucic, R.C., Letsinger, R.L., Mirkin, C.A., *Science*, **1997**, 277, 1078.
- [28] Özkar, S., Finke, R.G., *Langmuir*, **2002**, 18, 7653.
- [29] Özkar, S., Finke, R.G., *Langmuir*, **2003**, 19, 6247.
- [30] Ott, L.S., Finke, R.G., *Coordination Chemistry Reviews*, **2007**, 251, 1075–1100.
- [31] Zahmakıran, M., Kodaira, T., Özkar, S., *Applied Catalysis B: Environmental*, **2010**, 96, 533.
- [32] Sullivan, J. A., Keith A.F., Holger, H., *Catalysis Today*, **2009**, 145, 108–113.
- [33] Shankar, R., Shahi, V., *Journal of Organometallic Chemistry*, **2008**, 693, 307–315.
- [34] Wilcoxon, J.P., Martino, T., Klavetter, E., Sylwester, A.P., *Nanophase Mater.* **1994**, 771–780.
- [35] Yue, B., Wang, X., Xinpeng, A., Yang, J., Li, L., Lu, X., Ding, W., *Fuel Processing Technology*, **2010**, 91, 1098–1104.
- [36] Yi, C., Hua, R., *Tetrahedron Letters*, **2006**, 47, 2573–2576.
- [37] Zhang, J., Worley, J., Denomme, S., Kingston, C., Jakubek, Z.J., Deslandes, Y., Post, M., Simard, B., Braidy, N., Botton, G.A., *J. Phys. Chem. B*, **2003**, 107, 6920.
- [38] Belousov, V.M., Vasylyev, M.A., Lyashenko, L.V., Vilkova, N.Y., Nieuwenhuys, B.E., *Chemical Engineering Journal*, **2003**, 91, 143–150.
- [39] Hirai, H., Chawanya, H., Toshima, N., *Bull. Chem. Soc. Jpn.* **1985**, 58, 682–687.
- [40] Jose, D., Jagirdar, B. R., *Journal of Solid State Chemistry*, **2010**, 183, 2059–2067.
- [41] Zolotavin, P., Permenova, E., Sarkisov, O., Nadtochenko, V., Azouani, R., Portes, P., Chhor, K., Kanaev, A., *Chemical Physics Letters*, **2008**, 457, 342–346.

- [42] Hunter, R.J., *Foundations of Colloid Science*, Vol. 1, Oxford Univ. Press, New York, **1987**.
- [43] Bard, A.J., Faulkner, L.R., *Electrochemical Methods*, Wiley, New York, **1980**.
- [44] Stabilization of Pigment Suspension-Electrostatic Stabilization, <http://www.inkline.gr/inkjet/newtech/tech/dispersion/>, last visited on December 2010.
- [45] Napper, D.H., *Polymeric Stabilization of Colloidal Dispersions*, Academic Press, London, **1983**.
- [46] Metin, Ö., Özkar, S., *Journal of Molecular Catalysis A: Chemical*, **2008**, 295, 39–46.
- [47] Tadd, E., Zeno, A., Zubris, M., Dan, N., Tannenbaum, R., *Macromolecules*, **2003**, 36, 6497.
- [48] King, S., Hyunh, K., Tannenbaum, R., *J. Phys. Chem. B*, **2003**, 107, 12097.
- [49] Chauhan, B.P.S., Rathore, J.S., Chauhan, M., Krawicz, A., *J. Am. Chem. Soc.*, **2003**, 125, 2876.
- [50] Crooks, R.M., Zhao, M., Sun, L., Chechik, V., Yeung, L.K., *Acc. Chem. Res.*, **2001**, 31, 181.
- [51] Phan, N.T.S., Van Der Sluys, M., Jones, C.W., *Adv. Synth. Catal.*, **2006**, 348,609.
- [52] Steric Stabilization, <http://www4.ncsu.edu/~hubbe/Defnitsns/StericSt.htm>, last visited on December 2010.
- [53] Breck, D.W., *Zeolite Molecular Sieves, Structure, Chemistry and Use*, John Wiley&Sons, Inc., New York, **1974**.
- [54] Kulprathipanja, S., *Zeolites in Industrial Separation and Catalysis*, Wiley-WCH, Weinheim, **2010**.
- [55] Van Bekkum, H., Flanigen, E.M., Jansen, J.C., *Introduction to Zeolite Science and Practice*, Elsevier Science Publishers, Netherlands, **1991**.
- [56] Framework Type Codes, [www.iza-structure.org](http://www.iza-structure.org), last visited on December 2010.
- [57] Van Bekkum, H., Corma, A., Cejka, J.,Schfith, F., *Introduction to Zeolite Science and Practice*, Elsevier, Prague, **2005**.

- [58] (a) Pillai, U. R.; Sahle-Demessie, E. *Appl. Catal., A*, **2003**, *245*, 103 (b) Buonomenna, M. G., Drioli, E., *Organic Process Research & Development*, **2008**, *12*, 982–988.
- [59] (a) Hudlicky, M., *Oxidations in Organic Chemistry*, ACS, Washington DC, **1990**. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, **1981**.
- [60] Chemicalland21, <http://www.chemicalland21.com/arokorhi/specialtychem/perchem/BENZALDEHYDE.htm>, last visited on December 2010.
- [61] Wikipedia, <http://en.wikipedia.org/wiki/Benzophenone>, last visited on December 2010.
- [62] Weissermel, K.; Arpe, H.-J., *Industrial organic chemistry*, 3rd ed, VCH, New York, **1997**.
- [63] Wikipedia, <http://en.wikipedia.org/wiki/Benzaldehyde>, last visited on December 2010.
- [64] Muzart, J., *Chem. Rev.* **1992**, *92*, 113–140.
- [65] Lee, T. V., *Comprehensive organic synthesis*; Pergamon: Oxford, **1991**, *7*, 291–303.
- [66] Menger, F. M.; Lee, C. *Tetrahedron Lett.* **1981**, *22*, 1655–1656
- [67] (a) Poliakoff, M., Fitzpatrick, J.M., Farren, T. R., Anastas, P. T., *Science*, **2002**, *297*, 807. (b) The use of stoichiometric amounts of inorganic oxidants (notably Cr(VI) and Mn(VI)), which are toxic, in the oxidation of alcohols for industrial processes generates 15–20 kg of hazardous metal waste (deactivated oxidants) of Cr and Mn per kg of product. Please see:  
(c) Sheldon, R. A., Arends, I. W. C. E., Ten Brink, G. J., Dijkman, A., *Acc. Chem. Res.*, **2002**, *35*, 774. (d) Palmisano, G., Ciriminna R., Pagliaro M., *Adv. Synth. Catal.*, **2006**, *348*, 2033.
- [68] Zhan, B.Z., Thompson, A., *Tetrahedron*, **2004**, *60*, 2917–2935.
- [69] Berndtsson, A., Nyholm, R., Martensson, N., Nilsson, R., Hedman, J., *Phys. Status Solid B*, **1979**, *93*, 103.
- [70] Storck, S., Bretinger, H., Maier, W.F., *Appl. Catal., A*, **1998**, *174*, 137.
- [71] Mikhail, R.S.H., Brunauer, S., Bodor, E.E., *J. Colloid Interface Sci.*, **1968**, *26*, 45.

- [72] Bleloch, A., Johnson, B. F. G., Ley, S. V., Price, A. J., Shephard, D. S., Thomas, A. W., *Chem. Commun.*, **1999**, 1907.
- [73] Hinzen, B., Lenz, R., Ley, S. V., *Synthesis*, **1998**, 977.
- [74] Pagliaro, M., Ciriminna, R., *Tetrahedron Lett.*, **2001**, 42, 4511.
- [75] Matsushita, T., Ebitani, K., Kaneda, K., *Chem. Commun.*, **1999**, 265.
- [76] Zhan, B. Z., White, M. A., Sham, T. K., Pincock, J. A., Doucet, R. J., Rao, K. V. R., Robertson, K. N., Cameron, T. S., *J. Am. Chem. Soc.* **2003**, 125, 2195.
- [77] Choi, E., Lee, C., Na, Y., Chang, S., *Org. Lett.*, **2002**, 4, 2369.
- [78] Neumann, R., Levin, M., *J. Org. Chem.*, **1991**, 56, 5707.
- [79] Ji, H. B., Ebitani, K., Mizugaki, T., Kaneda, K., *Catal. Commun.*, **2002**, 3, 511.
- [80] Yamaguchi, K., Mori, K., Mizugaki, T., Ebitani, K., Kaneda, K., *J. Am. Chem. Soc.*, **2000**, 22, 7144.
- [81] Kaneda, K., Yamashita, T., Matsushita, T., Ebitani, K., *J. Org. Chem.*, **1998**, 63, 1750.
- [82] Son, Y. C., Makwana, V. D., Howell, A. R., Suib, S. L., *Angew. Chem., Int. Ed.* **2001**, 40, 4280.