

Preface

The generation of catalysts consisting of small metallic particles dispersed over a support has a long history in catalysis as a means of maximizing the available metallic surface area and assessing whether such particles have properties which differ from those of the bulk metal. It is accepted that for metallic catalysts, control at the atomic level is needed to design active sites because the chemical and catalytic properties of atoms at terraces, corners, and edges of a metal crystallite are different, and can be different from atoms at the metal-support interface. The location of the metal cluster on the support may be also important if its properties are affected by its proximity to the support defects. These problems become even more acute if one has to consider multimetallic rather than monometallic systems. The application of highly sensitive techniques like high resolution electron microscopy and XPS to highly dispersed metal catalysts lead to a better understanding of structural and electronic properties of supported small particles and allowed the determination of the bulk and surface composition of bimetallic clusters. Bimetallic catalysts have played an important role in heterogeneous catalysis. They have been extensively for fundamental investigations and have had a major technological impact, especially in the petroleum industry. A complicating feature in catalytic studies on metal alloys is the possibility of a difference between surface and bulk compositions. The focus of this dissertation is the synthesis and characterization of noble metal and metal oxide nanoparticles and their chemistry including catalytic properties. The subject in this work can be divided at least into two parts. The Part I is treated by the *Chapter I.1* dealing with the structural physical and electronic properties of transition metal nanoparticles. The surface and relevant bulk properties are also discussed which may be helpful to understand the content in the Part II (*Chapters II.1-II.6*). Some portions of the text occur in multiple places in different chapters to help readers understand without needing to shuffle through the entire document. The essentials of characterization techniques are covered in the chapters on instrumentation, characterization sections and spectra interpretation. Whenever appropriate, relationships among various topics are indicated.

In general terms, the scope of *Nanomaterials in Catalysis: Study of Model Reactions*, is

limited to topics which are, to some extent at least, relevant to industrial processes. The whole of heterogeneous catalysis fall within its scope, nevertheless the field of catalysis is so wide and detailed, and its ramifications are so numerous, that the production of the entire subject is well beyond the capability of any single author. Ancillary subjects such as surface science, materials properties and other fields of catalysis are given adequate treatment but not to extent to obscuring the central theme. *Nanomaterials in Catalysis: Study of Model Reactions* concentrates in the catalytic study of the metal nanoparticles in model reactions covered in the *Chapters II.1-II.6*. It is not expedient to impose a preconceived ordered structure. Instead each chapter is dealt when is most appropriate to do so. It will be sufficient if the entire subject in this work has been properly covered in the following chapters:

Chapter I.1. Because of the multidisciplinary nature of the nanomaterials, it would be difficult to cover all areas of interest. Accordingly, the shape, the size, and composition of the nanocrystals would play an important role in modulating its properties. These materials show very interesting properties that have been attributed to the high volume fraction of interfacial structures that are different from the crystalline structures of the core. Various synthesis methods or techniques can be grouped into two categories: thermodynamic equilibrium approach and kinetic approach. Here the synthesis of nanoparticles through thermodynamically approach was based on the formation of monosized metallic silver by a combination of a low concentration of solute and polymeric monolayer adhered onto the growth surfaces. For the kinetic approach we synthesized metal nanoparticles by kinetically confining the reaction in a restrict space.

Chapters II.1 and II.2. This chapter is an attempt to study the silver nanoparticles in the styrene epoxidation. Amongst the metal supports catalysts, silver occupies a unique position. Ethylene epoxidation has been produced almost exclusively by partial oxidation of ethylene over a silver catalyst. The study of the silver-oxygen system is complicated by the fact that oxygen is often present in multiple states including atomic, molecular, and subsurface states. The key role of oxygen adsorption on silver has been realized since the early studies, and several publications deal with the number and nature of

adsorbed oxygen species, under reaction conditions, and their role in the epoxidation and combustion routes.

Chapter II.3. Propylene oxide (PO) is one of the important bulk chemicals, which is used for producing polyurethane and polyols. Gold supported on TiO_2 catalysts were reported for the first time by Haruta and co-workers as selective catalyst for direct epoxidation of propene. Recently Lambert et al. also showed that copper catalysts also show promise for the epoxidation of propene. Here we present the study of the Au-Cu alloy nanoparticles in the propene epoxidation. The incorporation of copper seems to affect the gold dispersion giving longer distance of the perimeter interface which is probably indispensable for the epoxidation of propylene.

Chapter II.4. The target of this chapter was to investigate phase development in the V_2O_5 catalyst system consisting of TiO_2 (anatase) and MCM-41 supports. Among these metal oxides, vanadium oxide catalysts have attracted much attention due to their unique catalytic properties and commercial applicability for various chemical processes. Here it is described the effect of alkaline metal (Na) promotion on $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{MCM-41}$ in the selective oxidation of ethanol to acetaldehyde. We have observed that depending of the supported used the vanadia become an effective catalyst for selective oxidation of alcohols. The incorporation of alkaline ions such as Na result an increase of the catalytic activity and selectivity to acetaldehyde.

Chapter II.5. It is well know that clay minerals undergo spontaneous exfoliation in water. This chapter reports evidences on platelet defects induced by the use of ultrasounds or high mechanical stirring during reconstruction of hydrotalcites in water. Exfoliation is regarded as an effective way of maximizing the accessibility and utility of the LDH host layers as well as introducing physicochemical properties effects. Here, the catalytic properties of the activated hydrotalcites have been investigated in the base-catalyzed epoxidation of styrene.

Chapter II.6. Skeletal of hydrocarbons, skeletal isomerization and hydrogenolysis, occur

over a number of metallic catalysts. These reactions provide very good examples of the way in which reaction selectivity is related to catalyst structure. From works, realized by Dr. G. Maire and Dr. F. G. Garin, which has involved the use of both dispersed metal catalysts and single crystal catalysts, together with carbon isotopic tracer studies, some of the main mechanistic features of these processes are now reasonable well understood and this is the subject of this chapter. Here we describe the study of the hydrogenolysis of methylcyclopentane over Ir-Au/ γ -Al₂O₃. Methylcyclopentane (MCP) is a recognized probe molecule in the investigation of the structure sensitivity of several hydrocarbon conversions catalyzed usually by noble metal-based catalysts. The Ib metals can be considered as almost inactive in these reactions as compared with the group VIII metals. We reported some phenomena in which in our opinion indicate the Au metal plays a strong role in the adsorptive and catalytic properties of Ir even in bimetallic systems of immiscible components such as the case of Ir-Au metal system.

Abstract

Metal nanoparticles catalysts considered in this work included systems consisting essentially of a single metal component (Ag) and bimetallic system. Bimetallic systems of miscible (Au-Cu and Au-Ag) and immiscible components (Ir-Au) have been investigated. The study of these materials with chemical probes including chemisorption and selected catalytic reaction, in conjunction with physical and chemical methods such as electron microscopy, X-ray diffraction (XRD), temperature programmed reduction (TPR), UV-vis, photoelectron spectroscopy (XPS) has been performed to contribute the knowledge of their structures. The fact that surface composition can differ substantially from bulk composition was also studied. High resolution electron microscopy (HRTEM) provided independent evidence of the highly dispersed nature of the metal clusters. Concepts concerning the effect of additives on the structure and physicochemical and catalytic properties of oxide catalysts in selective oxidation reactions were considered.

This work was also carried out in an attempt to study the different oxygen species formed on silver. Of particular interest is to understand the role and nature of the elusive subsurface O species in the function of silver as an oxidant catalyst. The effect of additives on acid-base and redox properties and on their bearing on catalytic performance was discussed, with particular emphasis on alkaline metal additives such as cesium and sodium. The phenomena occurring in monophasic and supported mixed oxide containing the additives, including modification of structure, segregation, defect formation and spill-over of the reactants was also described.

The nature of the surface of the bimetallic systems was the question of interest. Will the individual clusters be monometallic or will they contain atoms of both metals and therefore be bimetallic? It is interesting to consider how the state of dispersion the metal catalysts affects the relationship between chemisorption capacity or catalytic activity and catalyst composition. The bimetallic clusters discussed thus far have been combination of a Group VIII and a Group IB metal. In spite of the great importance in petrochemistry, skeletal hydrocarbon reactions, such as hydrogenolysis of methylcyclopentane, offers an interesting fingerprint of the dependence of specific rate on catalyst structure. The first reported case of a reaction with large dependence on catalyst structure was performed for neopentane on platinum. This result led Boudart to classify reactions on metals as: (i)

“facile” or “structure-insensitive” reactions, for which the specific rate does not depend upon the size of the metal particle, and (ii) “demanding” or “structure sensitive” reactions, for which the specific rate is highly dependent on the metal dispersion. The rate per surface metal atom is the fundamental interest. Thus, the metal dispersion is extremely important parameter to be determined. An experimental scheme based on selective H₂ chemisorption was developed to investigate the surface composition of bimetallic system. With this capability, the activity of such a catalyst was referred to the amount of metal in the surface rather than to the metal content of the catalyst as a whole. The interaction between catalytically active metal oxide particles and oxide carriers greatly influences their structure and size. Vanadia catalysts constitute also a relevant example of the influence of this interaction. Accordingly, it was decided to study the effect of the support (TiO₂ and MCM-41) with the aim of understanding the interrelations on the catalytic properties of V₂O₅ as a way to improve its performance for the selective oxidation of ethanol.

Finally, the catalytic role of the different basic sites in hydrotalcite interlayer was envisaged through the study of the styrene epoxidation in liquid phase. Hydrotalcite-like compounds are not only interesting for their industrial applications, but are also beautiful examples of the scientific preparation of catalysts. All the stages of the preparation of a catalyst based on hydrotalcite-like precursor need precise chemical foundations in order to avoid inhomogeneties and/or chemical segregations, which would be detrimental to the properties of the final compounds. Layered double hydroxides (LDHs), also known as hydrotalcites or anionic clays, are a class of ionic lamellar compounds made of positive-charged hydroxide layers with charge balancing anions and water molecules sandwiched between layers. Exfoliated Mg-Al layered double hydroxide in water was investigated in the styrene epoxidation. The change in the basic properties during the rehydration process of the calcined samples as well the influence on catalytic activity was studied. Hydrotalcites are very attractive for this type of oxidation reaction because their ability to give Lewis type acid-base bifunctional catalysts or basic catalysts with Brönsted type sites, proceeding from the mixed oxide and the meixnerite-like structures, respectively.

Resumen

En este trabajo se han sintetizado y estudiado diferentes catalizadores a base de nanopartículas metálicas con diferentes tamaños y morfologías. Se han estudiado tanto sistemas monometálicos como bimetálicos con componentes de diferentes miscibilidad (por ejemplo sistemas Au-Cu y Au-Ag de total miscibilidad, así como Ir-Au de prácticamente total inmiscibilidad) con la finalidad de estudiar el cambio que producen tanto en el tamaño como en la morfología de las nanopartículas obtenidas.

Los nanomateriales obtenidos han sido estudiados mediante el empleo de diferentes técnicas de caracterización como pueden ser, fisisorción, quimisorción microscopia electrónica (SEM-TEM), difracción de rayos X (XRD), reducción a temperatura programada (TPR), espectroscopia ultravioleta-visible (UV-vis), espectroscopia fotoelectrónica (XPS), etc., así como mediante diferentes ensayos catalíticos modelo con la finalidad de correlacionar las propiedades físico-químicas de dichos materiales con los métodos de síntesis de éstos.

Se ha hecho especial énfasis en el estudio de las diferentes especies de oxígeno que presentan estos nanomateriales en superficie, así como su correlación con la actividad catalítica que presentan en diferentes reacciones de oxidación selectiva de olefinas. Por otra parte, la modificación de las propiedades ácido-base de dichos materiales y su carácter redox cuando se adiciona metales alcalinos del tipo sodio y cesio, también ha sido exhaustivamente estudiado.

La formación de sistemas bimetálicos y su homogeneidad, así como el efecto de dispersión y el cambio en sus propiedades físico-químicas que hace un metal sobre el otro, ha sido también objeto de estudio en este trabajo. Este hecho se ha puesto en evidencia en el estudio de reacciones de hidrogenolisis del metilciclopentano que permite una buena comprensión de la actividad catalítica, así como de la dependencia de la estructura en la actividad catalítica previamente ya descrita por Boudart.

La interacción entre las especies metálicas catalíticamente activas y los soportes empleados también pueden ejercer una notable influencia en la estructura y tamaño de la especie activa, y por consiguiente en el comportamiento catalítico. En este contexto, se han estudiado la interacción de óxido de vanadio en diferentes soportes como TiO_2 y MCM-4, para comprender el comportamiento catalítico del V_2O_5 en otra reacción test como es la de

oxidación selectiva del etanol.

Finalmente, el papel de los diferentes sitios básicos de materiales tipo hidrotalcita, el estudio de la exfoliación de dichos materiales y el cambio en sus propiedades básicas después de diferentes protocolos de rehidratación han sido estudiados en otra reacción test como es la reacción de epoxidación del estireno en fase líquida.

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Figure II.5.11 Titration by benzoic acid for the determination of the base amount of the HT catalysts. Reaction rate versus amount of benzoic acid added. (a) HT-rm(4h) and (e) HT-rm(24h) (f) HT-rus(25min) and (g) HT-rus(50min).

Figure II.6.1 X-ray diffraction of the samples investigated in this study. (A) Co-impregnated (CI) catalysts (a: Ir₁-Au₈; b: Ir₁-Au₄; c: Ir₁-Au₂; d: Ir₁-Au₁; e: Ir₂-Au₁; f: Ir₄-Au₁; g: Ir₈-Au₁; h: γ -Al₂O₃), (B) Sequential Impregnated (SI) catalysts (a: Ir₁-Au₈; b: Ir₁-Au₄; c: Ir₁-Au₂; d: Ir₁-Au₁; e: Ir₂-Au₁; f: Ir₄-Au₁; g: Ir₈-Au₁; h: γ -Al₂O₃), (C) Monometallic Ir catalysts (a: Ir_{0.125}; b: Ir_{0.25}; c: Ir_{0.5}; d: Ir₁; e: Ir₂; f: Ir₄; g: Ir₈; h: γ -Al₂O₃). (D) Mean gold particle size as a function of the Au loading in the bimetallic Ir-Au/ γ -Al₂O₃ catalysts.

Figure II.6.2 TEM images of Ir₂-Au₁ (CI) (a), Ir₂-Au₁ (SI) (b) and Ir₂ catalysts (c). The bars correspond to 100 nm.

Figure II.6.3 Irreversible hydrogen adsorption isotherms of the CI, SI and Ir monometallic samples at 310 K. (A) CI samples: (a) Ir₈-Au₁; (b) Ir₄-Au₁; (c): Ir₂-Au₁; (d) Ir₁-Au₁; (e) Ir₁-Au₂; (f) Ir₁-Au₄; (g) Ir₁-Au₈. (B) SI samples: (a) Ir₈-Au₁; (b) Ir₄-Au₁; (c): Ir₂-Au₁; (d) Ir₁-Au₁; (e) Ir₁-Au₂; (f) Ir₁-Au₄; (g) Ir₁-Au₈. (C) Monometallic Ir samples: (a) Ir₈; (b) Ir₄; (c) Ir₂; (d) Ir₁; (e) Ir_{0.5}; (f) Ir_{0.25}; (g) Ir_{0.125}. (D) Dispersion (H/Ir) values versus atomic Au/Ir ratio for (a) CI catalysts, (b) SI catalysts, (c) monometallic Ir catalysts.

Figure II.6.4 Evolution of initial rate (MCP molecules reacted s⁻¹ g_{Ir}⁻¹) versus Au/Ir atomic

ratios. (a) CI catalysts, (b) SI catalysts, (c) monometallic Ir catalysts.

Figure II.6.5 Conversion vs. time curves in the methylcyclopentane reaction at 457K: (a) CI catalysts, (b) SI catalysts, (c) monometallic Ir catalysts.

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