

Chapter 1

Introduction

1.1 Statement of the Problems

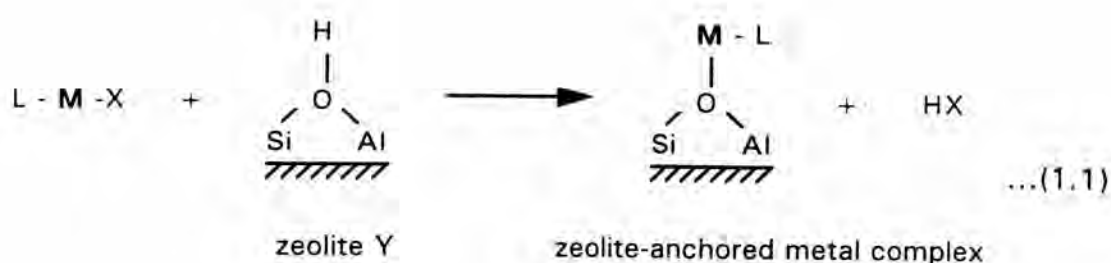
The catalytic systems in commercial processes are classified as either homogeneous and heterogeneous catalytic systems. Advantages of a homogeneous system generally include high efficiency under mild reaction and high accessibility for a substrate to reach the active site of the catalyst center. However, the homogeneous system can exhibit the problems of product contamination and catalyst loss, and the products are not easily separated from the catalyst. In a heterogeneous system, it is facile to separate a product from the catalyst. However, in supported metal systems it is difficult to avoid aggregation on the surface and agglomeration in the reaction media under catalytic conditions. New alternative is so-called "a hybrid system" which combines advantages and diminishes disadvantages of homogeneous and heterogeneous catalytic systems.

Zeolites are particularly attractive hosts for the design of hybrid systems.¹ The well-defined channelled porous microstructure, the ion exchange capability and the high thermal stability make zeolites have attractive advantages over amorphous supports such as polymers, silica, alumina and activated carbon.

Several methods for immobilization of catalytically active organometallics into zeolites include physisorption of uncharged metal carbonyls,²⁻³ ion exchange of metal ions and cationic complexes,⁴⁻⁸ and size encapsulation of large chelated complexes.⁹⁻¹² These conventional immobilization methods have faced the problems of migration of metal ions to the external surface, leaching of the unbound carbonyl compounds and pore blocking by the intrazeolite clumpy species. The effective systems have not yet been completely reached.

1.2 Anchoring Approach

Anchoring¹³ is a novel method to solve the aforementioned problems. The precursor must have ligand reactive to protons in zeolites to form neutral products and tightly bind between the metal center and oxygen rings of the zeolite frameworks. A general reaction can be described as follows :



L-M-X = organometallic precursor

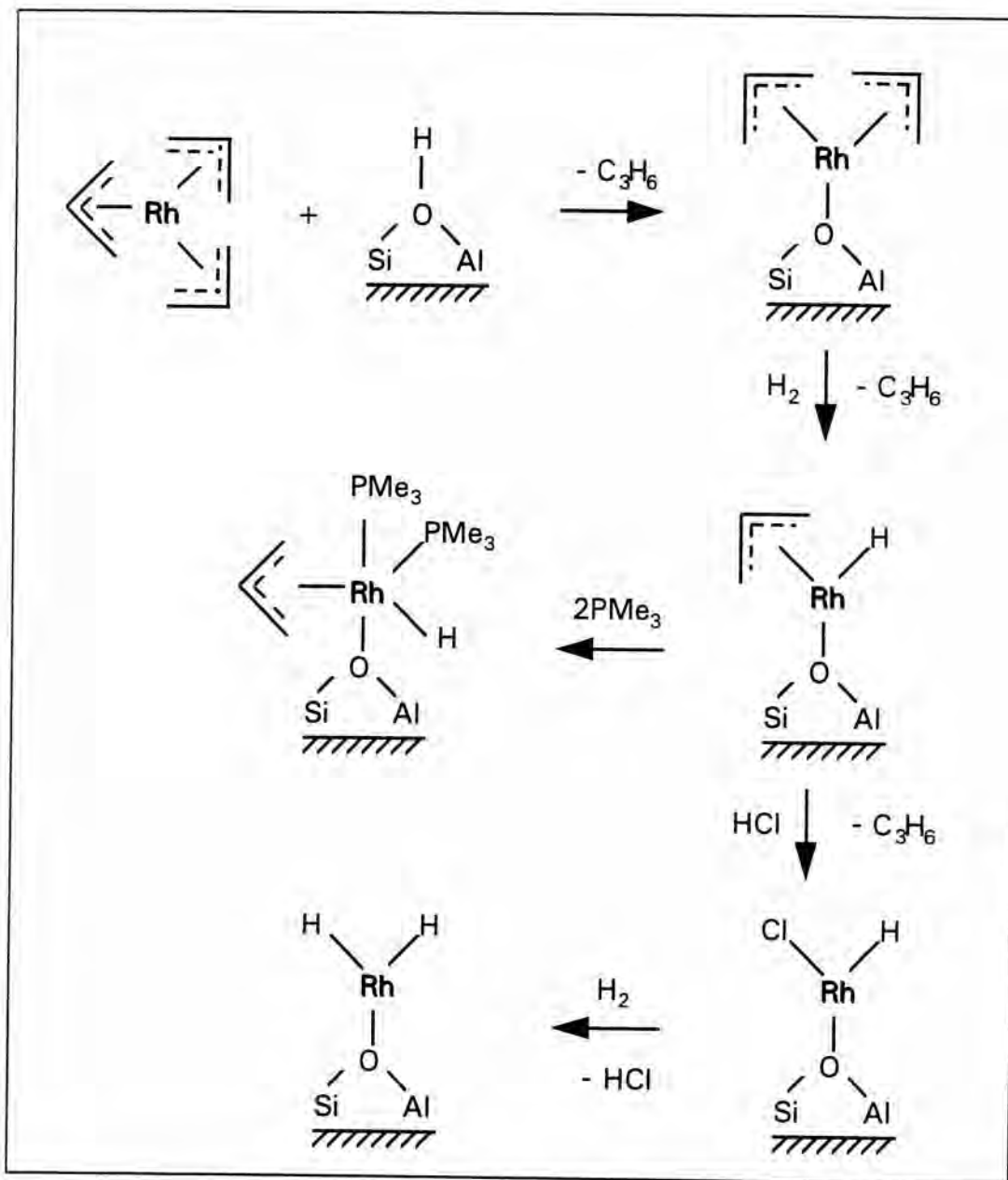
L = ligands inert to surface hydroxyl groups

X = reactive ligands such as alkyl, allyl and alkoxide

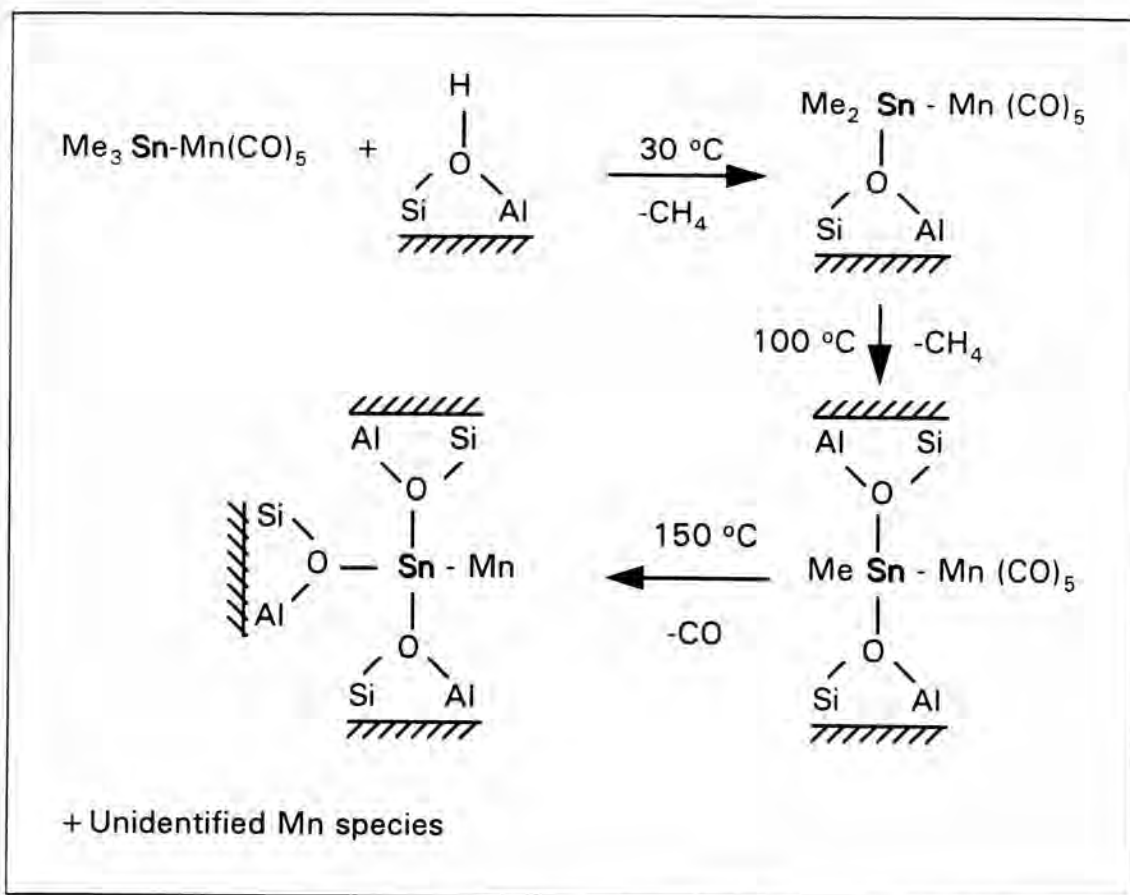
HX = conjugate product such as methane, olefins and alcohol

The anchoring and catalytic potential of intrazeolite organometallics are demonstrated by Schwartz's tris(π -allyl)rhodium.¹⁴ Reaction of this complex with hydroxyl groups of zeolite X leads to the loss of one propylene group, determined by GC/MS, leaving the bis(π -allyl)rhodium fragment bonded to a lattice oxygen through the metal center (see Scheme 1.1). Subsequent hydrogen treatment results in the formation of the allyl hydride, which shows high catalytic activity for olefin hydrogenation. Other reactions of intrazeolite allylrhodium complexes are also shown in Scheme 1.1. More recently, A. Borvornwattananont and T. Bein¹⁵ found that heterobimetallic compound $\text{Me}_3\text{SnMn}(\text{CO})_5$ can be anchored into the cages of acidic zeolites at room temperature under retention of the Sn-Mn bond. The structure and thermal stability of the intrazeolite metal

complexes were examined using EXAFS, FTIR and TPD-MS spectroscopies and shown in Scheme 1.2.



Scheme 1.1 : Proposed intrazeolite chemistry of allylrhodium complexes



Scheme 1.2 : Proposed intrazeolite chemistry of $\text{Me}_3\text{SnMn(CO)}_5$ derivatives.

Furthermore, organometallic species are usually larger than the 6-ring windows of sodalite cages and double 6-ring cages of faujasite-type structure, so all intrazeolite organometallic species will stay only in the supercages. The advantages of the anchoring method are the complete utilization of the intrazeolite species, the accessibility of the substrates to the catalytically active centers, and site isolation of each intrazeolite catalyst species individually. An important issue is whether the anchoring

bonds will stabilize the organometallic within the zeolite cages under catalytic condition.

1.3 Objectives

1. To synthesize zeolite Y for catalytic system
2. To synthesize the novel hybrid catalytic system from $\text{Rh}(\text{acac})(\text{CO})_2$ and zeolite Y
3. To determine the catalytic property of the intrazeolite catalyst for the hydroformylation of olefins

Zeolite Y has been an important component in petroleum process technology as catalysts in fluid catalytic cracking (FCC)¹⁶⁻¹⁸ or in hydrocracking,¹⁹ and as catalyst supports in Fischer-Tropsch synthesis²⁰⁻²¹ or in oxidation of alkenes.²²⁻²³ This invention is concerned the synthesis of Y typed zeolite. The published synthetic procedures are mostly uncommented recipes. Only meager information is given regarding reaction steps but the important reaction conditions are not clearly presented. Our synthetic procedure is adapted from the U.S. Patent No. 4,178,352²⁴ to provide the optimum condition for the synthesis of zeolite Y.

Zeolite Y was chosen as the catalytic support because its attractive advantages are numerous. The most important properties of zeolite Y are as follows :

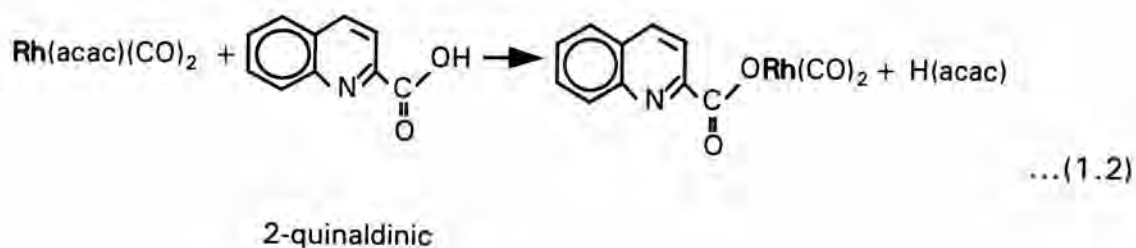
(i) Shape and size selectivity properties. Only molecules with dimension less than a critical size can enter the pores and reach the catalytic sites.

(ii) Well-defined active sites. Crystalline zeolite Y being crystalline has regular structures that can be characterized by X-ray technique. The locations of balancing cations are often well identified and the sites of catalytic activity, are thus well defined.

(iii) Exchangeable cation sites. The normal cations can be readily exchanged to more applicable ones for preparation of catalysts.

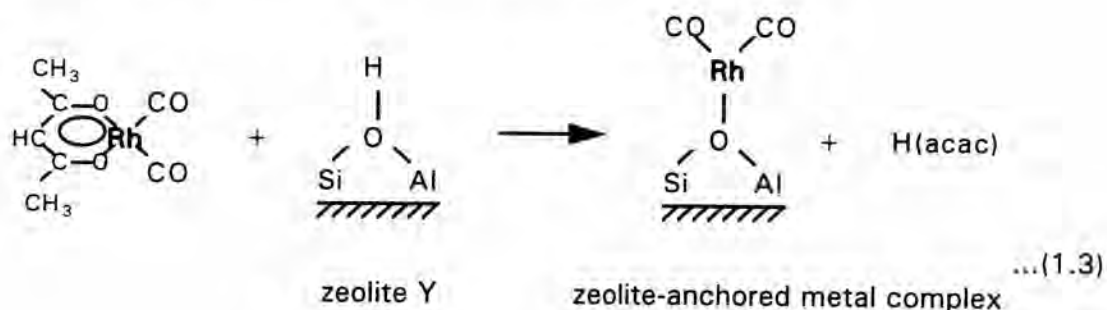
(iv) Pore system at molecular level. The pore system can potentially isolate each catalyst species individually and prevent dimerization and agglomeration of the catalyst species.

$\text{Rh}(\text{acac})(\text{CO})_2$ was chosen as a catalyst precursor because it can react with internal surface hydroxyl groups of the zeolite framework. It was reported that $\text{Rh}(\text{acac})(\text{CO})_2$ reacted with acids, such as 2-quinaldinic acid,²⁵ in solution as shown in Equation 1.2 :



if a proton exchanged zeolite is considered to be a solid acid, the similar substitution reaction is expected to occur. The acetylacetonate ligand is a

good leaving group on attack with Brønsted acid to form stable molecule i.e. acetylacetonone. Eventually, the center rhodium atom attaches to the zeolite framework. The model for anchoring $\text{Rh}(\text{acac})(\text{CO})_2$ into zeolite cages can be illustrated as shown in Equation 1.3 :



Due to its small molecule size²⁶ as depicted in Figure 1.1, this precursor theoretically diffuses readily into the zeolite supercages with 7.4 Å pore opening but not into either the small sodalite cages or double 6-rings of zeolite Y. The latter cages have pore opening of 2.2 Å.

Furthermore, the rhodium complexes have been used as catalyst precursors in hydroformylation of olefins.²⁷⁻³⁰ We hope that after the anchoring of $\text{Rh}(\text{acac})(\text{CO})_2$ to the zeolite framework, the intrazeolite rhodium species are still the active center for hydroformylation of olefins.

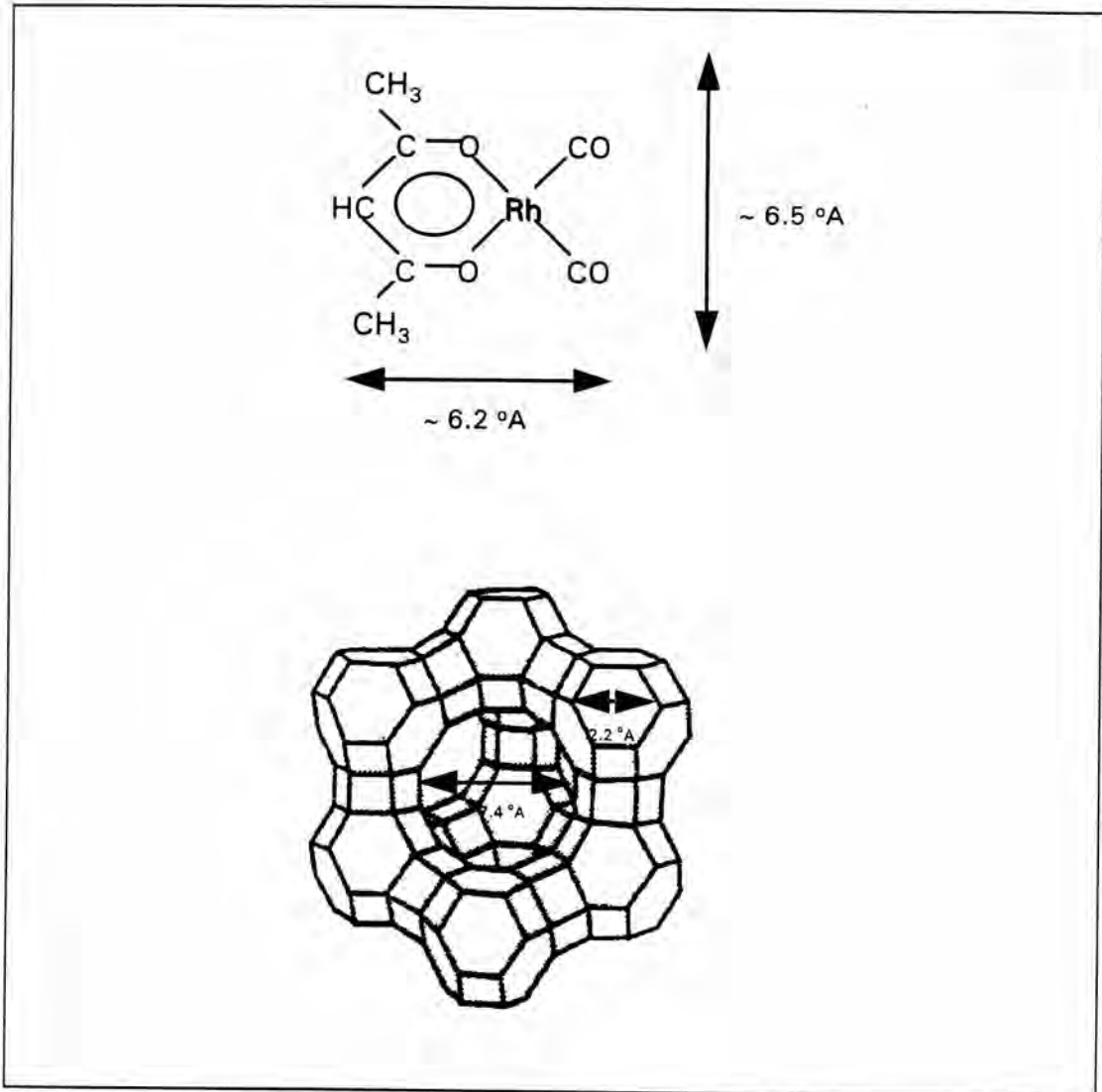


Figure 1.1 : Molecular geometry of $\text{Rh}(\text{acac})(\text{CO})_2$ and pore openings of the zeolite Y.