

CHARACTERIZATION OF BIMETALLIC Pt-Ru ON ALUMINA, SILICA AND MCM-41

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Abstract

Bimetallic Pt-Ru on alumina, silica and MCM-41 were prepared by impregnating each support with a solution mixture of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ followed by drying and calcination at 400°C for 2 h. The metal loading in each material confirmed by X-ray fluorescence spectroscopy was not different from the pre-calculated values. Hydrogen adsorption was carried out to determine metal particle size. The adsorption capacity indicated that the dispersion of Pt was higher than Ru on all supports while those of the bimetallic materials were between the values of monometal. In addition, metal dispersion on Al_2O_3 was higher than on SiO_2 and MCM-41. From the temperature-programmed reduction, Pt and Ru did not form bimetallic particles.

Keywords: Pt-Ru, alumina, silica, MCM-41

Introduction

There are three major components in heterogeneous catalyst: active component, support, and promoter. In general, a catalytic reaction takes place on the surface of the active component due to an interaction between the adsorbed reactants on active sites. Active components generally used are metals, oxides and sulfides. The support is normally a porous and inert material, chemically and mechanically, which helps to disperse the active component to increase surface area and thus, activity. The dispersion of active and usually expensive

components on support will minimize the cost of catalyst production and maximize the catalyst efficiency. Finally, the role of promoter is to improve the catalyst efficiency by improving physical or chemical properties of either the active component or the support.

About 75% of industrial catalysts, including metals, oxides, and sulfides, are supported nanoparticles and the most important ones are supported metals. The properties of supported metals are influenced by the size and composition of the metal particles, their

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interactions with support and other components such as promoters or poisons, and the reactive environment. The relationships between the catalyst structure and the catalytic activity are complex. Several researchers are working in this area to gain better understanding which could lead to the development of new catalysts and more efficient catalytic process. Desired catalysts should have high catalytic activity and decrease reaction steps in order to lower the production energy, cost, and wastes. Research in catalysis has improved understanding in a catalyst role as well as a reaction mechanism which could lead to industrial application.

Supported platinum catalysts modified by incorporation of a second metal have been reported in many applications. Examples are Pt-CuO/SiO₂ doped hydrous TiO₂ catalyst and Pt-Au catalyst which were used as emission-control catalysts for lean NO_x catalysis (Ballinger and Chen, 2001; Chandler and Pignolet, 2001). Pt-Re on alumina containing between 0.1 and 0.8 wt% of each metal has been used in naphtha reforming process. The combination of both metals which increases the stability of catalytic performance gives longer lifetime (Antos *et al.*, 1995).

The uniform, narrow size distribution and highly dispersed nanoparticles supported on various types of carbon (carbon black, fullerene soot, desulfurized carbon black, carbon nanotube) showed an average diameter between 1.0 and 1.5 nm. The Pt/Ru compositions of nanoparticles were similar to those of precursors, namely, 1:5 and 2:4, respectively. The local metal coordination number revealed that Pt preferred to segregation to the particle surfaces and nanoparticles were formed by metals from more than one precursor molecules (Nashner *et al.*, 1997, 1998; Hills *et al.*, 1999; Rajesh *et al.*, 2000).

Uniform bimetallic Rh-Ir particles could be obtained by synthesis of their carbonyl precursor in zeolite Y cavity (Ichikawa, 2000). However, the procedure was complex, required several preparation steps, and was not suitable for large scale.

An important step in a catalyst preparation is the reduction of metal oxides obtained after

calcinations to metallic particles by hydrogen or other gas reductants. Supported Pt-Ru catalysts had a reduction temperature range between 473 and 823 K in hydrogen with an average particle size about 1.4 - 7.7 nm (Nashner *et al.*, 1997, 1998; Hill *et al.*, 1999). The preparation from metal cluster precursors gave a reduction temperature in H₂ at about 673 K and resulted in metallic particles with an extremely narrow particle size distribution and lower average diameter (Nashner *et al.*, 1997, 1998; Hills *et al.*, 1999). Supports that have been used for Pt-Ru catalysts are various types of carbon, silica and zeolite but no other support materials such as γ -Al₂O₃ and MCM-41. Thus, it is interesting to use those supports in this research.

The goals of this research were to prepare supported bimetallic Pt-Ru on alumina, silica and MCM-41 from a mixture of Pt and Ru complex by impregnation and to characterize the resulting materials by X-ray fluorescence spectroscopy (XRF), hydrogen adsorption, and temperature-programmed reduction (TPR) to understand their chemical and physical properties. The Pt/Ru ratios chosen were 1:1, 1:2, and 4:5 and the supports were γ -Al₂O₃, SiO₂, and MCM-41.

The hydrogen chemisorption technique has been widely used to determine metal dispersion on support. The surface area of the active, selective catalysts that are either amorphous or containing extremely small crystallites and particle sizes is also calculated from hydrogen chemisorption by approximating a cross-sectional area of a surface metal atom. This technique measures monolayer hydrogen adsorption capacity of supported metals. The stoichiometry of chemisorption must be known to estimate the available catalytic surface area. The hydrogen molecule generally dissociates to two hydrogen atoms, each of which is assumed to adsorb onto one metal site. This technique or other probe gases chemisorption techniques have been applied to study many supported metals including Pt, Pd, Rh, Ru, Ir, Fe, Ni and Co (Farrautao and Bartholomew, 1997).

The reduction of metal oxides under flowing hydrogen can be investigated by the

temperature-programmed reduction (TPR). The TPR results show the temperature needed to complete reduction and can indicate whether the two metals are in contact or not. If two metals such as Rh and Fe are in contact, the reduction peaks of both metals will shift. In the Rh-Fe oxide particle, rhodium oxide will first become metallic and cause hydrogen to dissociatively adsorb. Then the adsorbed hydrogen migrates to iron oxide in contact with metallic rhodium and reduces the oxide instantaneously (Niemantsverdriet, 2000). In this research, platinum oxide is expected to become metallic first. If platinum is in contact with Ru, the reduction temperature of Ru will decrease due to the migration of hydrogen on neighboring Pt causing reduction of Ru.

Materials and Methods

Al_2O_3 (Aldrich, 150 m^2/g) was calcined at 400°C for 2 h prior to use as supports. Amorphous silica (JRC-SiO-6) was ground and sieved to get particle sizes between 40 to 60 mesh, washed with deionized water to remove dust, and dried at 120°C. MCM-41 was synthesized by the procedures described by Kumar *et al.* (2001) and Suriyakrai *et al.* (2002).

Monometallic and bimetallic Pt and Ru catalysts were prepared by an impregnation of the supports, using metal salts of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as the metal precursors. Then each sample was dried and calcined in muffle furnace at 400°C for 2 h. Total metal loading of catalysts was fixed at 1 wt% and also varied Pt:Ru molar ratios of bimetallic catalysts as 1:1, 4:5, and 1:2.

The metal loading and chemical composition of supported catalysts were investigated by X-ray fluorescence spectrophotometer (Shimadzu EDX-700). The ground supported catalysts, about 40 mg, were pressed with 150 - 250 kg_f/cm^2 to be disc prior to detecting metal compositions by XRF.

The metal dispersion was investigated by hydrogen chemisorption at room temperature with 10% H_2 in N_2 gas. About 1 mg of the sample was placed on quartz wool in a U tube connected

to a hydrogen chemisorption apparatus using TCD detector. The sample was reduced in hydrogen flow at 450°C for 1 h, and then purged hydrogen with nitrogen gas to clean sample surfaces at 400°C. After that, the sample was cooled down to room temperature and determined hydrogen chemisorption with injection of 10% H_2 in N_2 gas.

In addition, the temperature-programmed reduction was used to identify the reduction profiles of each catalyst by using 10% H_2 in Ar as a reductant. 100 mg of the sample was placed on the quartz wool in a U tube connected to the TPR apparatus using TCD detector and pretreated with the flowing of nitrogen gas at about 250°C for 30 min. The sample was cooled down nearly to -70°C by dry ice in methanol prior to reducing with 10% H_2 in Ar until 500°C.

Results and Discussion

Supported Monometallic Pt and Ru, and Bimetallic Pt-Ru on Al_2O_3 , SiO₂ and MCM-41

The metal loadings of supported Pt, Ru, and Pt-Ru on Al_2O_3 support were confirmed by XRF analysis as shown in Table 1. The total loading was approximately 1 wt% for all catalysts and was not different from the calculated values. The agreement is an advantage of catalyst preparation by impregnation method.

The H/M and H/Pt ratio were calculated from the hydrogen adsorption experiment. The monometallic Pt adsorbed hydrogen in a larger amount than that of monometallic Ru. The hydrogen adsorption for all bimetallic Pt-Ru catalysts were higher than that of monometallic Ru/ Al_2O_3 , but lower than that of monometallic Pt/ Al_2O_3 indicating that the adsorption was mainly occurred on Pt metal. The hydrogen adsorption trend for bimetallic Pt-Ru catalysts with metal ratio of 1:2 and 4:5 reversed from monometallic Ru/ Al_2O_3 in which the samples were calcined at 400°C had higher hydrogen adsorption. It was possible that, at high temperature, each metal prefers to form monometallic particles instead of alloy. In other

words, Pt and Ru in a mixed phase migrate away from each other more easily at high temperature.

Table 2 displays the metal loading and metal dispersion of Pt, Ru and Pt-Ru catalysts on silica and MCM-41. Because MCM-41 is a mesoporous form of SiO_2 , the trend of hydrogen adsorption was similar to that of amorphous SiO_2 . In this set of samples, the total metal loading was also confirmed by XRF to be close to 1 wt%. Hydrogen adsorption of monometallic Ru and Pt on silica and MCM-41 was also similar to that on alumina support, in which Pt could adsorb hydrogen significantly better than Ru. The adsorption of bimetallic catalysts fell between monometallic Ru and Pt. In all cases of silica and MCM-41, the samples dried at 120°C gave higher hydrogen adsorption than those calcined at 400°C indicating that metal sintering was more feasible on the silica-based support.

From Tables 1 and 2 monometallic Pt showed the highest dispersion on Al_2O_3 after calcined at 400°C for 2 h and also bimetallic Pt-Ru on Al_2O_3 also showed the higher metal dispersion than those on the other supports. The metal dispersions of monometallic Ru on all supports determined by hydrogen chemisorption using N_2 as a carrier gas were low. The strong adsorption between N_2 and Ru surfaces might lead to low adsorption of hydrogen on ruthenium surfaces. On the other hand, chloride trace from salt precursors might adsorb strongly on ruthenium surfaces and block the adsorption of hydrogen.

From the information obtained from the hydrogen adsorption study, the sites mainly responsible for hydrogen adsorption for bimetallic Pt-Ru catalysts on any support were platinum. Thus, the metal dispersion reflected the dispersion of Pt on the support. The presence of Ru metal reduced the efficiency of hydrogen adsorption. Consequently, as the Ru content decreased, metal dispersion studied by hydrogen chemisorption increased. The metal particle sizes could be estimated from the metal dispersion (D or H/M values) by the formulae below (Bergeret and Gallezot, 1997).

$$\begin{aligned} \text{For Pt,} \quad & d(\text{nm}) = 116/D(\%) \\ \text{For Ru,} \quad & d(\text{nm}) = 134/D(\%) \end{aligned}$$

The calculated results are exhibited in Table 3. Ru showed very large particle sizes of more than 44 nm, whereas the Pt on Al_2O_3 showed smaller particle sizes varied from 1.5 - 1.8 nm. It could be inferred that Pt had more dispersion on Al_2O_3 than that on the other supports. Because the metal particle size was calculated from the dispersion, the poor metal dispersion was hypothetically consistent with large particle size of which the surface area was lower.

Characterization of Supported Pt-Ru by Temperature-Programmed Reduction (TPR)

Pt-Ru/ Al_2O_3

Results from the temperature programmed reduction of alumina supported Pt-Ru are displayed in Figure 1. There were at least three reduction peaks of Ru at 132°C, 176°C, and 192°C. These broad peaks indicated that there were at least three forms of ruthenium oxides on alumina support. The peak broadening was a result from the large particle size of oxides. The area under the peak was proportional to the hydrogen consumption during the metal oxide reduction. For 1%Ru/ Al_2O_3 , the first peak was tall, symmetric, and broad, possibly corresponding to a broad range of particle sizes with the similar Ru oxidation state. The second and the third peaks were next to each other and broad, corresponding to the more stable oxidation state of Ru which was reduced at higher temperature. For bimetallic Pt-Ru/ Al_2O_3 , the concentration of Ru was lower than the monometallic case. As a result, the hydrogen consumption for Ru reduction was less than that of Pt. The starting reduction temperature of bimetallic Pt-Ru with 1:2 and 1:1 molar ratios was similar to the monometallic one and both cases showed two reduction peaks of Ru at 129°C and 160°C compared to 120°C and 153°C, respectively. The first Ru reduction peaks, however, were shifted slightly to lower temperature. As the Ru loading decreased, the reduction of Ru was completed at the lower temperature.

Monometallic 1.1%Pt/ Al_2O_3 showed the broad reduction peaks at a higher temperature than ruthenium, i.e. at 239°C and 388°C. The reduction, however, started at approximately

180°C. The two reduction peaks implied that there were at least two forms of platinum oxides. The first peak could be the upper part of the oxide particle which was not directly connected to alumina, while the second peak could be the interface between platinum oxides and alumina. The broad peak was also caused by a large range of particle size. This could be the drawback of catalyst prepared by impregnation in which the particle size was difficult to control.

When Pt was mixed with Ru in Pt-Ru/Al₂O₃, the reduction peaks of Pt did not shift to a lower

temperature. This phenomenon was a sign that Pt and Ru did not form alloy and they deposited on alumina support separately. This has led to another conclusion that the preparation of Pt-Ru/Al₂O₃ catalysts from mixed metal salts by impregnation failed to initiate alloy particle of Pt and Ru.

Pt-Ru/SiO₂

With similar experimental conditions, the TPR profiles of monometallic Pt, Ru and Pt-Ru on SiO₂ were obtained and showed in Figure 2. Broad reduction peaks of Ru were fused together with maxima around 162°C and 194°C

Table 1. Metal loading and metal dispersion of Pt, Ru, and Pt-Ru catalysts on alumina support

Material	Pt:Ru mole ratio	Pt/wt%	Ru/wt%	H/M	H/Pt
Ru/Al ₂ O ₃	0:1	-	0.99	0.008	-
Pt-Ru/Al ₂ O ₃	1:2	0.60	0.66	0.316	0.982
	4:5	0.56	0.33	0.546	1.161
	1:1	0.69	0.33	0.419	0.812
Pt/Al ₂ O ₃	1:0	1.12	-	0.771	0.771

Table 2. Metal loading and metal dispersion of Pt, Ru, and Pt-Ru catalysts on silica and MCM-41

Material	Pt:Ru mole ratio	Pt/wt%	Ru/wt%	H/M	H/Pt
Ru/SiO ₂	0:1	-	0.93	0.030	-
Pt-Ru/SiO ₂	1:2	0.47	0.55	0.139	0.452
	4:5	0.49	0.30	0.120	0.261
	1:1	0.49	0.23	0.081	0.154
	1:0	0.94	-	0.418	0.418
Ru/MCM-41	0:1	-	0.94	0.000	-
Pt-Ru/MCM-41	1:2	0.55	0.56	0.111	0.325
	4:5	0.61	0.43	0.122	0.287
	1:1	0.64	0.35	0.221	0.452
Pt/MCM-41	1:0	1.10	-	0.463	0.463

Table 3. Particle size of Pt and Ru calculated from metal dispersion

Material	Pt/wt%	Ru/wt%	Particle size (nm)
Ru/Al ₂ O ₃	-	0.99	156.9
Pt/Al ₂ O ₃	1.12	-	1.5
Ru/SiO ₂	-	0.93	44.5
Pt/SiO ₂	0.94	-	2.8
Ru/MCM-41	-	0.94	-
Pt/MCM-41	1.10	-	2.5

corresponding to two oxidation forms of ruthenium with large particle sizes. In contrast, no reduction peaks of monometallic Pt on silica were observed. This was because the oxides of platinum were reduced at lower temperature than the experimental conditions. PtO_x is known to have weak interaction with silica and can be easily reduced.

Because monometallic catalyst contained 1 wt% Ru, which was higher than that in bimetallic Pt-Ru, the reduction peak area of monometallic Ru was larger than that of the bimetallic. Bimetallic Pt-Ru with 1:2, 4:5, and 1:1 molar ratios showed that a single reduction peak corresponded to Ru at 195°C, 172°C, and 160°C, respectively. When the Ru content decreased, the Ru reduction peak shifted slightly to a lower temperature when compared

to the second broad peak of monometallic Ru, whereas the first reduction peak at 162°C disappeared. This result indicated that only one form of ruthenium oxide possibly existed in the bimetallic system.

There was a difference in the TPR profiles of Pt on SiO_2 when compared with the other supports. Pt showed a small reduction peak at 49°C which was lower than Ru. When Pt was mixed with Ru in bimetallic catalysts, the reduction peaks of Pt slightly shifted to higher temperature and Pt reduction peak shifted slightly to lower temperature when the amount of Ru increased.

From these results, it could be concluded that oxides of Pt on SiO_2 were reduced more easily than Ru on SiO_2 . This referred to the weak interaction between Pt and SiO_2 .

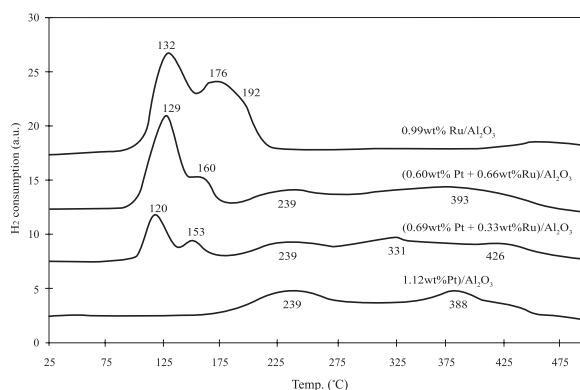


Figure 1. TPR profiles of supported Pt, Ru, and Pt-Ru catalysts on Al_2O_3

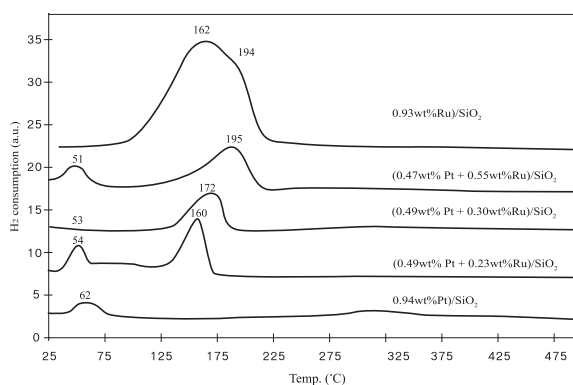


Figure 2. TPR profiles of supported Pt, Ru, and Pt-Ru catalysts on SiO_2

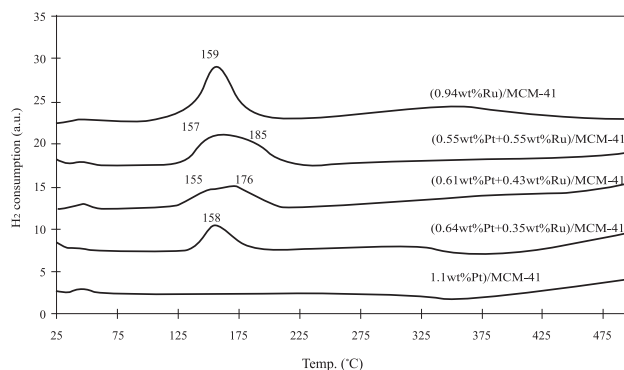


Figure 3. TPR profiles of supported Pt, Ru, and Pt-Ru catalysts on MCM-41

Pt-Ru/MCM-41

The TPR profiles of monometallic Pt, Ru, and Pt-Ru on MCM-41 were shown in Figure 3. There were two reduction peaks of Ru. The first peak was detected at 159°C while a very broad peak centered at about 356°C. The second peak could be the reduction of the MCM-41 support. Bimetallic Pt-Ru with 1:2 and 4:5 molar ratios showed seemingly two overlapped reduction peaks of Ru at 157°C and 186°C compared to 155°C and 176°C, respectively. Only Pt-Ru with the 1:1 molar ratio had one reduction peak of Ru at 158°C. It was difficult to observe the reduction peak of monometallic platinum on MCM-41. There was only a very broad peak at above 350°C which was probably the support reduction. All three bimetallic Pt-Ru catalysts did not show any reduction peaks of Pt. This broad peak might result from the interaction between the novel metal and the MCM-41.

Conclusions

From hydrogen adsorption, platinum formed smaller particle sizes and dispersed on Al_2O_3 better than on SiO_2 and MCM-41. The Pt dispersion was better than Ru on all supports. The preparation of Pt-Ru from H_2PtCl_6 and RuCl_3 on all supports failed to yield bimetallic Pt-Ru particles. Both Pt and Ru particles did not form alloy and dispersed separately on all supports.

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