Preparation and Reaction Studies of Pt/Al₂O₃ Model Catalysts

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Abstract — Surface of Pt/Al₂O₃ model catalyst was produced on an aluminum foil with surface area of 1 cm². The aluminum surface was oxidized under 10^{-5} Torr oxygen and platinum was deposited on top of the oxide layer using a plasma evaporation source. Conversion of 1-butene was performed on the model catalyst surface. Isomerization was the major reaction in 1-butene conversion on the aluminum oxide layer. Addition of Pt on the aluminum oxide layer induces hydrogenation of 1-butene. Selectivity for the hydrogenation increases as the amount of Pt on alumina increases.

요　약 — 알루미늄 박편 위에 Pt/Al₂O₃ 모델 촉매를 만들었다. 알루미늄 표면을 10^{-5}Torr의 산소 압력 하에서 산화시킨 후, plasma evaporation source를 사용하여 Pt을 증착시켰다. 이 모델 촉매 표면에서 일어나는 1-butene의 반응을 연구하였다. 산화알루미늄 표면에서는 이성질화 반응이 일어 났으나, Pt을 증착시킨 산화알루미늄 표면에서는 수소첨가반응이 일어남이 관찰되었다. 알루미나 표면의 Pt이 증가함에 따라 수소첨가반응으로의 선택성이 증가되었다.

1. Introduction

Surface science has evolved from the study of surface structure and surface-gas interaction in ultrahigh vacuum (UHV). Catalytic reactions, on the other hand, take place in high pressure range (10³~ 10⁵ Torr). Development of UHV systems equipped with an internal or an external high-pressure reactor bridged the gap between UHV and high-pressure reaction [1]. For UHV/high-pressure reaction studies, single crystal or metal foil catalysts are generally used. Single crystal catalysts have about 1 cm² surface area and they have very uniform surface structure and composition. These model catalysts are fabricated easily by depositing second or third materials on the catalyst surfaces [2]. These surfaces can be characterized by modern surface science techniques. By performing the reaction over the catalyst, whose surface structure and composition are known, effect of the surface structure and the composition on the catalytic reactions can be studied on a molecular level. Instrumentation of the combined UHV/high-pressure reactor system has

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been extensively reviewed [3].

Catalytic reforming produces gasoline from naphtha and is a key process in petroleum refining [4]. Typical industrial reforming catalysts have platinum or other metal components dispersed on γ-Al₂O₃. Because of its acidic propety, alumina support is not only a catalyst carrier but a catalyst itself. For this reason, the reforming catalyst has been called dual functional or bifunctional [5]. Hydrogenation-dehydrogenation reactions take place at metallic sites and isomerization reactions are catalyzed at acidic sites. However, there are not many experimental evidences for the dual functionality of the reforming catalyst [6].

Metal oxides are widely used for heterogeneous catalysis but surface science studies of oxide catalysts have not been performed extensively [7]. Because of insulating and brittle properties of metal oxides, utilization of surface electron spectroscopies is quite limited. In addition to that, heating and cleaning of metal oxide surfaces cause several experimental problems [8]. The best way to overcome these problems is to produce thin oxide films on metal substrates instead of using metal oxide itself.

Use of planar alumina as a model for alumina-based catalysts is gaining more attention [9]. The advantage of using planar alumina instead of bulk alumina is that uniform film of aluminum oxide can be produced and modern surface science techniques can be used to characterize the surface. Aluminum oxide films have been prepared by direct oxidation of aluminum foils and single crystals [10, 11] or by oxidizing deposited aluminum on the second metal such as Pt [12], Ru [13] or Mo [14]. The thickness of the oxide film can be controlled from seve-

ral monolayers to 1000 Å and various planar aluminum oxides have been prepared and studied.

We report the preparation of Pt/Al₂O₃ model catalysts. The aluminum oxide surface was produced by direct oxidation of the aluminum foil. Platinum was deposited on top of the aluminum oxide layer using a plasma evaporation source. Reaction of 1-butene over the Pt/Al₂O₃ model catalyst surface has been studied. Isomerization of 1-butene over aluminum oxide surfaces will be discussed. Isomerization of 1-butene over alumina is the classical example
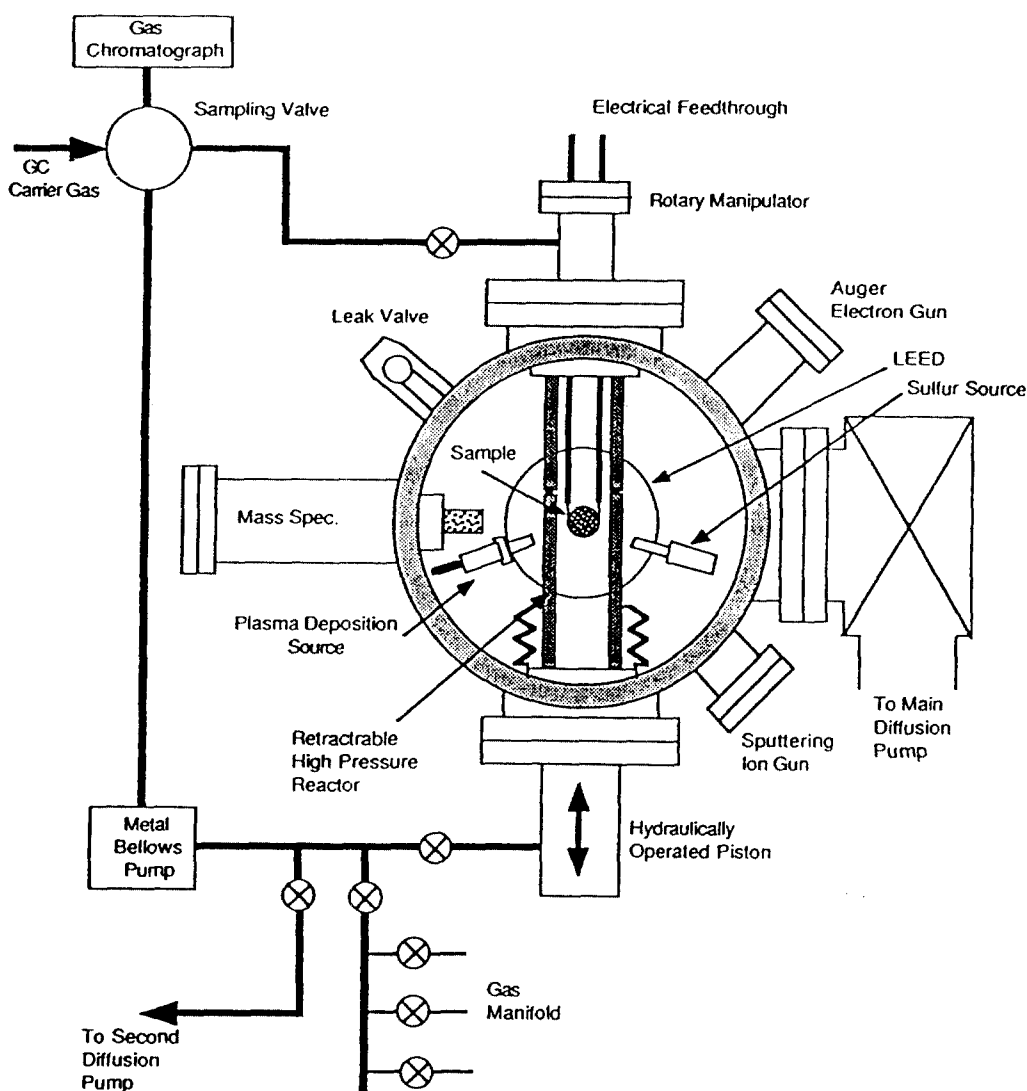

Fig. 1. Schematic diagram of an ultrahigh vacuum/high pressure reactor system.

of an acid-catalyzed reaction which takes place on
the aluminum oxide surface [14]. We will also dis-
cuss the change of the activity and selectivity of
the alumina catalyst in the presence of platinum.

2. Experiment Method

All of the experiments described in this paper
were conducted in a combined ultrahigh vacuum
(UHV)/high pressure reactor system. This system
was designed for both surface science studies in
ultrahigh vacuum and catalytic reaction studies in
high pressure [16]. The schematic of the system
is shown in Fig. 1. The system was equipped with
an Auger electron spectrometer (AES), a low-energy
electron diffraction (LEED) optics, a quadrupole
mass spectrometer, a metal evaporation source, and
an internal isolation cell for catalytic reactions. After
the preparation and characterization of the catalysts
in UHV, the internal isolation cell was closed and
pressurized with reactant gases for reaction studies.
The accumulation of products was monitored using
a gas chromatograph and the turnover rate was de-
termined.

An aluminum foil sample was spot-welded on gold
rods. The sample was resistively heated and the
temperature was monitored using thermocouple
spot-welded directly to the sample. The sample was
cleaned using cycles of Ar ion sputtering at room
temperature and annealing at 600℃ until no impu-
rities could be detected by AES. The aluminum su-
rface was oxidized by exposing to 10^{-5} Torr of oxy-
gen.

Platinum was deposited on the aluminum oxide
surface using a plasma evaporation source. The
principle of the plasma evaporation source has been
fully described elsewhere [17]. Briefly, the arc dis-
charge is initiated by a high-voltage (15 kV) pulse
applied to the trigger electrode located between a
cathode and an anode. The platinum plasma is for-
med between a Pt cathode and a stainless steel
anode by the arc discharge. Dense metal plasma
plumes away from the cathod toward the substrate.
The deposition rate was controlled by changing the
plasma pulse rate. The amount of platinum deposi-
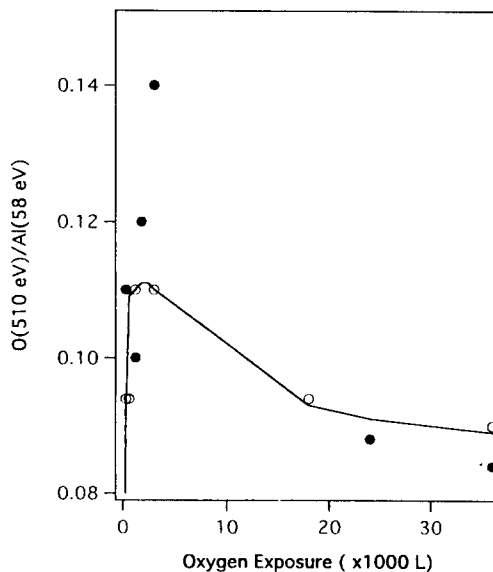ted on the substrate was estimated by integrating

Fig. 2. Change of AES peak to peak height ratio of
the O *KLL* transition (510 eV) to Al $L_{2,3}$ *VV*
transition (58 eV). The oxygen pressure was
10^{-5} Torr and oxidation temperature was 500
℃. The closed circles represent oxidation at
25℃.

the Pt plasma current collected by the substrate
that was negatively biased by 50 V. The deposition
rate was also calibrated from the separated experi-
ment [17]. It was determined by inspecting the ac-
tual amount of platinum deposited on the Re (0001)
surface using AES and LEED. Pt was deposited on
both sides of the aluminum foil for reaction studies.

3. Results and Discussion

3.1. Preparation of Pt/Al₂O₃ Model Catalyst Sur-
faces

The aluminum foil was oxidized in 10^{-5} Torr of
oxygen. Oxidation of aluminum was monitored by
AES. The Al $L_{2,3}$ *VV* AES peak shifted from 68 eV
to 58 eV after oxidation. The interaction of oxygen
with aluminum has been extensively studied using
several surface-sensitive techniques [10, 11]. It was
generally found that oxygen atoms are initally che-
misorbed on both surface and subsurface binding
sites without formation of Al_2O_3 [11]. Extended ex-
posure to oxygen produces three dimensional oxide

clusters. Fig. 2 shows the change of AES peak-to-peak height ratio of oxygen *KLL* transition (510 eV) to aluminum $L_{2,3}$ *VV* transition (58 eV). Black dots in Fig. 2 represent the change of oxygen to aluminum peak ratio for O_2 adsorption at 300 K and open circles for O_2 adsorption at 773 K. At 300 K, the oxygen peak intensity increased up to 500 L (1 L = 1 × 10⁻⁶ Torr sec exposure) of oxygen exposure. This is the inital chemisorption stage of adsorbed oxygen. The AES peak ratio of O (510 eV) to Al (58 eV) remained almost constant after 30000 L of oxygen exposure. It is believed that the aluminum oxide layer was formed at this stage. No metallic aluminum Auger transition feature (68 eV) was detected at this stage. When the oxidation temperature was 773 K, it was observed that oxide formation took place at lower exposure of oxygen. In this work, aluminum oxide layer was produced by exposing 35000 L of oxygen on aluminum at 773 K.

Platinum was deposited on both sides of the oxided aluminum foil using a plasma evaporation source as described previously.

3.2. Conversion of 1-Butene on Pt/Al₂O₃

Conversion of 1-butene over Al_2O_3 surfaces was performed in the presence of hydrogen. The Al_2O_3 layer was prepared by oxidizing aluminum foil in 10⁻⁵ Torr of oxygen for 1 hour at 773 K. The pressure of 1-butene was 200 Torr and the same pressure of hydrogen was used. When the reaction temperature was lower than 373 K, selectivity for cis-2-butene over trans-2-butene was about 1.5. It was proposed that 1-butene is adsorbed on the alumina

surface as a gauche form [18]. The adsorption sites are a surface O^2 ion and underlying Al^{3+} ions. From this intermediate species, cis-2-butene is easy to be formed. At temperatures higher than 373 K, however, more trans-isomer was formed. At these temperatures, thermodynamically more stable isomer (trans-2-butene) could be easily produced. That can be explained in terms of activation energy change. Fig. 3 shows the Arrhenius plots for 1-butene isomerization on Al_2O_3 in the temperature range of 333 to 493 K. When the reaction temperature was
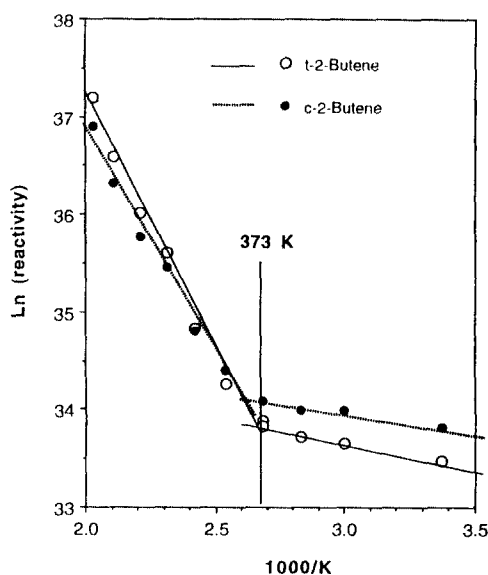

Fig. 3. Arrhenius plots for 1-butene isomerization on Al_2O_3. The pressure of 1-butene and hydrogen was 200 Torr.

Table 1. Comparison of initial turnover rates of 1-butene conversion on Pt/Al₂O₃ model catalysts

Coverage (×10¹⁵ Pt atoms/cm²)	Reactivity(×10¹⁶ molecules/sec/cm²)			Selectivity (hydrogenation/isomerization)
	Hydrogenation	Isomerization		
	n-Butane	t-2-Butene	c-2-Butene	
0	—	0.11	0.11	—
0.2	2.9	0.81	0.65	2.0
0.5	4.4	1.2	0.96	2.0
1.0	11	2.2	1.9	2.7
2.0	13	2.2	2.0	3.1
4.0	16	2.2	2.1	3.7

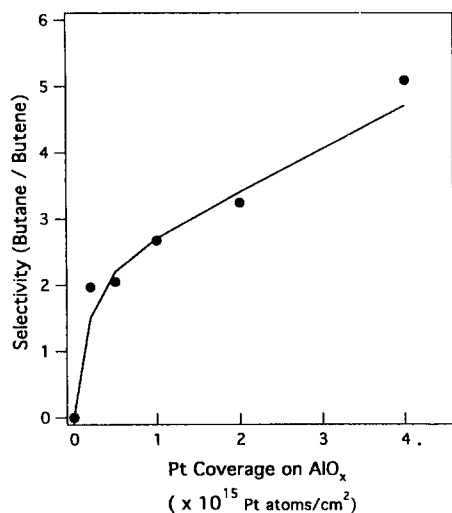Reaction conditions: T = 140℃, $P_{1\text{-butene}}$ = 200, Torr, P_{H2} = 200 Torr.

Fig. 4. Conversion of 1-butene over Pt/Al₂O₃ model catalyst surfaces. It shows the selectivity for hydrogenation (n-butane) over isomerization (cis- and trans-2-butene). The pressure of 1-butene and hydrogen was 200 Torr and the reaction temperature was 413 K.

lower than 373 K, activation energies for isomerization to trans-2-butene and cis-2-butene were 47 kJ/mole and 40 kJ/mole, respectively. When the catalyst temperature was higher than 373 K, the activation energies became much lower. At temperatures higher than 373 K, the activation energies for isomerization to trans-2-butene and cis-2-butene were 3.9 kJ/mole and 4.2 kJ/mole, respectively. The activation energy is so low at temperatures higher than 373 K that the isomerization reaction is thermodynamically controlled and the trans isomer is a dominant product.

The same reaction was performed over Pt-covered Al_2O_3 surfaces at 413 K. The products of the reaction were cis-2-butene, trans-2-butene, and n-butane. The addition of Pt on Al_2O_3 increased the reactivity of isomerization. When the surface was covered by 2×10^{14} Pt atoms/cm², the initial turnover rate for isomerization was increased from 0.22×10^{16} to 1.46×10^{16} molecules/sec/cm². When Pt was added on Al_2O_3, the hydrogenation of 1-butene to n-butane was the dominant reaction. The product distribution of 1-butene conversion on Pt /Al₂O₃ model catalyst surfaces is summarized in

Table 1. With more platinum on the Al_2O_3 surface, hydrogenation became more important. Fig. 4 shows the change of the selectivity of hydrogenation as a function of Pt coverage on Al_2O_3. When the surface was covered by 2×10^{14} Pt atoms/cm², the selectivity for hydrogenation over isomerization was 2.0. The selectivity was increased to 3.7 when the Al_2O_3 surface was covered with 4.0×10^{15} Pt atoms/cm². These results clearly demonstrate the dual functionality of the Pt/Al₂O₃ catalyst.

4. Conclusion

Based on the results and discussion given above, the following conclusions can be made:

(1) The model Pt/Al₂O₃ catalyst was successfully produced by oxidizing aluminum foil at 500°C in 10^{-5} Torr of oxygen followed by depositing Pt on the top of the aluminum oxide layer.

(2) Isomerization was the major reaction of 1-butene conversion on the aluminum oxide layer and the result was similar to the reaction on bulk alumina. Addition of Pt on the aluminum oxide layer induced the hydrogenation of 1-butene, Selectivity of hydorgenation increased as Pt coverage increased.

(3) These results demonstrate that the small surface area model catalyst is useful for the study of catalytic reactions on metal oxide surfaces.

5. Acknowledgments

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