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# Development of Highly Active New Hydrodesulfurization Catalysts for Prevention of Acid Rain - Supported Noble Metal Catalysts -

Masatoshi SUGIOKA\*, Yasuharu KANDA\*, Takao KOBAYASHI\* and Yoshio UEMICHI\*

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The catalytic activities and performance of noble metals supported on various carriers such as metal oxides, carbons, zeolite, Al-pillared clays and mesoporous silica for the hydrodesulfurization (HDS) of thiophene as a model HDS reaction for petroleum were investigated in order to develop highly active new HDS catalysts. It was revealed that sulfided Rh supported on SiO<sub>2</sub>, amorphous carbon (Am.C), Pt supported on HZSM-5, MCM-41 and Rh supported on Al-PILM (montmorillonite) showed high and stable activities for the HDS of thiophene. The activities of these catalysts were higher than that of commercial CoMo/Al<sub>2</sub>O<sub>3</sub> HDS catalyst. Therefore, some kind of supported noble metal catalysts have high potential for new HDS catalysts for petroleum.

Keywords: Acid rain prevention, Hydrodesulfurization, Petroleum, New catalyst, Noble metal

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## 1 INTRODUCTION

Hydrodesulfurization (HDS) of petroleum feedstocks is one of the most important processes to produce clean fuels in the petroleum industry<sup>(1)(2)</sup>. The CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst is widely used in the HDS process of petroleum. Recently, the development of highly active HDS catalysts, which are more active than commercial CoMo/Al<sub>2</sub>O<sub>3</sub> HDS catalyst, has been claimed in the petroleum industry to produce much lower sulfur content fuels against the serious problems of environmental pollution on a global scale by acid rain caused by burning petroleum.

Various catalysts have been proposed as new HDS catalysts<sup>(3)(4)(5)(6)</sup>. We showed that noble metals supported on zeolites and related materials exhibit high activity for the HDS of organic sulfur compounds and these catalysts have high potential as second generation HDS catalysts<sup>(7)(8)(9)(10)(11)(12)</sup>.

In the present paper, we describe our systematic studies on the catalytic activities and performance of

noble metals (NM = Pt, Pd, Rh, Ru) supported on various carriers such as metal oxides, carbons, zeolite, Al-pillared clays and mesoporous silica for the HDS of thiophene in order to develop highly active new HDS catalysts.

## 2 EXPERIMENTAL

Hydrodesulfurization (HDS) of thiophene (TP) over noble metals supported on various carriers was carried out in a conventional fixed bed flow reactor under 1 atm. Thiophene was introduced into the reactor by passing hydrogen (30ml/min) through a TP trap cooled at 0°C in the HDS of thiophene. The H<sub>2</sub>/thiophene molar ratio (mol/mol) was 30. Reaction products in the HDS of thiophene were analyzed by gas chromatography (FID).

Noble metals supported on metal oxides, carbons, zeolite, Al-pillared clays and mesoporous silica were prepared by an impregnation method using noble metal chloride aqueous solutions and the amount of NM loading was 5 wt%. Catalysts except on carbon carriers were calcined at 500°C for 4 hrs in air and were reduced at 450°C for 1 hr. Presulfiding treatment of the

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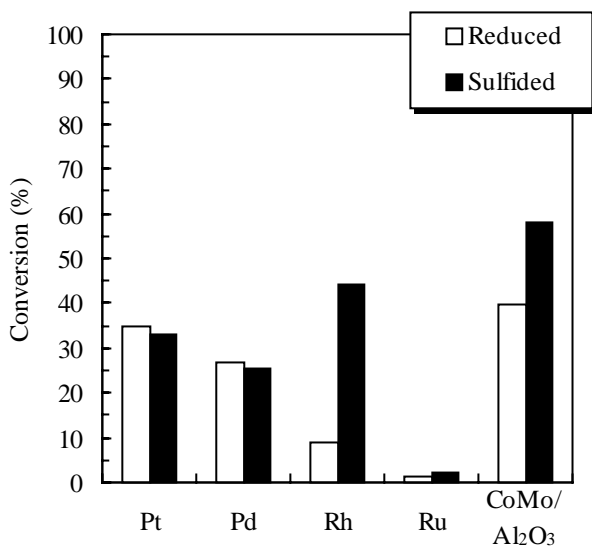
catalysts was performed by 5 vol% H<sub>2</sub>S-H<sub>2</sub> mixture at 400°C for 1 hr.

### 3 RESULTS AND DISCUSSION

#### 3.1 Catalytic Activities of Noble Metals Supported on Various Carriers

##### 3.1.1 NM supported on metal oxides

The catalytic activities of noble metals supported on metal oxides (MO<sub>x</sub>) such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> for the HDS of thiophene were examined at 350°C with and without presulfiding. It was revealed that the order of steady activity of NM/Al<sub>2</sub>O<sub>3</sub> catalysts was Pt/Al<sub>2</sub>O<sub>3</sub> > Pd/Al<sub>2</sub>O<sub>3</sub> > Rh/Al<sub>2</sub>O<sub>3</sub> >> Ru/Al<sub>2</sub>O<sub>3</sub>. Pt/Al<sub>2</sub>O<sub>3</sub> showed the highest activity. Further, the activities of Rh/Al<sub>2</sub>O<sub>3</sub> catalyst was remarkably enhanced by the presulfiding and the order of activity after sulfiding was Rh/Al<sub>2</sub>O<sub>3</sub> > Pt/Al<sub>2</sub>O<sub>3</sub> > Pd/Al<sub>2</sub>O<sub>3</sub> >> Ru/Al<sub>2</sub>O<sub>3</sub>. It was, however, found that the sulfided Rh/Al<sub>2</sub>O<sub>3</sub> catalysts did not show higher activity than CoMo/Al<sub>2</sub>O<sub>3</sub> as shown in Fig.1.

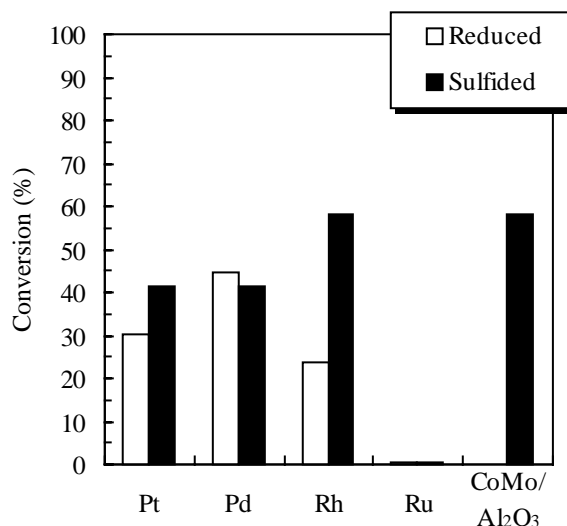


W/F = 37.9 g·hr/mol, H<sub>2</sub>/Thiophene = 30

Fig. 1 Catalytic activities of noble metals supported on Al<sub>2</sub>O<sub>3</sub> for the HDS of thiophene at 350°C.

In the HDS of thiophene on NM/SiO<sub>2</sub> catalysts, the order of activity was Pd/SiO<sub>2</sub> > Pt/SiO<sub>2</sub> > Rh/SiO<sub>2</sub> >> Ru/SiO<sub>2</sub>. After presulfiding, the activity of Rh/SiO<sub>2</sub> was considerably enhanced and the order of activity was Rh/SiO<sub>2</sub> > Pt/SiO<sub>2</sub>, Pd/SiO<sub>2</sub> >> Ru/SiO<sub>2</sub>. It was found that the activity of sulfided Rh/SiO<sub>2</sub> was comparable to that of CoMo/Al<sub>2</sub>O<sub>3</sub> as shown in Fig.2.

The reaction products in the HDS of thiophene over NM/MO<sub>x</sub> catalysts were mainly C<sub>4</sub> hydrocarbons and hydrogen sulfide. This result indicates that NM/MO<sub>x</sub> catalysts have high activity in hydrodesulfurization and low activity in hydrocracking for C<sub>4</sub> hydrocarbons.



W/F = 37.9 g·hr/mol, H<sub>2</sub>/Thiophene = 30

Fig. 2 Catalytic activities of noble metals supported on SiO<sub>2</sub> for the HDS of thiophene at 350°C.

##### 3.1.2 NM supported on carbons

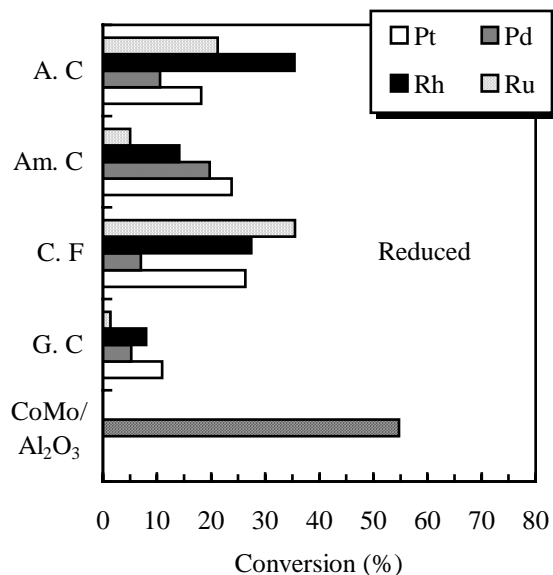
The catalytic activities of noble metals supported on various carbons such as active carbon (A.C), amorphous carbon (Am.C), carbon fiber (C.F) and graphite (G.C) for the HDS of thiophene were examined at 350°C. It was revealed that the activities of NM/C catalysts were changed by the kind of noble metals and the type of carbons. The NM/C catalysts without sulfiding showed lower activity than CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst as shown in Fig.3. However, the activities of Rh/Am.C catalyst was remarkably enhanced by the presulfiding and its activity was higher than that of CoMo/Al<sub>2</sub>O<sub>3</sub> as shown in Fig.4. The hydrocarbon products in the HDS of thiophene over NM/C catalysts were mainly C<sub>4</sub> hydrocarbons.

##### 3.1.3 NM supported on zeolite

The catalytic activities of noble metals supported on HZSM-5 zeolite for the HDS of thiophene were examined at 400°C. The order of the activities of NM/HZSM-5 catalysts was Pt/HZSM-5 > Rh/HZSM-5 > Pd/HZSM-5 >> Ru/HZSM-5. Pt/HZSM-5 showed the highest activity and its activity was higher than that of CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst as shown in Fig.5. The high and stable activity of Pt/HZSM-5 catalyst during the HDS of thiophene was maintained after reaction for 20 hrs, but other NM/HZSM-5 catalysts showed the deactivation with reaction time. Further, the activity of Pt/HZSM-5 was hardly affected by presulfiding, indicating that the Pt/HZSM-5 catalyst has high sulfur tolerant property for hydrogen sulfide and sulfur compounds.

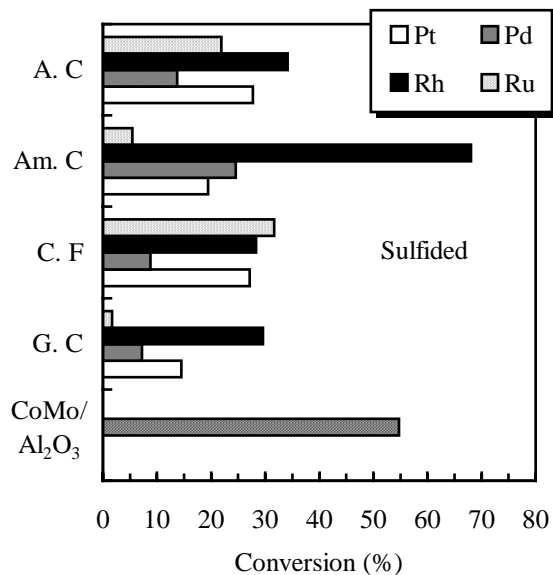
The hydrocarbon products in the HDS of thiophene over Pt/HZSM-5 catalyst were C<sub>4</sub> hydrocarbon (50 %)

with large amount of cracking products of  $C_4$  hydrocarbons ( $C_2$  10%,  $C_3$  40%). This indicates that Pt/HZSM-5 catalyst has the activities of both hydrodesulfurization of thiophene and hydrocracking of hydrocarbons.



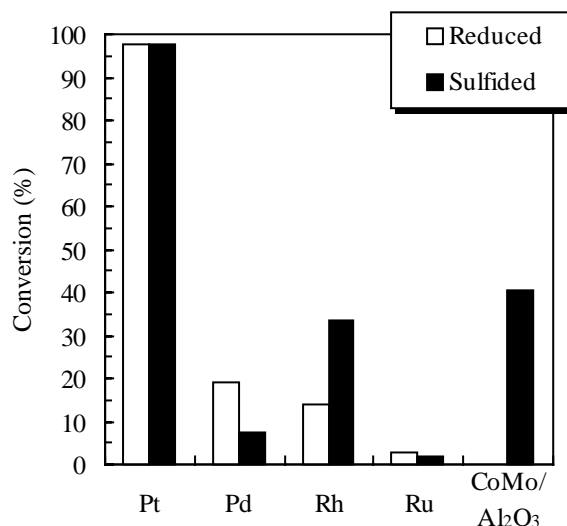
W/F = 37.9 g·hr/mol,  $H_2$ /Thiophene = 30

Fig. 3 Catalytic activities of noble metals supported on various carbons for the HDS of thiophene at 350°C before sulfiding.



W/F = 37.9 g·hr/mol,  $H_2$ /Thiophene = 30

Fig. 4 Catalytic activities of noble metals supported on various carbons for the HDS of thiophene at 350°C after sulfiding.



W/F = 19.0 g·hr/mol,  $H_2$ /Thiophene = 30

Fig. 5 Catalytic activities of noble metals supported on HZSM-5 for the HDS of thiophene at 400°C.

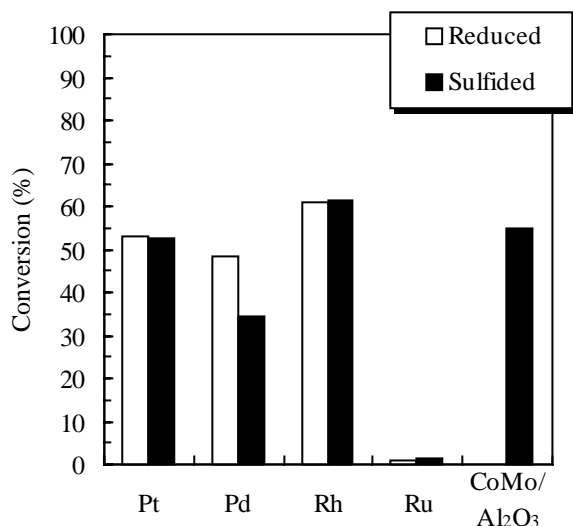
### 3. 1. 4 NM supported on pillared clays

The catalytic activities of noble metals supported on Al-pillared clays (Al-PILCs) were examined at 350°C. In the HDS of thiophene over NM/Al-PILM (montmorillonite), the order of catalytic activity of NM/Al-PILM was Rh/Al-PILM > Pt/Al-PILM > Pd/Al-PILM >> Ru/Al-PILM. The catalytic activity of Rh/Al-PILM was the highest and its activity was higher than that of CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst as shown in Fig.6. However, Pt/Al-PILH (hectorite) showed the highest activity in the HDS of thiophene among NM/Al-PILH catalysts and this activity was comparable to that of CoMo/Al<sub>2</sub>O<sub>3</sub>. In the HDS of thiophene over NM/Al-PILS (saponite), sulfided Rh/Al-PILS showed the highest activity and this activity was higher than that of CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. It was revealed that the activities of NM/Al-PILCs catalysts were considerably varied by the kind of NM and type of clays.

The hydrocarbon products in the HDS of thiophene over NM/Al-PILCs catalysts were mainly  $C_4$  hydrocarbons. This result indicates that noble metal/Al-PILCs catalysts have high activity in hydrodesulfurization and low activity in hydrocracking for  $C_4$  hydrocarbons.

### 3. 1. 5 NM supported on mesoporous silica

The catalytic activities of noble metals supported on mesoporous silica MCM-41 for the HDS of thiophene were examined at 350°C. The order of the activities of NM/MCM-41 catalysts for the HDS of thiophene was Pt/MCM-41 > Pd/MCM-41 > Rh/MCM-41 >> Ru/MCM-41.



W/F = 37.9 g·hr/mol, H<sub>2</sub>/Thiophene = 30

Fig. 6 Catalytic activities of noble metals supported on Al-PILM for the HDS of thiophene at 350°C.

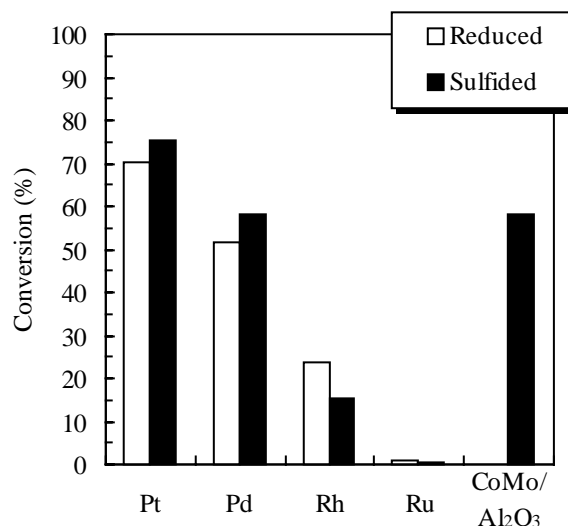
The Pt/MCM-41 catalyst showed high and stable activity for the HDS of thiophene and the activity of Pt/MCM-41 catalyst was higher than that of CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst shown in Fig.7. However, the activities of NM/MCM-41 catalysts were a little bit decreased by presulfiding.

In the HDS of thiophene over Pt/MCM-41 catalyst, the hydrocarbon products were mainly C<sub>4</sub> hydrocarbons and the selectivity of saturated C<sub>4</sub> hydrocarbon (n-butane, about 90%) were markedly higher than that on other supported NM catalysts. This indicates that Pt/MCM-41 catalyst has high hydrogenating activity for unsaturated C<sub>4</sub> hydrocarbons even in the presence of hydrogen sulfide formed in the HDS reaction.

### 3. 2 Catalytic Performance of Supported Noble Metal Catalysts

It was revealed that the sulfided Rh supported on SiO<sub>2</sub> and amorphous carbon (Am.C), Pt supported on HZSM-5 and MCM-41, and Rh supported on Al-PILM showed higher activity than CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. Therefore, these supported NM catalysts have high possibility of usage as highly active new hydrodesulfurization catalysts for petroleum.

Furthermore, the hydrocarbon products in the HDS of thiophene over sulfided Rh/SiO<sub>2</sub> and Rh/Am.C catalysts, Rh/Al-PILM and Pt/MCM-41 were mainly C<sub>4</sub> hydrocarbons. This indicates that these catalysts have high hydrodesulfurization activity and low hydrocracking activity for hydrocarbons. That is to say, these supported NM catalysts promote predominantly hydrodesulfurization reaction without hydrocracking of petroleum.



W/F = 37.9 g·hr/mol, H<sub>2</sub>/Thiophene = 30

Fig. 7 Catalytic activities of noble metals supported on MCM-41 for the HDS of thiophene at 350°C.

On the other hand, the hydrocracking products (C<sub>2</sub>, C<sub>3</sub>) of C<sub>4</sub> hydrocarbons were significantly formed in the HDS over Pt/HZSM-5 catalyst. This indicates that Pt/HZSM-5 catalyst has high activities for both HDS of organic sulfur compounds and hydrocracking of hydrocarbons. Namely, Pt/HZSM-5 catalyst has high potential for both hydrocracking and hydrodesulfurization of petroleum.

### 3. 3 Mechanism of HDS of Thiophene over Supported NM Catalysts

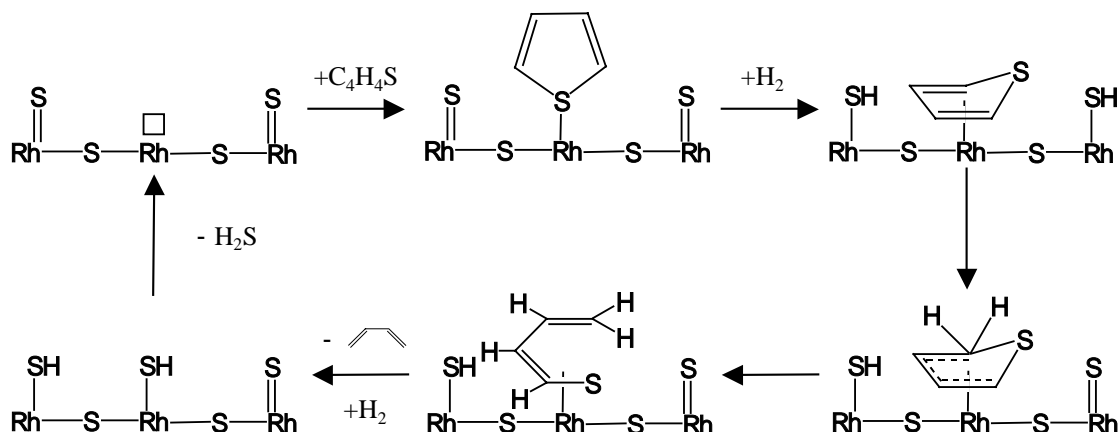
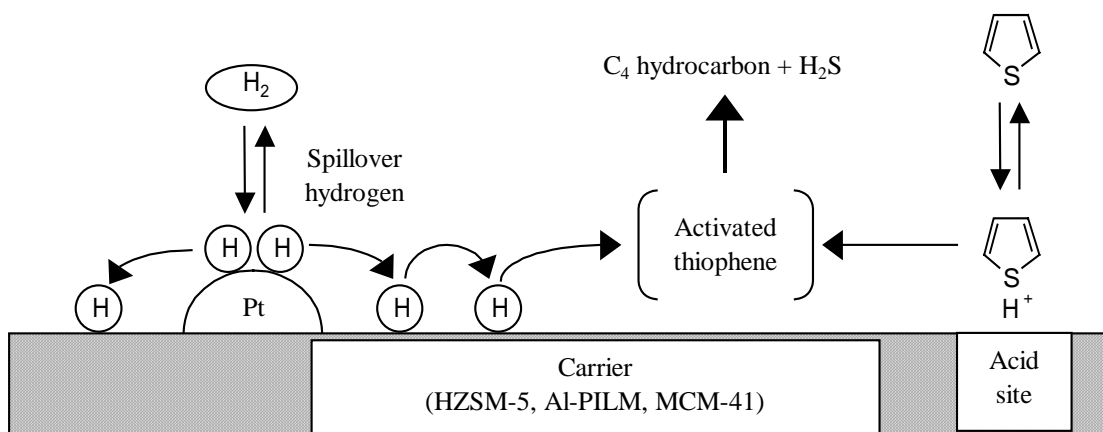
#### 3. 3. 1 Sulfided Rh supported on metal oxides and carbons

It was revealed that the catalytic activities of Rh supported on metal oxide and carbon such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and amorphous carbon (Am.C) for HDS of thiophene were remarkably enhanced by presulfiding with hydrogen sulfide. This indicates that metallic Rh on these carriers is sulfided into Rh sulfide species (Rh<sub>2</sub>S<sub>3</sub>) and the coordinatively unsaturated site of Rh<sub>2</sub>S<sub>3</sub> acts as active site for the activation of thiophene, whereas sulfur atom of Rh<sub>2</sub>S<sub>3</sub> acts as active site for the activation of hydrogen.

On the basis of this concept, we propose a possible mechanism for HDS of thiophene over sulfided Rh supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Am.C as shown in Scheme 1.

#### 3. 3. 2 Pt supported on zeolitic carriers

It was revealed that Pt supported on zeolitic carriers such as HZSM-5, Al-ALPM and MCM-41 showed high catalytic activities for HDS of thiophene and the activities of these Pt catalysts were hardly affected by presulfiding. This indicate that Pt supported on these

Scheme 1 Possible mechanism of thiophene HDS over sulfided Rh supported on  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and Am.C.

Scheme 2 Possible mechanism of thiophene HDS over Pt supported on HZSM-5, Al-PILM and MCM-41.

carriers exists metallic state even after presulfiding. On the other hand, it has been well known that HZSM-5, Al-PILM and MCM-41 have acid site, mainly Brønsted acid site, on their surface. We assumed that Pt catalyst supported on these acidic carriers acts as bifunctional catalyst for the HDS of thiophene, in which Pt acts as the active site for the activation of hydrogen to form spillover hydrogen and the acid site of the carriers acts as the active site for the activation of thiophene.

On the basis of this concept, we propose a possible mechanism for the HDS of thiophene on Pt supported on HZSM-5, Al-PILM and MCM-5 as shown in Scheme 2.

#### 4. CONCLUSIONS

It was revealed that sulfided Rh supported on  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and Am.C, and Pt supported on HZSM-5,

Al-PILM and MCM-41 showed high catalytic activities for the HDS of thiophene. Therefore, these catalysts have high potential for highly active new hydrodesulfurization of organic sulfur compounds in petroleum feedstocks.

Furthermore, it can be possible to develop much more highly active noble metal-based HDS catalysts on the basis of the proposed mechanisms for HDS of thiophene over supported NM catalysts.

#### ACKNOWLEDGMENTS

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### 酸性雨防止のための新規高活性水素化脱硫触媒の開発 担持貴金属触媒

杉岡 正敏\*, 神田 康晴\*, 小林 隆夫\*, 上道 芳夫\*

新規の高活性水素化脱硫触媒の開発を目的として、種々の担体(金属酸化物, 炭素, ゼオライト, Al-層間架橋粘土, メソポーラスシリカ)に担持した貴金属担持触媒の活性および特性を、石油の水素化脱硫(HDS)反応のモデル反応であるチオフエンのHDS反応により検討した。その結果、硫化処理を施したRh担持SiO<sub>2</sub>、無定形炭素(Am.C)、Pt担持HZSM-5、MCM-41 およびRh担持Al-PILM(モンモリロナイト)が高活性かつ安定な活性を示すことが明らかとなった。これらの触媒の活性はHDSプロセスに工業的に用いられているCoMo/Al<sub>2</sub>O<sub>3</sub>触媒の活性を上回るものであった。このことから、ある種の担持貴金属触媒は新規のHDS触媒として高い可能性を有している。

キーワード：酸性雨防止、水素化脱硫、石油、新規触媒、貴金属

\*応用化学科

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