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# Hydrodesulfurization of Thiophene over Platinum Supported on Metal Oxide Catalysts

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

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## Abstract

The catalytic activities of platinum (Pt) supported on various metal oxides ( $\text{MO}_x$ ;  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and  $\text{ZnO}$ ) for hydrodesulfurization (HDS) of thiophene were investigated. HDS activities of supported Pt catalysts were examined at  $350^\circ\text{C}$  by using conventional fixed bed flow reactor under atmospheric pressure. The order of HDS activities of  $\text{Pt}/\text{MO}_x$  was as follows;  $\text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{SiO}_2 > \text{Pt}/\text{TiO}_2 > \text{Pt}/\text{MgO} > \text{Pt}/\text{ZnO}$ . Catalytic properties of  $\text{MO}_x$  supports and  $\text{Pt}/\text{MO}_x$  were evaluated by nitrogen adsorption, decomposition of 2-propanol (2-PA), XRD and hydrogen adsorption. It was revealed that HDS activities of  $\text{Pt}/\text{MO}_x$  catalysts were not correlated to BET surface area and acid-base properties of  $\text{MO}_x$  but these were strongly correlated to the dispersion of Pt on  $\text{MO}_x$ .

Keywords: Hydrodesulfurization, Metal oxides, Noble metal, Supported platinum catalyst

## 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  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst is widely used in the HDS process of petroleum. Recently, the development of highly active HDS catalysts, which are more active than commercial  $\text{CoMo}/\text{Al}_2\text{O}_3$  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<sup>(3)(4)</sup>.

Supported noble metal catalysts have been proposed as new HDS catalysts<sup>(5)(6)(7)</sup>. We reported that noble metals, especially platinum, supported on zeolites<sup>(8)(10)(12)</sup> and related materials<sup>(9)(11)(13)(14)</sup> exhibit high activity for the HDS of organic sulfur compounds and these catalysts have high potential as second generation HDS catalysts.

In the present work, we investigated the catalytic

performance of Pt supported on various metal oxides ( $\text{MO}_x$ ) such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and  $\text{ZnO}$  for the HDS of thiophene as a model reaction of HDS of petroleum feedstocks.

## 2 EXPERIMENTAL

$\text{Pt}/\text{MO}_x$  catalysts were prepared by an impregnation method using hydrogen hexachloroplatinate hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) aqueous solution and the amount of Pt loading was 5 wt%. After impregnation, the catalysts were calcined at  $500^\circ\text{C}$  for 4 hrs in air and were reduced at  $450^\circ\text{C}$  for 1 hr. Presulfiding treatment of the catalyst was performed by 5 vol%  $\text{H}_2\text{S}-\text{H}_2$  mixture at  $400^\circ\text{C}$  for 1 hr.

Hydrodesulfurization of thiophene over  $\text{Pt}/\text{MO}_x$  was carried out at  $350^\circ\text{C}$  in a conventional fixed bed flow reactor under 1 atm. Thiophene was introduced into the reactor by passing hydrogen (30ml/min) through a thiophene trap cooled at  $0^\circ\text{C}$  in the HDS of thiophene. The  $\text{H}_2$ /thiophene molar ratio (mol/mol) was 30. Reaction products in the HDS of thiophene were analyzed by gas chromatography (FID).

BET surface area was measured by nitrogen

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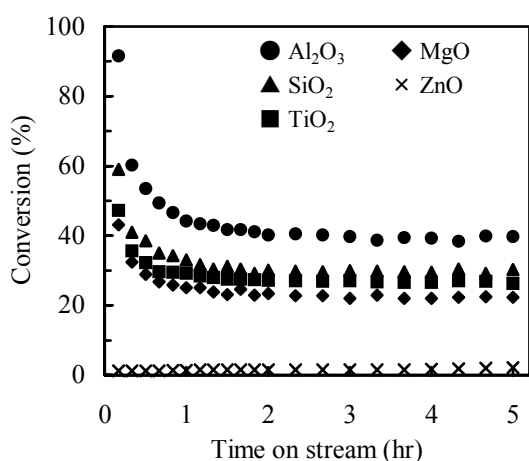
adsorption at liquid nitrogen temperature ( $-196^{\circ}\text{C}$ ). Acidic and basic properties of  $\text{MO}_x$  were evaluated by decomposition of 2-propanol (2-PA) using pulse reactor at  $200^{\circ}\text{C}$ . Helium was employed as a carrier gas. Dispersion of Pt on  $\text{MO}_x$  was measured by hydrogen adsorption method at  $25^{\circ}\text{C}$ . Catalysts were pretreated by evacuation at  $500^{\circ}\text{C}$  for 1 hr, and then reduced by hydrogen (200 Torr) at  $450^{\circ}\text{C}$  for 1 hr and evacuation at the same temperature for 1 hr. XRD patterns of supported Pt catalysts were measured by using Rigaku diffractometer with  $\text{Cu K}\alpha$  radiation.

### 3 RESULTS AND DISCUSSION

#### 3.1 Catalytic Activities of Pt Supported on $\text{MO}_x$ for HDS of Thiophene

The catalytic activities of Pt supported on various  $\text{MO}_x$  such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and  $\text{ZnO}$  for the HDS of thiophene were examined at  $350^{\circ}\text{C}$ . It was found that  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst showed the highest initial activity among  $\text{Pt}/\text{MO}_x$  catalysts, but this activity was decreased with reaction time as shown in Fig. 1, probably due to the poisoning by hydrogen sulfide and/or carbon deposit. The order of the HDS activities of  $\text{Pt}/\text{MO}_x$  catalysts after reaction for 2 hrs was as follows:  $\text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{SiO}_2 > \text{Pt}/\text{TiO}_2 > \text{Pt}/\text{MgO} \gg \text{Pt}/\text{ZnO}$ .

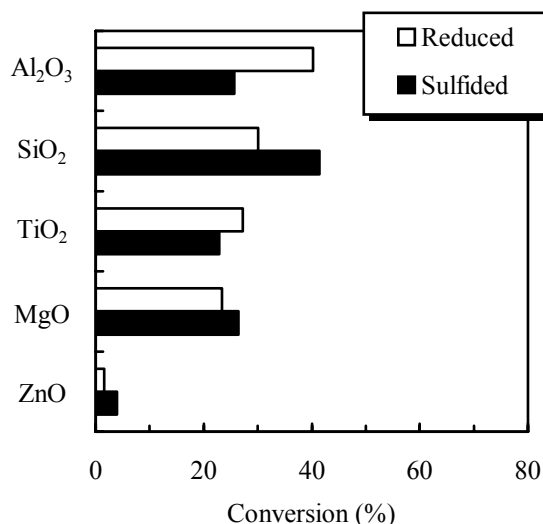
The reaction products in the HDS of thiophene over reduced  $\text{Pt}/\text{Al}_2\text{O}_3$  were mainly  $\text{C}_4$  hydrocarbons (butanes 93%, butenes 6%) and trace amount of  $\text{C}_1$ - $\text{C}_3$  hydrocarbons as shown in Table 1. These results indicate that high catalytic activity of  $\text{Pt}/\text{Al}_2\text{O}_3$  for thiophene HDS was attributed to high hydrogenating ability for unsaturated  $\text{C}_4$  hydrocarbons formed in the HDS of thiophene in the presence of hydrogen sulfide.



W/F =  $37.9 \text{ g} \cdot \text{hr}/\text{mol}$ ,  $\text{H}_2/\text{Thiophene} = 30$

Fig. 1 Hydrodesulfurization of thiophene over  $\text{Pt}/\text{MO}_x$  catalysts at  $350^{\circ}\text{C}$ .

We reported in the previous paper<sup>(15)</sup> that HDS activities of  $\text{Rh}/\text{Al}_2\text{O}_3$  and  $\text{Rh}/\text{SiO}_2$  catalysts were considerably enhanced by presulfiding treatment. Thus, we examined the catalytic activities of presulfided  $\text{Pt}/\text{MO}_x$  for HDS of thiophene at  $350^{\circ}\text{C}$ . The catalytic activity of  $\text{Pt}/\text{SiO}_2$  was enhanced by the presulfiding treatment and this activity was the almost same as that of  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst as shown in Fig. 2. However, HDS activities of other  $\text{Pt}/\text{MO}_x$  were decreased ( $\text{Pt}/\text{Al}_2\text{O}_3$ ,  $\text{Pt}/\text{TiO}_2$ ) or hardly changed ( $\text{Pt}/\text{MgO}$ ,  $\text{Pt}/\text{ZnO}$ ) by presulfiding treatment.



W/F =  $37.9 \text{ g} \cdot \text{hr}/\text{mol}$ ,  $\text{H}_2/\text{Thiophene} = 30$

Fig. 2 Catalytic activities of Pt supported on  $\text{MO}_x$  for the HDS of thiophene at  $350^{\circ}\text{C}$ .

#### 3.2 Characterization of $\text{MO}_x$ Supports and $\text{Pt}/\text{MO}_x$ Catalysts

##### 3.2.1 BET Surface Area of $\text{MO}_x$

We also carried out the characterization of  $\text{MO}_x$  and  $\text{Pt}/\text{MO}_x$  in order to clarify the cause of high activity of  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst in the HDS of thiophene. Figure 3 shows the BET surface area of  $\text{MO}_x$  and HDS activity of  $\text{Pt}/\text{MO}_x$  catalyst.  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  have high surface area (ca.  $300 \text{ m}^2/\text{g}$ ). However, surface area of  $\text{MgO}$  and  $\text{ZnO}$  were lower than these of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . Figure 4 shows the relationship between BET surface area of  $\text{MO}_x$  and HDS activities of  $\text{Pt}/\text{MO}_x$  catalysts. These results indicate that HDS activity of  $\text{Pt}/\text{MO}_x$  was independent of BET surface area of  $\text{MO}_x$  as supports.

##### 3.2.2 Acidic and Basic Properties of $\text{MO}_x$

Since propylene and water are formed on acidic sites of solid acid catalysts and acetone and hydrogen are formed on basic sites of solid base catalysts in the decomposition of 2-propanol (2-PA), the acidic and basic properties of various  $\text{MO}_x$  can be evaluated by the decomposition of 2-PA. We examined the catalytic

activity and selectivity of various  $\text{MO}_x$  in the decomposition of 2-PA at 200°C. We found that  $\text{Al}_2\text{O}_3$  showed high activity for the dehydration of 2-PA, but other  $\text{MO}_x$  showed very low activity for the decomposition of 2-PA as show in Fig. 5. These results indicate that  $\text{Al}_2\text{O}_3$  has high acidity and other  $\text{MO}_x$

have very low acidity and basicity. Figure 6 shows the relationship between catalytic activities of  $\text{MO}_x$  for 2-PA dehydration and HDS activities of Pt/ $\text{MO}_x$  catalysts. It was revealed that HDS activity of Pt/ $\text{MO}_x$  catalyst was not correlated to the acidic and basic properties of  $\text{MO}_x$ .

Table 1 Product distribution over Pt/ $\text{MO}_x$  catalysts in HDS of thiophene at 350°C.

Catalyst	HDS (%)	< C <sub>3</sub> (%) <sup>a)</sup>	C <sub>4</sub> (%) <sup>b)</sup>	C <sub>4</sub> <sup>=</sup> (%) <sup>c)</sup>	1,3-C <sub>4</sub> <sup>=</sup> (%) <sup>d)</sup>
Pt/ $\text{Al}_2\text{O}_3$ (reduced)	40.3	0.7	93.0	6.3	0.0
Pt/ $\text{Al}_2\text{O}_3$ (presulfided)	25.7	1.1	84.4	14.5	0.0
Pt/ $\text{SiO}_2$ (reduced)	30.1	1.0	71.7	27.3	0.0
Pt/ $\text{SiO}_2$ (presulfided)	41.4	0.3	77.3	22.4	0.0
Pt/ $\text{TiO}_2$ (reduced)	27.2	2.7	59.6	37.7	0.0
Pt/ $\text{TiO}_2$ (presulfided)	22.9	1.0	60.8	38.2	0.0
Pt/MgO (reduced)	23.4	2.9	74.1	23.0	0.0
Pt/MgO (presulfided)	26.4	0.8	83.8	15.4	0.0
Pt/ZnO (reduced)	1.6	8.6	9.0	77.8	4.6
Pt/ZnO (presulfided)	3.9	7.0	15.1	77.0	0.9

a) C<sub>1</sub>-C<sub>3</sub> hydrocarbons, b) butanes, c) butenes, d) 1,3-butadiene

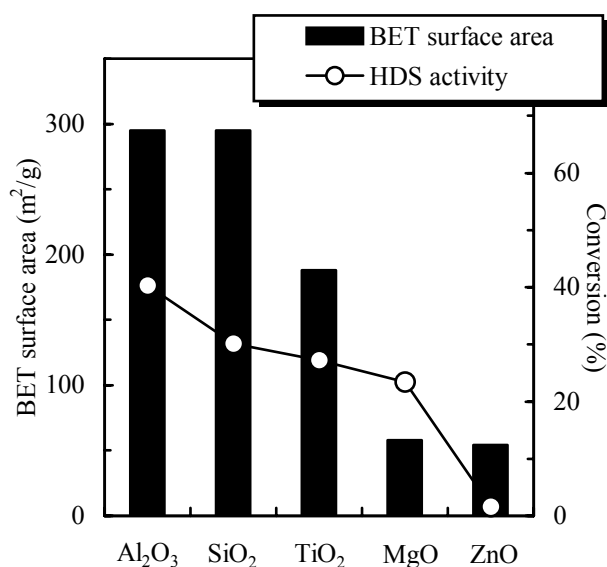


Fig. 3 BET surface area of  $\text{MO}_x$  and HDS activities of Pt/ $\text{MO}_x$  catalysts.

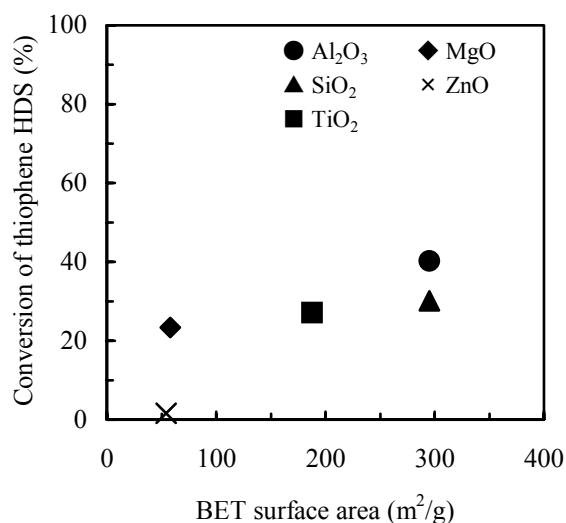


Fig. 4 Relationship between BET surface area of  $\text{MO}_x$  and HDS activities of Pt/ $\text{MO}_x$  catalysts.

### 3. 2. 3 Dispersion of Pt on Metal Oxides

Figure 7 shows the XRD patterns of Pt/ $\text{MO}_x$  catalysts before reduction. The peaks of Pt were not observed on  $\text{Al}_2\text{O}_3$ , but these on  $\text{SiO}_2$  were observed as shown in Fig. 7 (a). This indicates that the dispersion of Pt on  $\text{Al}_2\text{O}_3$  was higher than that on  $\text{SiO}_2$ . The peak height of Pt on  $\text{TiO}_2$  and MgO was larger than that on  $\text{SiO}_2$  as shown in Fig. 7 (b) and Fig. 7 (c). In the Pt/ZnO, the peaks of Pt were not observed, but peaks of  $\text{Zn}_2\text{PtO}_4$  were observed as shown in Fig. 7 (d). This result indicates that dispersion of Pt on ZnO was remarkably lower than these on other  $\text{MO}_x$ .

Furthermore, we examined the dispersion of Pt on  $\text{MO}_x$ . Figure 8 shows the dispersion of Pt on  $\text{MO}_x$  measured by hydrogen adsorption method at 25°C. It was found that dispersion of Pt on  $\text{MO}_x$  was changed by the kind of  $\text{MO}_x$ . The order of the Pt dispersion on  $\text{MO}_x$  was as follows; Pt/ $\text{Al}_2\text{O}_3$  > Pt/ $\text{SiO}_2$  > Pt/ $\text{TiO}_2$  > Pt/MgO >> Pt/ZnO. This order was the same as that of the HDS activities of Pt/ $\text{MO}_x$  catalysts. The catalytic activities of Pt/ $\text{MO}_x$  were strongly correlated to the dispersion of Pt on  $\text{MO}_x$  as shown in Fig. 9. This means that HDS activity of Pt/ $\text{MO}_x$  catalyst was remarkably controlled by the dispersion of Pt on  $\text{MO}_x$  supports.

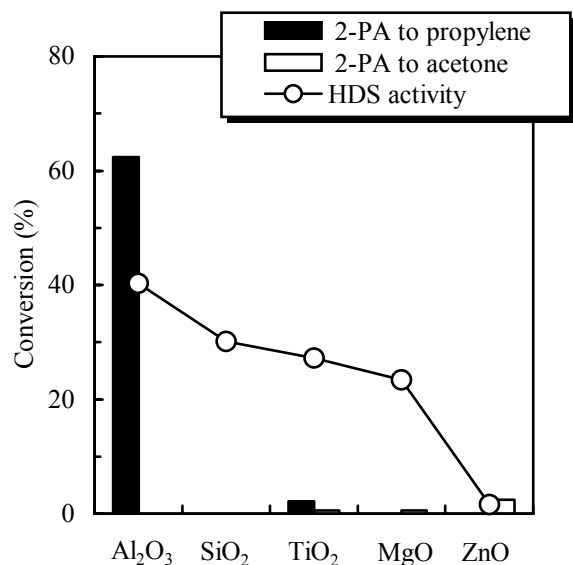


Fig. 5 Catalytic activities of MO<sub>x</sub> for decomposition of 2-propanol (2-PA) and HDS activities of Pt/MO<sub>x</sub> catalysts.

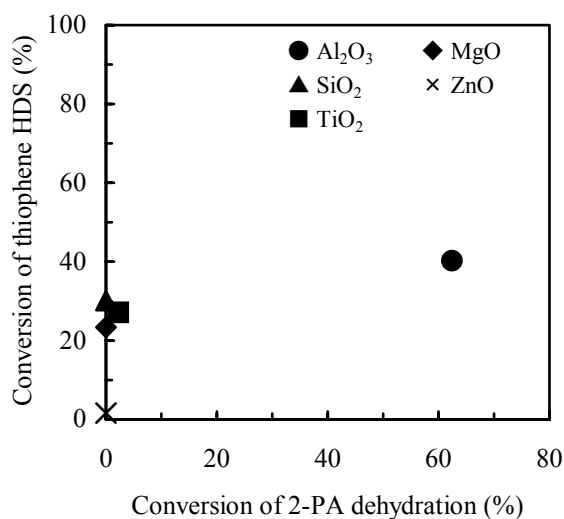


Fig. 6 Relationship between catalytic activities of MO<sub>x</sub> for 2-propanol (2-PA) dehydration and HDS activities of Pt/MO<sub>x</sub> catalysts.

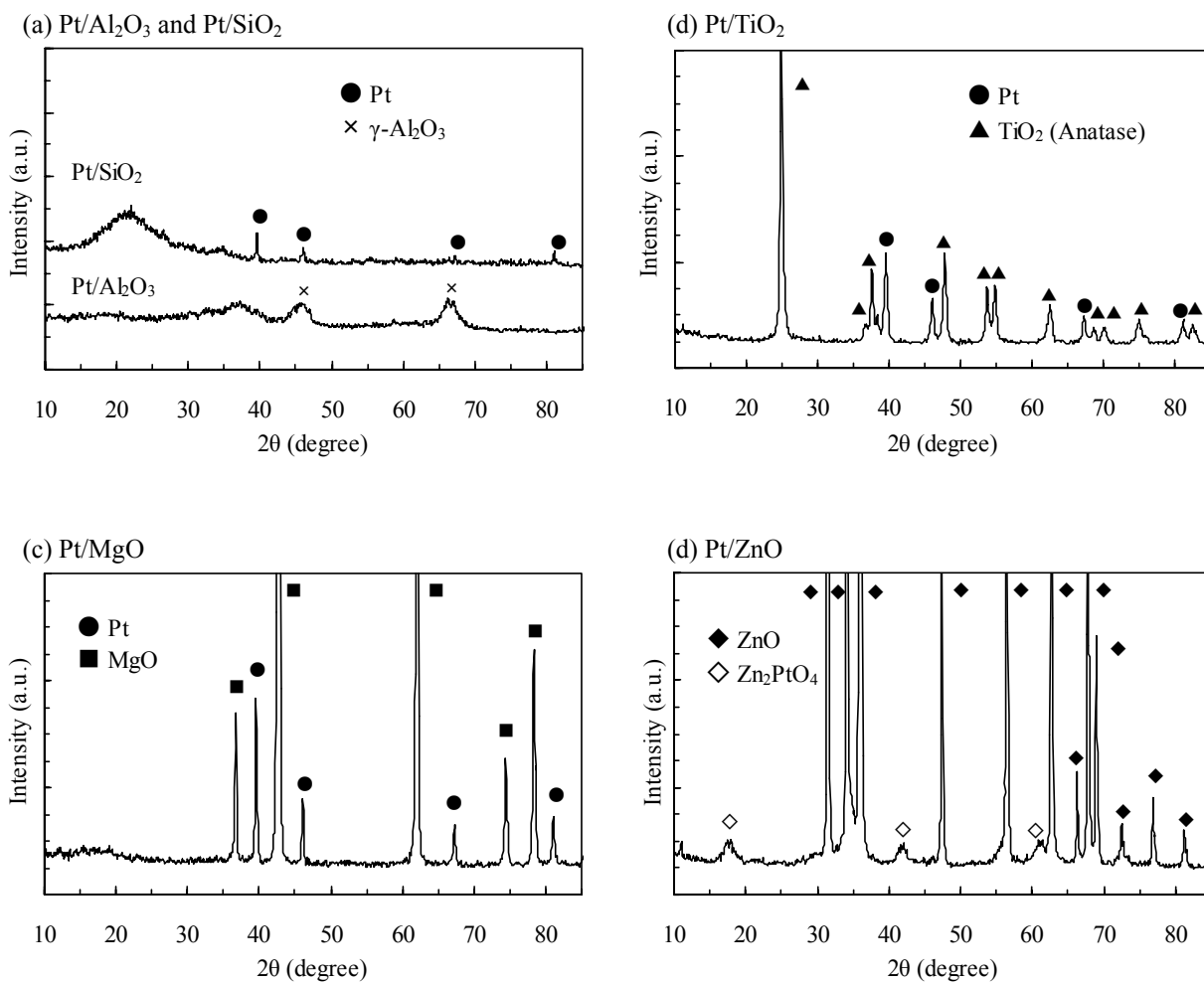


Fig. 7 XRD patterns of Pt supported on MO<sub>x</sub> (a) Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>, (b) Pt/TiO<sub>2</sub>, (c) Pt/MgO and (d) Pt/ZnO before reduction.

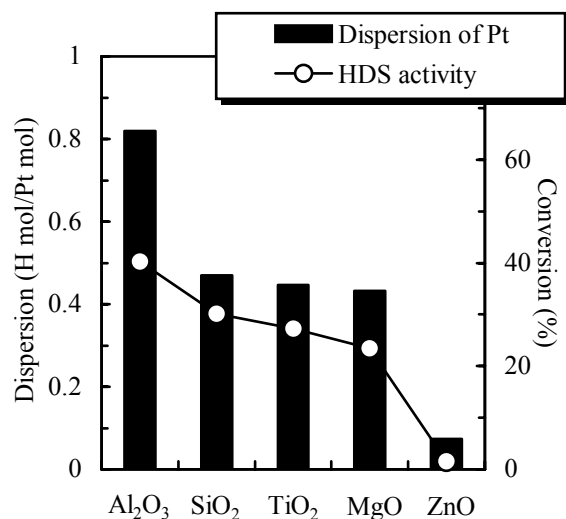


Fig. 8 Dispersion of Pt on MO<sub>x</sub> and HDS activities of Pt/MO<sub>x</sub> catalysts.

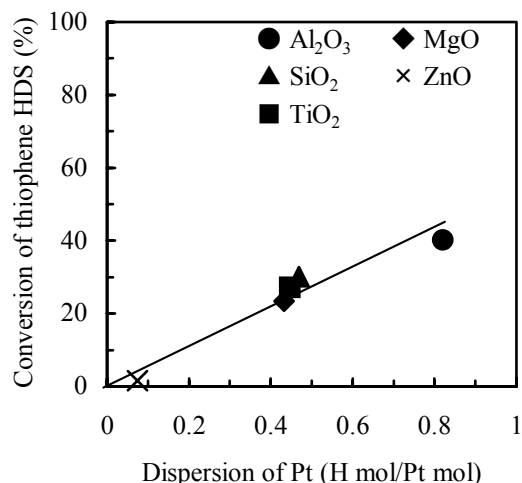


Fig. 9 Relationship between dispersion of Pt on MO<sub>x</sub> and HDS activities of Pt/MO<sub>x</sub> catalysts.

#### 4 CONCLUSION

It was found that HDS activities of Pt/MO<sub>x</sub> catalysts were not correlated to BET surface area and acid-base properties of MO<sub>x</sub>. However, the activities of Pt/MO<sub>x</sub> catalysts were strongly correlated to the dispersion of Pt on MO<sub>x</sub>. It is concluded that high dispersion of Pt on MO<sub>x</sub> supports is essential to prepare highly active MO<sub>x</sub>-supported Pt catalysts for the HDS of petroleum feedstocks.

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白金担持金属酸化物触媒によるチオフェンの水素化脱硫反応

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種々の金属酸化物( $\text{MO}_x$ ;  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{ZnO}$ )に担持した白金(Pt)触媒のチオフェン水素化脱硫(HDS)反応に対する活性( $350^\circ\text{C}$ )について検討した。担持白金触媒のHDS活性は常圧固定床流通式反応装置を用いて検討した。その結果, Pt/ $\text{MO}_x$ のHDS活性の序列はPt/ $\text{Al}_2\text{O}_3$  > Pt/ $\text{SiO}_2$  > Pt/ $\text{TiO}_2$  > Pt/ $\text{MgO}$  > Pt/ $\text{ZnO}$ となることがわかった。  $\text{MO}_x$ 担体の表面積, 酸塩基特性およびPtの分散度を窒素吸着法, 2-プロパノールの分解反応, XRDおよび水素吸着法で評価したところ, Pt担持 $\text{MO}_x$ 触媒のHDS活性は $\text{MO}_x$ のBET表面積および酸塩基特性には依存しないが, Ptの分散度に強く依存することが明らかとなった。

キーワード: 水素化脱硫, 金属酸化物, 貴金属, 担持白金触媒

\*応用化学科

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