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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 (MO_x ; Al_2O_3 , SiO_2 , TiO_2 , MgO and ZnO) for hydrodesulfurization (HDS) of thiophene were investigated. HDS activities of supported Pt catalysts were examined at 350°C by using conventional fixed bed flow reactor under atmospheric pressure. The order of HDS activities of Pt/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 MO_x supports and Pt/MO_x were evaluated by nitrogen adsorption, decomposition of 2-propanol (2-PA), XRD and hydrogen adsorption. It was revealed that HDS activities of Pt/MO_x catalysts were not correlated to BET surface area and acid-base properties of MO_x but these were strongly correlated to the dispersion of Pt on 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⁽¹⁾⁽²⁾. 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⁽³⁾⁽⁴⁾.

Supported noble metal catalysts have been proposed as new HDS catalysts⁽⁵⁾⁽⁶⁾⁽⁷⁾. We reported that noble metals, especially platinum, supported on zeolites⁽⁸⁾⁽¹⁰⁾⁽¹²⁾ and related materials⁽⁹⁾⁽¹¹⁾⁽¹³⁾⁽¹⁴⁾ 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 (MO_x) such as Al_2O_3 , SiO_2 , TiO_2 , MgO and ZnO for the HDS of thiophene as a model reaction of HDS of petroleum feedstocks.

2 EXPERIMENTAL

Pt/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°C for 4 hrs in air and were reduced at 450°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°C for 1 hr.

Hydrodesulfurization of thiophene over Pt/MO_x was carried out at 350°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°C in the HDS of thiophene. The 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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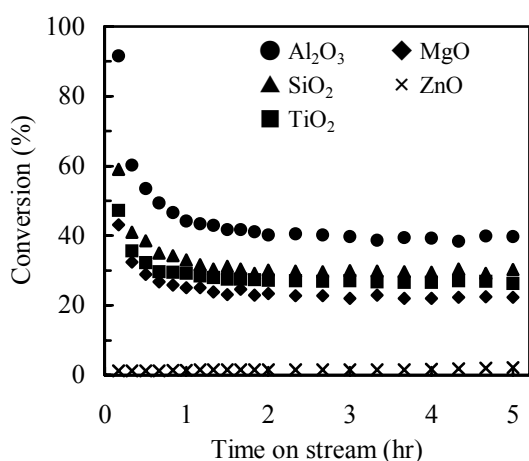
adsorption at liquid nitrogen temperature (-196°C). Acidic and basic properties of MO_x were evaluated by decomposition of 2-propanol (2-PA) using pulse reactor at 200°C . Helium was employed as a carrier gas. Dispersion of Pt on MO_x was measured by hydrogen adsorption method at 25°C . Catalysts were pretreated by evacuation at 500°C for 1 hr, and then reduced by hydrogen (200 Torr) at 450°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 MO_x for HDS of Thiophene

The catalytic activities of Pt supported on various MO_x such as Al_2O_3 , SiO_2 , TiO_2 , MgO and ZnO for the HDS of thiophene were examined at 350°C . It was found that $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst showed the highest initial activity among Pt/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 Pt/MO_x catalysts after reaction for 2 hrs was as follows: $\text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{SiO}_2 > \text{Pt}/\text{TiO}_2 > \text{Pt}/\text{MgO} \gg \text{Pt}/\text{ZnO}$.

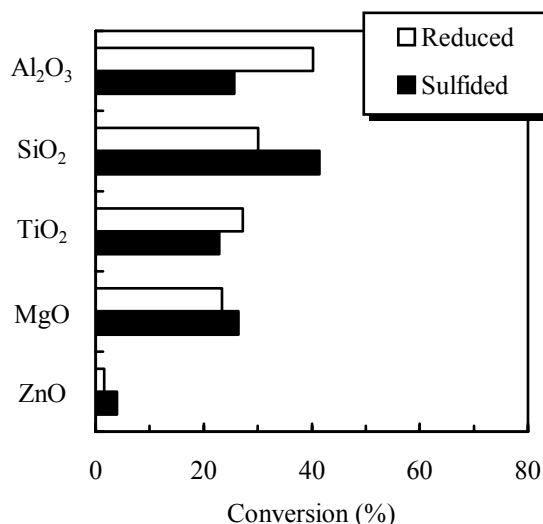
The reaction products in the HDS of thiophene over reduced $\text{Pt}/\text{Al}_2\text{O}_3$ were mainly C_4 hydrocarbons (butanes 93%, butenes 6%) and trace amount of C_1 - C_3 hydrocarbons as shown in Table 1. These results indicate that high catalytic activity of $\text{Pt}/\text{Al}_2\text{O}_3$ for thiophene HDS was attributed to high hydrogenating ability for unsaturated 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 Pt/MO_x catalysts at 350°C .

We reported in the previous paper⁽¹⁵⁾ that HDS activities of $\text{Rh}/\text{Al}_2\text{O}_3$ and Rh/SiO_2 catalysts were considerably enhanced by presulfiding treatment. Thus, we examined the catalytic activities of presulfided Pt/MO_x for HDS of thiophene at 350°C . The catalytic activity of Pt/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 Pt/MO_x were decreased ($\text{Pt}/\text{Al}_2\text{O}_3$, Pt/TiO_2) or hardly changed (Pt/MgO , Pt/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 MO_x for the HDS of thiophene at 350°C .

3.2 Characterization of MO_x Supports and Pt/MO_x Catalysts

3.2.1 BET Surface Area of MO_x

We also carried out the characterization of MO_x and Pt/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 MO_x and HDS activity of Pt/MO_x catalyst. Al_2O_3 and SiO_2 have high surface area (ca. $300 \text{ m}^2/\text{g}$). However, surface area of MgO and ZnO were lower than these of Al_2O_3 and SiO_2 . Figure 4 shows the relationship between BET surface area of MO_x and HDS activities of Pt/MO_x catalysts. These results indicate that HDS activity of Pt/MO_x was independent of BET surface area of MO_x as supports.

3.2.2 Acidic and Basic Properties of 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 MO_x can be evaluated by the decomposition of 2-PA. We examined the catalytic

activity and selectivity of various MO_x in the decomposition of 2-PA at 200°C. We found that Al_2O_3 showed high activity for the dehydration of 2-PA, but other MO_x showed very low activity for the decomposition of 2-PA as show in Fig. 5. These results indicate that Al_2O_3 has high acidity and other MO_x

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

Table 1 Product distribution over Pt/ MO_x catalysts in HDS of thiophene at 350°C.

Catalyst	HDS (%)	< C ₃ (%) ^{a)}	C ₄ (%) ^{b)}	C ₄ ⁼ (%) ^{c)}	1,3-C ₄ ⁼ (%) ^{d)}
Pt/ Al_2O_3 (reduced)	40.3	0.7	93.0	6.3	0.0
Pt/ Al_2O_3 (presulfided)	25.7	1.1	84.4	14.5	0.0
Pt/ SiO_2 (reduced)	30.1	1.0	71.7	27.3	0.0
Pt/ SiO_2 (presulfided)	41.4	0.3	77.3	22.4	0.0
Pt/ TiO_2 (reduced)	27.2	2.7	59.6	37.7	0.0
Pt/ 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) C₁-C₃ hydrocarbons, b) butanes, c) butenes, d) 1,3-butadiene

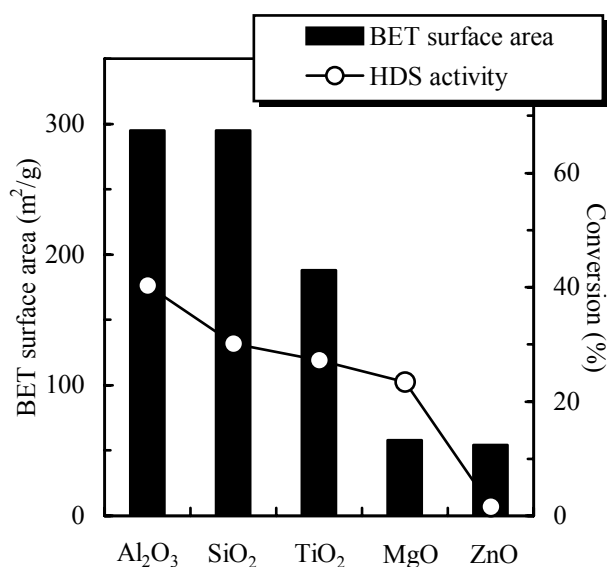


Fig. 3 BET surface area of MO_x and HDS activities of Pt/ MO_x catalysts.

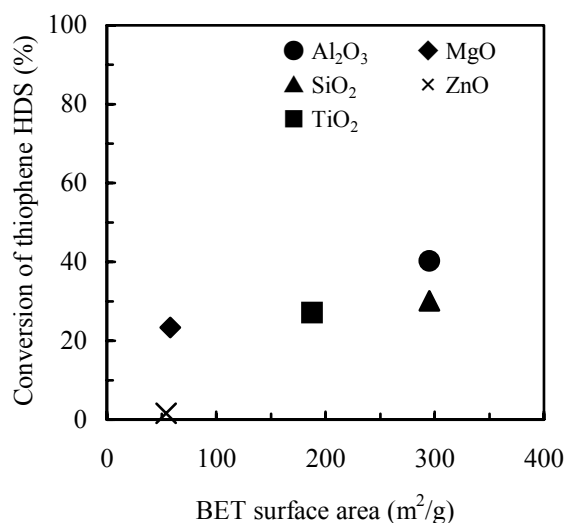


Fig. 4 Relationship between BET surface area of MO_x and HDS activities of Pt/ MO_x catalysts.

3. 2. 3 Dispersion of Pt on Metal Oxides

Figure 7 shows the XRD patterns of Pt/ MO_x catalysts before reduction. The peaks of Pt were not observed on Al_2O_3 , but these on SiO_2 were observed as shown in Fig. 7 (a). This indicates that the dispersion of Pt on Al_2O_3 was higher than that on SiO_2 . The peak height of Pt on TiO_2 and MgO was larger than that on 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 Zn_2PtO_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 MO_x .

Furthermore, we examined the dispersion of Pt on MO_x . Figure 8 shows the dispersion of Pt on MO_x measured by hydrogen adsorption method at 25°C. It was found that dispersion of Pt on MO_x was changed by the kind of MO_x . The order of the Pt dispersion on MO_x was as follows; Pt/ Al_2O_3 > Pt/ SiO_2 > Pt/ TiO_2 > Pt/MgO >> Pt/ZnO. This order was the same as that of the HDS activities of Pt/ MO_x catalysts. The catalytic activities of Pt/ MO_x were strongly correlated to the dispersion of Pt on MO_x as shown in Fig. 9. This means that HDS activity of Pt/ MO_x catalyst was remarkably controlled by the dispersion of Pt on MO_x supports.

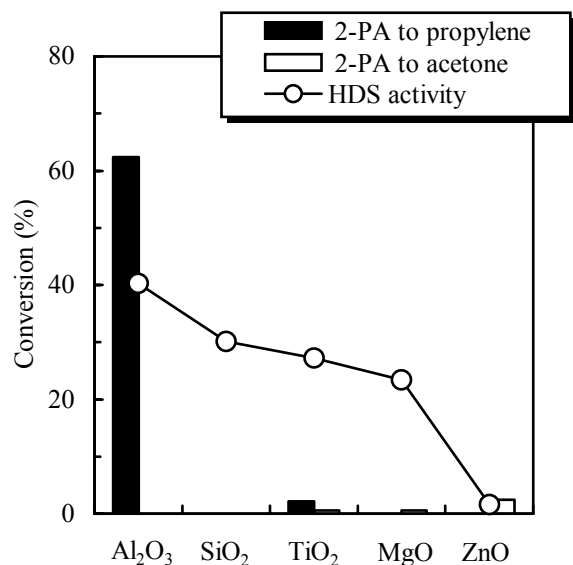


Fig. 5 Catalytic activities of MO_x for decomposition of 2-propanol (2-PA) and HDS activities of Pt/MO_x catalysts.

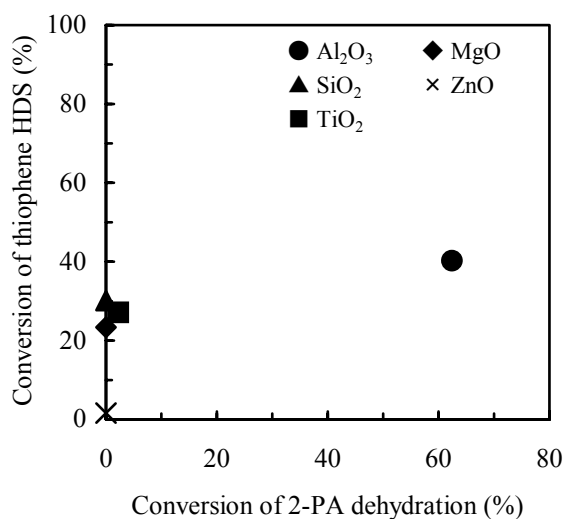


Fig. 6 Relationship between catalytic activities of MO_x for 2-propanol (2-PA) dehydration and HDS activities of Pt/MO_x catalysts.

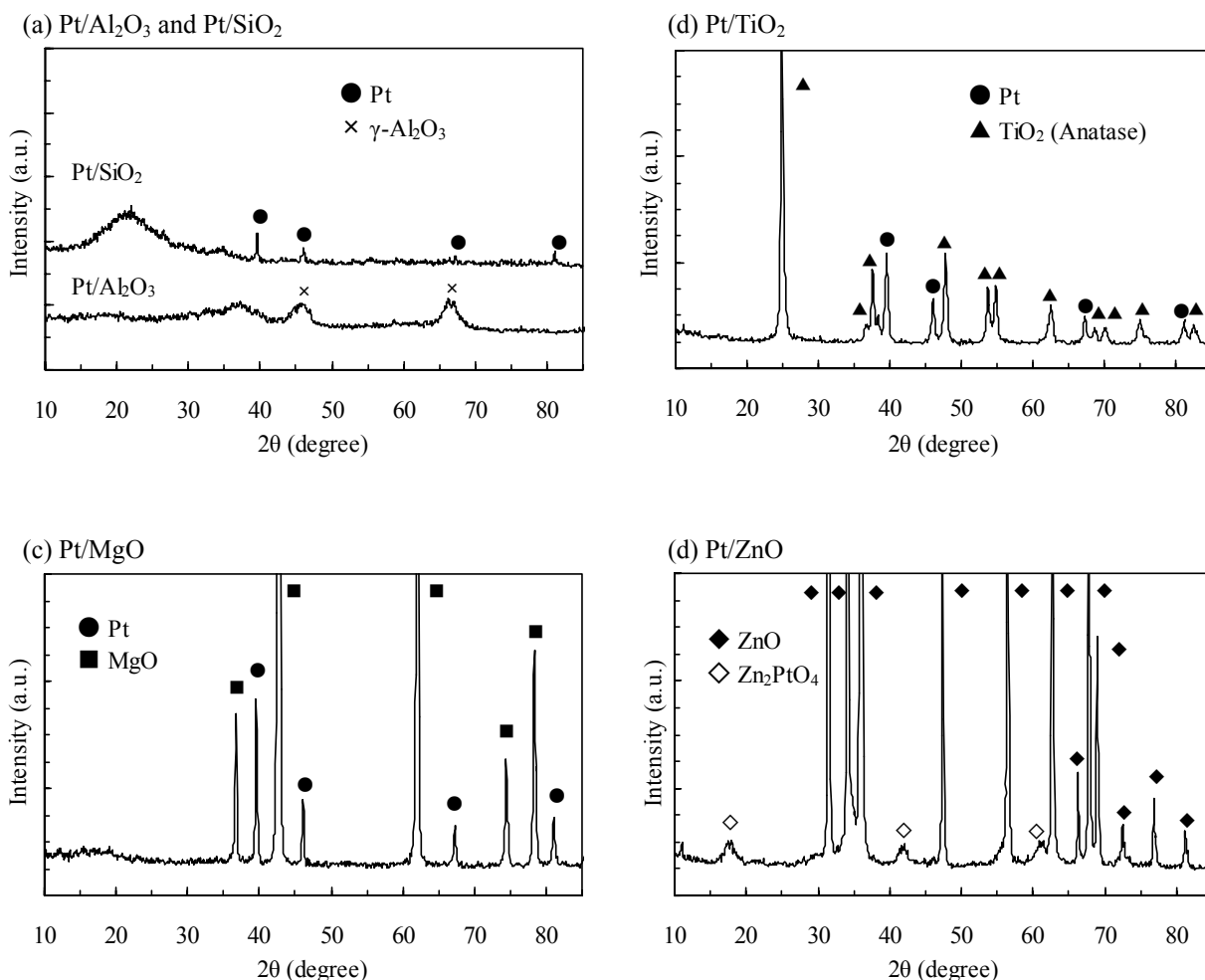


Fig. 7 XRD patterns of Pt supported on MO_x (a) Pt/Al₂O₃ and Pt/SiO₂, (b) Pt/TiO₂, (c) Pt/MgO and (d) Pt/ZnO before reduction.

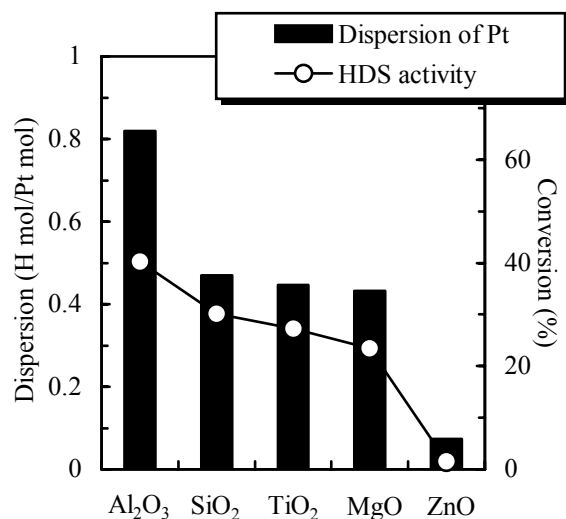


Fig. 8 Dispersion of Pt on MO_x and HDS activities of Pt/MO_x catalysts.

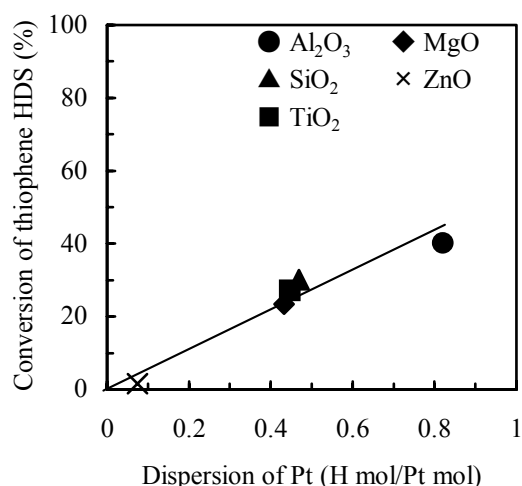


Fig. 9 Relationship between dispersion of Pt on MO_x and HDS activities of Pt/MO_x catalysts.

4 CONCLUSION

It was found that HDS activities of Pt/MO_x catalysts were not correlated to BET surface area and acid-base properties of MO_x. However, the activities of Pt/MO_x catalysts were strongly correlated to the dispersion of Pt on MO_x. It is concluded that high dispersion of Pt on MO_x supports is essential to prepare highly active MO_x-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

神田 康晴*, 小林 隆夫*, 上道 芳夫*, 杉岡 正敏*

種々の金属酸化物(MO_x ; Al_2O_3 , SiO_2 , TiO_2 , MgO , 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°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/ MO_x のHDS活性の序列はPt/ Al_2O_3 > Pt/ SiO_2 > Pt/ TiO_2 > Pt/ MgO > Pt/ ZnO となることがわかった。 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 MO_x 触媒のHDS活性は 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

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