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TiO_2-coated on Al_2O_3 support prepared by the CVD method for HDS catalysts

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Abstract

Mo–Co or Mo–Ni catalysts supported on alumina (Al_2O_3) have been widely used for hydrodesulfurization (HDS) of heavy petroleum fractions. In order to enhance the catalytic activities for HDS, a composite type support (TiO_2–Al_2O_3) prepared by the chemical vapor deposition (CVD) method has been studied. We found that Mo catalyst supported on TiO_2–Al_2O_3 showed much higher catalytic activity for HDS of dibenzothiophene derivatives than the catalysts supported on Al_2O_3.

Keywords: Mo–Co catalysts; Mo–Ni catalysts; Hydrodesulfurization

1. Introduction

The maximum allowed sulfur level of gas oil in Japan is currently to 0.5 wt.-%, but Japan will have to cut down the sulfur level to 0.05 wt.-% in 1997 to protect the environment from Diesel emissions. To meet this assignment, Japan has to develop a new catalyst for deep hydrodesulfurization (HDS) for gas oil that is available under mild conditions because of the cost requirements; a reaction temperature below 666 K would be preferable and the reaction pressure below 3.5 MPa would also be preferable.

Molybdenum oxide catalysts have been widely used in the petroleum industry for HDS and hydrocracking of heavy fractions of crude oil and for partial oxidation of aliphatic alcohol, polymerization, metathesis, isomerization and hydrogenation of alkenes. TiO_2-supported molybdena catalysts have become important due to their higher reducibility to a lower valence state of Mo, and because their HDS and hydrocracking were higher than those of Al_2O_3-supported molybdena catalysts [1]. The HDS of thiophene over the surface Mo species on TiO_2 possessed higher turnover numbers than the catalyst supported on Al_2O_3. The catalytic activity and selectivity were strongly dependent on the surface morphology [2].

However, TiO_2 supports have small specific areas and hard to make pellet. If we can create TiO_2 over-layers coated on Al_2O_3 supports, the catalytic activity for HDS may overcome the drawbacks of TiO_2 supports. We studied how to

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prepare composite types of TiO_2–Al_2O_3 support by chemical vapor deposition (CVD) method of $TiCl_4$ on the substrate. Then we have studied deep HDS of dibenzothiophene derivatives (dibenzothiophene: DBT, 4-methyldibenzothiophene: 4-MDBT, 4,6-dimethyldibenzothiophene: 4,6-DMDBT) as a model reaction under the mild conditions. Since dibenzothiophene derivatives are key sulfur compounds in the gas oil fraction, those molecules were relatively less active for HDS reactions [3].

2. Experimental

2.1. Catalyst preparation

The titania (TiO_2) support in this study was P-25 titania from Degussa, with surface area of ca. 51 m^2 g^{-1}. Alumina (Al_2O_3) support was JRC-ALO-4 alumina with a surface area of ca. 163 m^2 g^{-1}. (JRC: Japan Reference Catalyst). The composite type of TiO_2–Al_2O_3 support was prepared by the CVD method of $TiCl_4$ on Al_2O_3. Five grams of Al_2O_3 (JRC-ALO-4) substrate was placed into a quartz tubular reactor and pretreated 773 K under N_2 flow for 5 h, then cooled down to 473 K. The sample was exposed to $TiCl_4$ vapor at 473 K for 2–10 h, when $TiCl_4$ vapor was mixed with N_2. Then, the sample was hydrolyzed by water vapor with N_2 at 473 K for 2 h, followed by calcination under O_2 stream at 773 K for 2 h. Supported molybdena catalysts in this study were prepared by an equilibrium adsorption method [4,5]. Five g of support was impregnated at 323 K for 100 h with 0.007 N aqueous solution of ammonium heptamolybdate. The pH of the solution was adjusted with HNO_3 or NH_4OH solution. The suspended solution was occasionally shaken in a thermostat bath. After adsorption, the solids were separated from the solution by filtration. All the wet catalysts were dried at 373 K for 24 h and then calcined in air at 773 K for 24 h. The adsorbed amounts of molybdena (wt.-% MoO_3) were determined by XPS and XRF analysis.

2.2. Hydrodesulfurization reaction

HDS was carried out by using a high pressure flow reactor. The reactor was a 8 mm ID stainless steel tube packed with 200 mg catalyst diluted with quartz sand. The catalyst was dried at 773 K for 10 h under O_2 stream and was presulfided with a mixture of 5% H_2S in H_2 under atmospheric pressure at 573 K for 2 h. After pretreatment, the reactor was pressurized by H_2 at 3 MPa, then the reactant solution was carried out under the following conditions: reaction temperature, 573 K; LHSV, 5–6 h^{-1} and H_2 flow rate, 0.2 dm^3 min^{-1}. The initial concentration of DBT or mixture of DBT/4MDBT/4,6-DMDBT (1/1/1, mol base) in n-dodecane solution is 0.15 wt.-% at *S* base. After the HDS reaction reached steady state, the liquid products were collected from a gas–liquid separator and were analyzed by GC (FID). DBT, 4-MDBT and 4,6-DMDBT were synthesized by a method described by Gerdil and Lucken [6].

3. Results and discussion

3.1. Preparation of TiO_2–Al_2O_3 supports

We found that molybdena catalyst supported on TiO_2 showed much higher catalytic activity for HDS of DBT than catalysts supported on Al_2O_3. Ramirez and co-workers found that the HDS activity for thiophene was much higher than for Al_2O_3 [7]. However, TiO_2 supports have small specific areas [3]. If we can create TiO_2 over-layers coated on Al_2O_3 supports, the catalytic activity for HDS may overcome the drawbacks of TiO_2 support.

Table 1 shows surface properties of composite TiO_2-supports prepared by CVD method. The γ-Al_2O_3 was exposed with a gas flow of $TiCl_4$ in N_2 at a constant flow rate at different exposure time (2–10 h). After adsorption of $TiCl_4$, the sample was hydrolyzed by water vapor at 473 K for 2 h, then calcined under an

Table 1
Surface properties of TiO_2–Al_2O_3 as a function of exposure time of $TiCl_4$

Entry	Support	Exposure time/h [a]	TiO_2 (bulk)/wt.-% [b]	Ti 2p/Al 2p [c]	Specific area/m^2 g^{-1} [d]
1	Al_2O_3	0	0	–	163
2	TiO_2–Al_2O_3	2	2.3	0.031	157
3	TiO_2–Al_2O_3	4	4.2	0.044	154
4	TiO_2–Al_2O_3	6	7.7	0.073	150
5	TiO_2–Al_2O_3	8	10.8	0.096	147
6	TiO_2–Al_2O_3	10	11.0	0.110	145

[a] Alumina substrate (γ-Al_2O_3) exposed to $TiCl_4$ vapor at 473 K for 2–10 h.
[b] Determined by X-ray fluorescence analysis.
[c] Determined by X-ray photoelectron spectroscopy.
[d] Determined by N_2 adsorption (BET method).

O_2 stream at 773 K for 2 h. The bulk (XRF) and surface (XPS) composition of TiO_2 increased almost linearly with increasing exposure time. The adsorbed amounts of TiO_2 on Al_2O_3 are strongly dependent on the exposure time of $TiCl_4$. The specific area was decreased slightly with increasing exposure time. The results suggest that TiO_2 species are homogeneously dispersed over the external surfaces of γ-Al_2O_3.

Fig. 1 shows the pore size distribution of the supports before or after CVD treatments determined by N_2 adsorption. After CVD treatment, pore size distribution did not change significantly; only a small decrease of pore volume was observed after CVD treatment.

The IR spectra in Fig. 2 show the changes in the hydroxyl region as the loading of TiO_2 was increased over the Al_2O_3 substrate. The integrated intensities of the alumina O–H stretch region were decreased with increased loading of TiO_2. It is quite interesting that the relatively strong high frequency band of Al_2O_3 at about 3762 cm^{-1} was nearly completely eliminated at the early stage of CVD, then decreased the intensities of other hydroxyl groups at lower frequencies of O–H stretching of Al_2O_3. These spectra confirm that the Al_2O_3 hydroxyl groups are eliminated as they are replaced by a titania species during the CVD treatment. The gradual

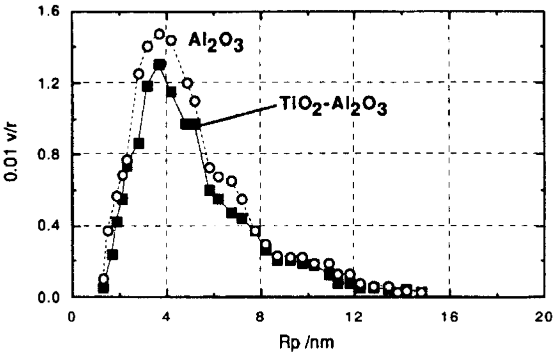


Fig. 1. Pore size distribution of γ-Al_2O_3 and composite TiO_2–Al_2O_3: TiO_2–Al_2O_3 was prepared by the CVD method for 8 h (TiO_2: 10.8 wt.-%).

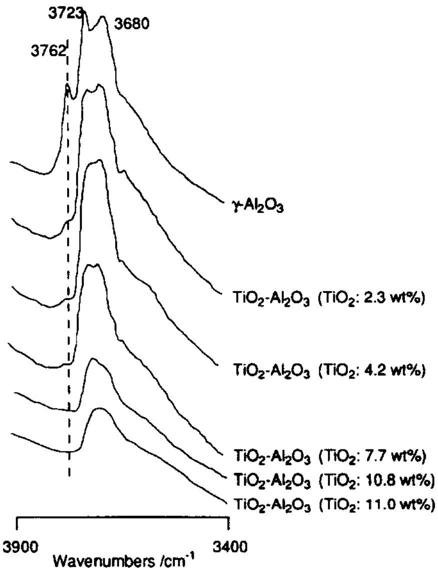


Fig. 2. IR spectra of the O–H region from the TiO_2–Al_2O_3 composite with increasing TiO_2 loading.

to almost complete replacement of hydroxyl groups is evident [8]. This information coupled with the data of Table 1 and Fig. 1 suggested that Ti atoms may be associated with the Al_2O_3 surface and may create Ti–O–Al bondings on the surface.

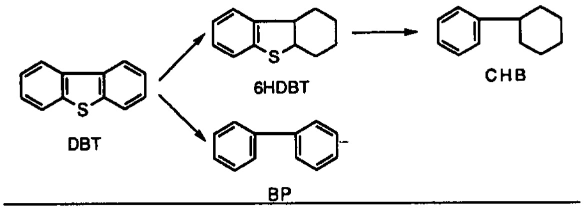
3.2. HDS reactions for dibenzothiophene derivatives

Although HDS of petroleum residues is widely practiced, the catalyst developments for HDS of gas oil fraction is in need for a similar technology. There are only a few published materials reporting the TiO_2 support effect for HDS catalysts [1,2,7,9–11]. Table 2 shows the catalytic activity for HDS of DBT over Mo catalyst supported on Al_2O_3, TiO_2 and TiO_2–Al_2O_3. The major product was biphenyl (BP) and cyclohexylbenzene (CHB) followed. We found that the Mo catalyst supported on TiO_2–Al_2O_3 prepared by CVD method showed much higher activity for HDS than the catalysts supported on Al_2O_3. When a composite type TiO_2–Al_2O_3 support, prepared by a normal impregnation method, was used the catalytic activity for HDS was less active than with the supports prepared by CVD method.

Table 3 shows the catalytic activity for HDS of dibenzothiophene derivatives (DBT, 4MDBT, 4,6-DMDBT) over Mo catalyst supported on Al_2O_3, TiO_2 and TiO_2–Al_2O_3. For these model reactions, the reactant solution was an equal mol of DBT, 4-MDBT and 4,6-DMDBT dissolved in n-dodecane (*S*: 0.15 wt.-%). The sequences of reactivities of sulfur compounds are DBT > 4-MDBT > 4,6-DMDBT. This results are confirmed from previous reports on the Co–Mo/Al_2O_3 system [3,12]. We found that Mo catalyst supported on composite TiO_2–Al_2O_3 showed much higher activity for HDS, especially for the HDS of 4,6-DMDBT.

The catalytic activity and selectivity are strongly dependent on the surface morphology [2]. Mo species supported on TiO_2–Al_2O_3 were sulfided to create coordinatively unsaturated site of surface MoS_2 at lower temperature region more easily than that of Al_2O_3 supports. Especially, Ni–Mo catalyst supported on TiO_2 showed much higher activities even for the HDS of 4,6-DMDBT, which hardly react with the active site of Ni–Mo/Al_2O_3. The results

Table 2
Catalytic activities for HDS [a] of Dibenzothiophene (DBT) [b]



Catalyst [c]	Conversion/%	Selectivity/%		
		BP	CHB	6HDBT
Mo/Al_2O_3	64.4	73.0	26.8	0.2
Mo/TiO_2	92.0	73.2	26.8	0.0
Mo/TiO_2–Al_2O_3 (CVD) [d]	97.5	73.4	26.4	0.2
Mo/TiO_2–Al_2O_3 (IMPREG) [d]	66.8	71.0	28.4	0.6

[a] Reaction conditions: reaction temperature: 573 K, Pressure: 3 MPa, LHSV = 5–6 h^{-1}.

[b] DBT was dissolved in n-dodecane (*S*: 0.15 wt.-%).

[c] MoO_3 loading is 6 wt.-% prepared by an equilibrium adsorption method.

[d] TiO_2 loading of TiO_2–Al_2O_3 support is 10.8 wt.-% prepared by the CVD method and an impregnation method (IMPREG).

Table 3
Catalytic activities for HDS [a] of DBT, 4-MDBT and 4,6-DMDBT [b]

Catalyst [c]	Conversion/%		
	DBT	4-MDBT	4,6-DMDBT
Mo/Al_2O_3	65.9	38.6	18.3
Mo/TiO_2	95.9	79.7	32.1
Mo/TiO_2–Al_2O_3 (CVD) [d]	85.9	70.0	49.6
Mo/TiO_2–Al_2O_3 (IMPREG) [d]	74.1	50.5	32.3
Ni–Mo/TiO_2	96.0	91.0	57.6

[a] Reaction conditions: reaction temperature: 573 K, Pressure: 3 MPa, LHSV = 5–6 h^{-1}.

[b] Equal mol of DBT, 4-MDBT and 4,6-DMDBT were dissolved in n-dodecane (*S*: 0.15 wt.-%).

[c] MoO_3 loading is 6 wt.-% prepared by an equilibrium adsorption method.

[d] TiO_2 loading of TiO_2–Al_2O_3 support is 10.8 wt.-% prepared by the CVD method and an impregnation method (IMPREG).

give quite important information for the future development of HDS catalyst of gas oil.

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