Preparation of metal sulfide catalysts supported on mesoporous and amorphous silica uniformly coated with TiO_2 and ZrO_2

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Abstract: Mesoporous silicas (MSs) and amorphous silicas (ASs) coated with TiO_2 or ZrO_2 layer were used as supports to prepare metal sulfide catalysts for hydrodesulfurization (HDS) of sulfur-containing aromatics. The TiO_2 coating on MSs and ASs of the catalysts increased HDS activity of 4,6-dimethyldibenzothiophene (4,6DMDBT), however, did not by the ZrO_2 coating. This difference in the activity between TiO_2 and ZrO_2 coating was attributed to the enhancement of hydrogenation ability from the correlation with the naphthalene hydrogenation activity of the catalysts.

Keywords: Mesoporous silica, TiO_2 coating, hydrodesulfurization

1. Introduction

Supported metal sulfides have been used as hydrodesulfurization (HDS) catalysts. It is well known that the HDS activities of Mo sulfide catalysts are greatly affected by the support, namely, support effect. However, it is difficult to understand the effects of the support on the catalytic activity because the oxide materials used as supports (Al_2O_3, SiO_2, TiO_2 etc.) are inherently heterogeneous and have different surface areas. Preparation of oxides with high surface is considered a great way to overcome these problems by the coating of surface of amorphous silicas (ASs) or mesopore walls of the mesoporous silicas (MSs) with the oxide layers. Detailed studies of the effects of the support on HDS performance using silica materials coated with oxides are promising for the clarification of support effect of HDS catalysts.

In this study, the TiO_2- and ZrO_2-coated silica materials were applied to catalyst supports for HDS of sulfur-containing aromatics to investigate the support effect of TiO_2- and ZrO_2-supported Mo sulfide catalysts on the catalytic properties for the HDS reaction. Furthermore, we will report the effect of TiO_2- and ZrO_2-coat of the Mo sulfide catalysts on the hydrogenation activity of aromatic compounds.

2. Experimental

CARiACT Q-10 was used as an AS. MSs having mesopores with the diameter of ca. 7 nm was prepared as previously reported [1] using triblock copolymer (Pluronic P-123 $EO_{20}PO_{70}EO_{20}$), tetraethoxysilane. The TiO_2 and ZrO_2 coating on ASs and MSs was carried out according to the procedure in our previous study [1]. The dried MS or AS was dispersed in a dry toluene by sonication. Titanium tetraisopropoxide (Ti/Si = 0.30) or zirconium tetra-n-butoxide in a dry toluene was added dropwisely to the suspension under dry N_2, and the mixture was stirred and washed. The coated silica was dried and calcined to remove the alkoxy groups. This coating procedure was repeated up to 3 times.

Mo oxide catalysts supported on the synthesized mesoporous materials (MoO_3/support) were prepared by a conventional impregnation method using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AHM) as precursor [1, 2]. The catalyst was dried at 100 °C for 16 h and calcined at 500 °C for 5 h. The Mo loading was fixed at 10wt% MoO_3. The MoO_3/support catalyst thus prepared was presulfided at 350 °C for 3 h in a 10% H_2S/H_2 flow at an atmospheric pressure.

The HDS reaction of 4,6-dimethyl-dibenzothiophene (4,6DMDBT) was carried out by batch mode using an autoclave reactor [1, 2]. The sulfided catalyst was suspended in a reactant solution (0.5wt% 4,6-DMDBT solved in tetrahydronaphthalene) in a glove bag filled with N_2. Then suspension was transferred to an autoclave in the glove bag. The HDS reaction was carried out 330 °C for 4,6-DMDBT. The initial H_2 pressure was 2.0 MPa and the reaction time was 3h. In order to understand the interaction between MoS_2 and the support, naphthalene hydrogenation (HYD) reaction was carried out by the same procedure as above using a reactant solution (1.0wt% naphthalene solved in n-decane) at 300 °C. The reactant and products were analyzed by a gas chromatography equipped with an FID detector. The conversion of DBT and 4,6-DMDBT and naphthalene was calculated from the decreased amount of the reactant.

3. Results and discussion

Table 1 shows the catalytic activities of Mo sulfide catalysts supported on AS and MS for the HDS of 4,6-DMDBT. The Mo/AS without oxide coating did not exhibit the HDS activity. However, Mo/AS coated with TiO_2 three times showed a higher activity, indicating the effectiveness of the TiO_2 coating over AS surface on the HDS activity as with the case of SBA-15 as reported previously[1]. Note that the HDS activity of Mo/MS is higher than that of AS for three times TiO_2 coatings, indicating better dispersion of Mo sulfide of Mo/MS due to high surface area. On the other hand, Mo/AS coated with ZrO_2 showed no HDS activity regardless of the number of coating. Mo/AS coated with ZrO_2 one time also showed no HDS activity. These results suggest strong support effect of Mo sulfide catalysts on HDS activity.

In the case of HDS of 4,6-DMDBT, the two methyl groups inhibit the interaction of the sulfur atom with the active site. Therefore, 4,6-DMDBT favors the hydrogenation (HYD) reaction pathway instead of the direct desulfurization (DDS) one because steric hindrance could be avoided[3]. According to our previous study, it is suggested that hydrogenation activity of catalysts for aromatic compounds is correlated with 4,6-DMDBT HDS activity[1]. To clarify the contribution of TiO_2 to reaction pathway for 4,6-DMDBT, reaction naphthalene HYD was carried out for the MS with hybridized coating TiO_2 and ZrO_2. The results were summarized in Table 2. In Table 2, Zr-Zr-Ti represents two times coating with ZrO_2 followed by TiO_2 coating. Table 2 clearly indicates lower HDS and HYD activity of Mo/MS/Ti-Ti-Zr exposing ZrO_2 on the support surface. On the other hand, Mo/MS/Ti-Ti-Zr exposing TiO_2 on the support surface showed higher HDS and HYD activity, indicating acceleration of HDS reaction through HYD pathway for or4,6-DMDBT.

Table 1. HDS activity of Mo sulfide catalysts supported on AS and MS for the HDS of 4,6-DMDBT

catalyst	coat		4,6DMDBT Conversion/%
	oxide	number	
Mo/AS	-	-	0.0
	TiO_2	1	0.0
		3	8.0
	ZrO_2	1	0.0
		3	0.0
Mo/MS	-	-	0.94
	TiO_2	3	21.3
	ZrO_2	1	0.0

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Table 2. Catalytic activities of Mo sulfide catalysts supported on MS with hybridized coating of TiO_2 and ZrO_2 for the HDS of 4,6-DMDBT and HYD of Naphthalene

catatyst	4,6DMDBT Conversion/%	Naphthalene Conversion/%
Mo/MS /Zr-Zr-Ti	8.74	29.9
Mo/MS /Ti-Ti-Zr	0	19.7

4. Conclusions

1. The TiO_2 coating of AS increased the HDS activity for 4,6-DMDBT HDS as well as MS, while The ZrO_2 coating of AS and MS did not show HDS activity for 4,6-DMDBT.
2. The improved HYD ability by TiO_2 coating increase of HDS activity for 4,6-DMDBT but Mo sulfide supported on SiO_2 or ZrO_2-coated surface showed low HYD ability leading to poor HDS activity.

References

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