High Surface Area Smectite Supported Cobalt Oxides as Active Catalysts for Thiophene Hydrodesulfurization

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Cobalt oxide loaded on high surface area smectites are prepared and tested in a pulse flow reactor for thiophene hydrodesulfurization (HDS). Smectites used were montmorillonite, saponite, porous saponite, hectorite and stevensite. Co-porous saponite showed the highest activity among Co-smectites, Co/Al_2O_3, and $CoMo/Al_2O_3$ so far studied. It suggests that the property of smectite has an influence on the catalyst activity.

Generally, HDS catalyst applied in industry are derived from oxides of an element of Group VIB (Mo or W) and Group VIII (Co or Ni) supported on γ-alumina. Catalytic activity is supposed to be connected with the presence of Group VIB elements while Group VIII elements are believed to act as promoters. However, it has been reported recently that only cobalt or nickel oxide loaded on some supports shows higher HDS activity than $CoMo$-Al_2O_3 catalysts as a few studies.[1-3] Duchet et. al. has reported the high HDS activity of carbon-supported cobalt sulfide.[1] In another report, Kloprogge et al. prepared nickel sulfide supported on Al-pillared montmorillonite catalysts and this catalyst showed a high thiophene HDS activity.[2] In a recent study, Sychev et al. has prepared chromia pillared montmorillonite from Na- and Ca-cationic forms of montmorillonite, and activated this in stream of H_2S/H_2 mixture gas. This showed high activity for thiophene HDS and the consecutive hydrogenation of butenes.[3] In the above references, montmorillonite is a well known clay used as catalyst support. However, other smectite clay minerals (saponite, hectorite, stevensite and so on) have not been used as a support of HDS catalyst in spite of their high surface areas. We investigated a series of cobalt oxide loaded smectite clay (Co-smectite) for HDS.

The montmorillonite (KUNIPIA F), saponite, porous saponite, hectorite and stevensite were obtained from KUNIMINE KOGYO Co. Ltd.. KUNIPIA F is a purified montmorillonite from natural clay and the others are synthesized ones. The synthetic clays were used for catalyst supports without further pretreatment.

Cobalt nitrate solution ($Co(NO_3)_2\ 6H_2O$ 29.0 g and distilled water 500 ml) was aged at 80 °C for 2 h. Ten g of smectite support was added to this solution and stirred at 80 °C for 1.5 h. The precipitated product thus obtained was filtered and washed by distilled water (500 ml) and ethanol (500 ml). The washed product was dried overnight at 120 °C and calcined overnight at 400 °C.

Co/Al_2O_3 or Co-Mo/Al_2O_3 catalysts were prepared by incipient wetness method with cobalt nitrate or cobalt nitrate and ammonium heptamolybdate. After impregnation, the catalyst was dried at 120 °C and calcined at 400 °C for 16 h.

Hydrodesulfurization experiments were carried out in a pulse flow reactor. Prior to the activity test, the catalyst (sample weight 0.1 g) was sulfided in-situ with a mixed gas flow (60 ml/min, 2 kg/cm^2) of 95% hydrogen and 5% hydrogen sulfide at 400 °C for 2 h. After sulfidation of the catalyst, the temperature and the gas flow rate were changed to the reaction condition (300 °C, H_2 60 ml/min, 2 kg/cm^2). The thiophene (0.3 ml) was injected and its conversion was measured by an on-line gas chromatograph. The major product of this reaction was C4 gas and the yields of by-products (C1, C2 and C3) were less than 1%. The material balance of reactant and product confirmed by the total GC peak area was more than 99%. The HDS performance of the catalyst was determined after the pulse reaction condition had been stabilized.

Table 1. Characterization of Co-Smectite catalysts

Support	BET surface area (m^2/g)	Total pore volume (ml/g)
Montmorillonite	26	0.027
Co-Montmorillonite	36	0.033
Saponite	224	0.21
Co-Saponite	240	0.21
porous-Saponite	514	0.42
Co- porous-Saponite	510	0.43
Hectorite	174	0.15
Co-Hectorite	278	0.25
Stevensite	250	0.20
Co-Stevensite	407	0.36
Co-Al_2O_3	203	0.42
$CoMo$-Al_2O_3	188	0.34

The surface area and the pore volume of catalysts were analyzed by means of nitrogen adsorption using NOVA 1200 (Quanta Chrome Corporation), and shown in Table 1.

Table 2 shows the thiophene HDS activity of Co-smectite catalysts at three levels of reaction temperature (300 °C, 350 °C and 400 °C). The smectite-supported catalyst shows higher activity than the alumina-supported catalyst. It is emphasized that Co- porous saponite has the highest activities in smectite-supported samples. Particular attention should be paid to the fact

Table 2. HDS activity of Co-Smectite catalysts

Support	Loaded metal as oxide (wt%)	Thiophene conversion/%[a]		
		300 °C	350 °C	400 °C
Montmorillonite[b]	3.1	25.7	50.7	69.6
Saponite[c]	5.0	73.1	78.5	86.2
porous-Saponite[c]	7.7	92.7	96.0	97.9
Hectorite[c]	7.8	67.0	80.0	88.5
Stevensite[c]	8.6	57.5	71.9	81.1
Al_2O_3	4	7.4	14.7	22.0
—	100[d]	7.2	11.5	17.2
Al_2O_3	Co 4 wt% Mo15 wt%	85.0	97.0	98.3

[a] Calculated from unreacted thiophene peak area of GC.
[b] Commercial montmorillonite, "KUNIPIA F".
[c] These clays were provided by KUNIMINE KOGYO Co. Ltd.
[d] Cobalt oxide was used as catalyst.

that at low reaction temperature (300 °C), HDS activity (92.7%) of this catalyst is higher than that (85.0%) of CoMo-Al_2O_3 which is known to be highly active for HDS.

The amount of loaded cobalt varies in each support, that is difficult to compare the activities directly. One can say smectites are capable to load more than 5 wt% of cobalt oxide and these smectite supports might have high cation exchange ability. As shown in Table 1, smectite supports except montmorillonite have higher BET surface area and higher pore volume than those of alumina support. These catalyst characteristics are one of the reasons for increasing HDS activity. However, HDS activity of hectorite is higher than that of stevensite, whereas surface area, pore volume and amount of loaded cobalt oxide of stevensite are higher than those of hectorite. The facts suggest that HDS activity is determined by not only the support characteristics above, but also another factor such as sulfiding behavior of cobalt oxide and dispersion of cobalt sulfide on smectite clay which might influence HDS reaction activity.

Results obtained by several investigators show that, on a unit surface area basis, unsupported Co_9S_8 are at least as active in the HDS of thiophene or dibenzothiophene.[4] On alumina the Co_9S_8 phase is probably poorly dispersed since its formation very probably arises from the sulfidation of Co_3O_4 aggregates or crystals present in the calcined oxidic precursor. In view of the high HDS activity as shown in Table 2, it is reasonable to assume that sulfurized Co-smectite catalysts contain highly dispersed cobalt sulfide in active state.

In conclusion, catalysts of cobalt oxide on high surface smectite was found to be one of very promising catalysts, especially for HDS reaction. Detailed characterization is required to explain the observed differences in catalytic activity for HDS in a further study.

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