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In-situ FT-IR Study of Nitric Oxide Adsorbed on Sulfided Co-Mo/Al_2O_3 Catalyst

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Infrared study was made of NO adsorbed on Co-Mo/Al_2O_3 catalyst subjected to sulfidation/reduction pretreatments. Both Co and Mo served as a site for NO adsorption. The amount of the adsorption depended on the pretreatment and was in the following order: sulfided > sulfided-then-reduced > reduced-then-sulfided > untreated. Higher adsorptive capacity coincided with higher hydrogenation activity.

Cobalt promoted molybdenum catalysts supported on alumina, in their sulfided states , are currently used in the hydrotreatment of petroleum fractions, and are considered prospective for use with the upgrading of coal-derived liquids. Although a variety of Co-Mo/Al_2O_3 catalysts have been a subject of fundamental studies,1) active structure of the catalyst components, involved in those reactions mentioned, still remains controversial. The present paper deals with the results of IR spectrometry of NO adsorption on Co-Mo/Al_2O_3 catalyst, in which NO was used as a probe molecule to diagnose catalyst's surface.2-4) We also try to correlate the adsorptive character of the catalyst to its hydrogenation activity.

Powder diffuse reflectance spectrometry in the infrared region was adopted, because of easier sample preparation and versatility toward colored materials. Illustrated in Fig.1 is the IR cell designed specially for in-situ measurement at elevated temperatures under flow-system. KBr window was mounted between air-tight graphite O-rings to prevent the window from mechanical breakage. A commercial Co-Mo/Al_2O_3 catalyst (4.4 wt% CoO and 14.9 wt% MoO_3), KF-742 supplied from Nippon Ketjen Co., was used as base material. Finely powdered catalyst sample (80 mg, 200 mesh under), placed in the IR cell, was sulfided with 5%H_2S/H_2 and/or reduced with H_2 at 400 °C for 5 h, followed by flushing the cell with Ar. The adsorption of NO was carried out at room temperature for 1 h. After thoroughly replacing the gas phase NO with Ar, IR spectra of the strongly adsorbed NO were measured using JIR-100 FT Spectrometer.

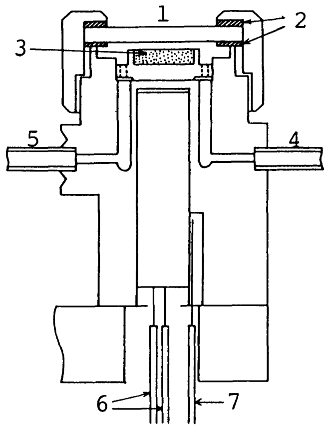

Fig.1. Side view of the cell: 1, KBr window; 2, graphite O-rings; 3, sample; 4, gas in-let; 5, gas out-let; 6, heater; 7, thermo-couple.

Figure 2 shows the IR spectra of NO adsorbed on Co-Mo/Al_2O_3 pretreated under three distinctly different procedures. In every cases studied, absorption emerged at 1720, 1820, and 1890 cm^{-1} (spectra b, c, d).

From a comparison with the spectra observed with NO adsorbed on Mo/Al_2O_3 and Co/Al_2O_3,5) we tentatively assign the low frequency band (1720 cm^{-1}) and the high frequency band (1890 cm^{-1}) as being due to NO adsorbed in a dimeric form on Mo and Co, respectively. The absorption around 1820 cm^{-1} may be ascribed to adsorbed NO on both Mo and Co. Also included in Fig.2 for comparison is the spectra observed with fresh catalyst (spectra a)). No characteristic absorption was recorded in the latter instance. Furthermore, no noticeable absorption was observed for the H_2-treated catalyst. As shown in Fig.2, signals due to adsorbed NO on Mo and on Co were both intense with sulfided catalyst (spectra b)). Reduction of the catalyst prior to its sulfidation decreased the intensity of the characteristic bands, especially the one ascribed to NO on Co (spectra c)). Conversely, reduction of the catalyst subsequent to its sulfidation weakened the intensity of the band ascribed to NO on Mo (spectra d)). These findings suggest that the sulfidation enhances NO adsorption and that varying the sulfidation/reduction sequence causes considerable effect on the relative amounts of surface Mo and Co which are active for NO adsorption. Capacity of the differently pretreated catalysts for NO uptake was in the following order: sulfided > sulfided-then-reduced > reduced-then-sulfided > reduced $\simeq$ fresh.

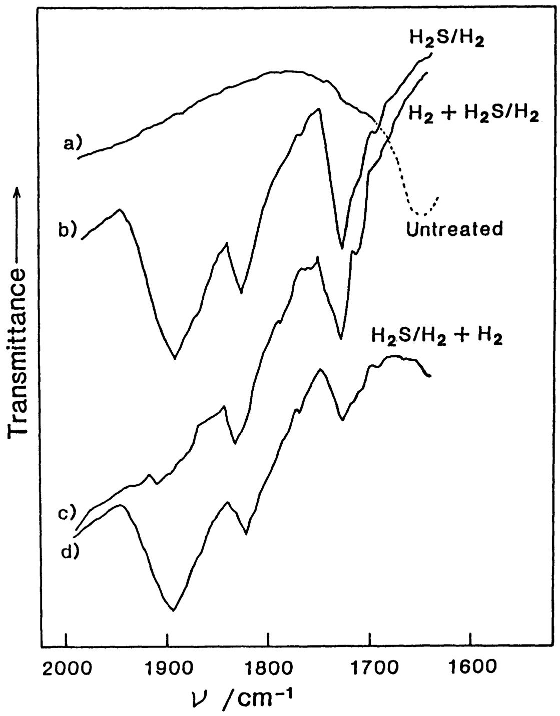

Fig.2. IR spectra of adsorbed NO on $Co-Mo/Al_2O_3$ catalysts: a) fresh; b) sulfided; c) reduced-then-sulfided; d) sulfided-then-reduced.

The catalysts so pretreated were tested for their activities for the hydrogenation of coal-derived heavy oil and o-xylene. Our preliminary result on the relative rates of the hydrogenation at 400 °C is listed in Table 1. The trend in the hydrogenation activity is thus found to coincide with the NO adsorption capacity (especially 1890 cm^{-1} band) of the particular catalysts used.

Table 1. Effect of catalyst pretreatment on coal-derived heavy oil and o-xylene hydrogenation rates

Catalyst	Relative rates	
pretreatment	heavy oil	o-xylene
H_2	(1.00)	13
$H_2 + H_2S/H_2$	2	20
$H_2S/H_2 + H_2$	5	23
H_2S/H_2	7	40

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