NO Adsorption Sites in Sulfided MoO_3/Al_2O_3 Catalysts

Characterization of active species by the adsorption of probe molecules is very informative particularly when the fractions of the active species are very small. MoO_3/Al_2O_3 catalysts have been extensively studied by many workers, because of industrial interests, by using various physicochemical techniques (1). Very recently, Lombardo et al. (2) reported the hydrogenations of olefins over reduced MoO_3/Al_2O_3 catalysts at 25°C and reached the conclusions that the hydrogenation sites, whose concentrations are very low, are effectively poisoned by NO. Furthermore, according to Millman and Hall (3), NO adsorbs on Mo to form dinitrosyl complex, in agreement with the more recent results by other workers (4). In connection with these findings, we tried to obtain further information on the NO adsorption sites in MoO_3/Al_2O_3 catalysts by modifying the catalysts by sulfidation.

The identical batches of MoO_3/Al_2O_3 catalysts were used as in the previous studies (5, 6). They were calcined at 550°C for 5 h in air. Self-supporting wafers of the MoO_3/Al_2O_3 catalysts were reduced with H_2 (100 Torr) or sulfided with H_2S/H_2 (1/10, 100 Torr) or thiophene/H_2 (1/17, 100 Torr) using an in situ ir cell at 400°C by repeated 20-min exposures (three to ten times), followed by evacuation for 1 h at the same temperature. Infrared spectra were recorded at room temperature on a Hitachi spectrophotometer (EPI-G). The amount of chemisorbed NO was volumetrically measured at room temperature in separate experiments.

The sulfidation degrees of the catalysts were determined by X-ray photoelectron spectroscopy (XPS) without exposing the catalyst to air or moisture (5). The peak area intensity ratio of the S2p level to the Mo3d level was converted to the S/Mo atomic ratio. The detailed procedures have been described elsewhere (5). The X-ray photoelectron spectra of reduced or sulfided catalysts did not show the presence of Mo with valence states lower than IV.

Figure 1 shows the ir spectra of NO adsorbed on reduced or sulfided MoO_3/Al_2O_3 catalysts. The spectral features were in excellent agreement with those reported by other workers (3, 4). The wavenumbers of the doublet peak were 1820 and 1710 cm^{-1}, which are ascribable to a dinitrosyl complex (3, 4), irrespective of the loading amount of MoO_3. However, on sulfidation, these wavenumbers shifted to lower values; 1780 and 1680 cm^{-1}, respectively, as shown in Fig. 1 and depended neither on the MoO_3 content nor on the sulfidation degree of Mo. NO ir signals due to NO adsorbed on H_2-reduced sites (1820 and 1710 cm^{-1}) were observed even when the catalyst was slightly sulfided (S/Mo = 0.36). Subsequent sulfidation of H_2-reduced catalysts with H_2S/H_2 showed the characteristic ir spectra of NO adsorbed on sulfided catalysts. The red shifts in the wavenumbers indicate the sulfidation of Mo available for NO adsorption. The replacement of oxygen atoms attached to Mo by sulfur atoms seems to increase the electron density on Mo, since the binding energies of the Mo3$d_{5/2}$ level for sulfided and reduced Mo(IV) were 229.0 and 229.9 eV, respectively. This explains the lower wavenumbers for NO adsorbed on sulfided Mo (more negatively charged nitrosyl) than those for NO adsorbed on H_2-reduced Mo.

Comparing the NO desorption temperature for reduced and sulfided catalyst systems, it was revealed that the adsorption of
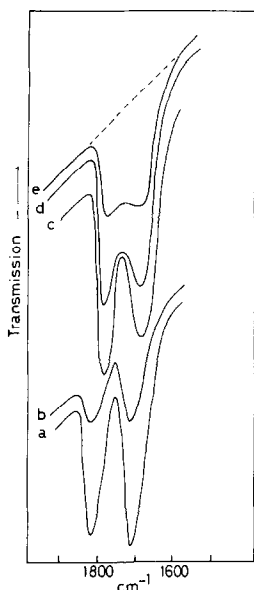
FIG. 1. Infrared spectra of adsorbed NO on MoO_3/Al_2O_3 catalysts reduced with H_2 or sulfided with H_2S/H_2 for 200 min at 400°C: (a) 16.7 wt%, reduced; (b) 9.1 wt%, reduced; (c) 4.8 wt%, sulfided; (d) 9.1 wt%, sulfided; (e) 13 wt%, sulfided. Broken line indicates a background spectrum.

NO on sulfided catalysts was as strong as that on reduced catalysts. The unresolved doublet peaks for high-Mo-content catalysts would be due to the enhanced absorption and scattering of infrared beam rather than to the presence of more than one kind of adsorption site.

Table 1 summarizes the amount of chemisorbed NO over reduced or sulfided catalysts. The fraction of Mo which adsorbs NO is very small (<3% of Mo, assuming dinitrosyl complex) and depends on the sulfidation degree of Mo (S/Mo; atomic ratio). Figure 2 shows the NO/Mo ratio as a function of S/Mo. The following points are noteworthy: (1) the amount of chemisorbed NO shows a maximum at ca. S/Mo = 1 and (2) it depends on the S/Mo regardless of the supported amount of MoO_3. Taking into account the previous results (5) that the anion vacancy concentration on sulfided MoO_3/Al_2O_3 catalysts increases with S/Mo up to S/Mo = 1 and that it decreases with further increase in S/Mo, these findings lead us to the conclusions that NO/Mo depends linearly on the vacancy concentration on Mo and that two NO molecules adsorb on a single Mo atom to form dinitrosyl complex. These conclusions are consistent with the results for reduced catalysts (2).

In contrast to MoO_3/Al_2O_3 catalysts, MoO_3/SiO_2 catalysts (10 wt% MoO_3) showed only very weak and unresolved ir spectra of adsorbed NO in spite of a higher extent of reduction of Mo. This may suggest that Mo in tetrahedral coordinations produces the NO adsorption sites, since MoO_3/SiO_2 catalysts do not contain such Mo species except at very low MoO_3 content (7). This hypothesis may be supported by the recent results of Zingg et al. (8), since the NO/Mo ratio decreases with a

TABLE 1

Amount of Chemisorbed NO over Reduced or Sulfided MoO_3/Al_2O_3 Catalysts

MoO_3 wt%	Treatment gas[a]	Amount of chemisorbed NO[b] (10^{-5} mol/g cat.)	NO/Mo (10^{-2} mol/g atom Mo)	Extent of sulfiding[c] (S/Mo)
13.0	H_2	0.96	1.06	0
4.8	H_2S/H_2	2.00	6.04	0.92
9.1	H_2S/H_2	2.68	4.25	1.27
13.0	H_2S/H_2	3.85	3.95	1.25
23.1	Thiophene/H_2	1.66	1.03	0.36

[a] Reduced or sulfided with 100 Torr of the treatment gas for 200 min (ten times the 20-min exposure) at 400°C.

[b] Measured at room temperature and 10 Torr of NO and corrected for the amount of physisorbed NO.
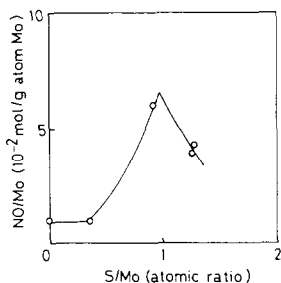
[c] S/Mo; atomic ratio determined by XPS.

FIG. 2. Dependence of the amount of chemisorbed NO on the sulfidation degree of Mo (S/Mo, atomic ratio). Adsorption temperature, 25°C; NO pressure, 10 Torr.

loading amount of MoO_3 for a series of sulfided catalysts as expected from their results that the fraction of tetrahedral Mo in total Mo decreases with a MoO_3 content.

Combining our results with those of Lombardo et al. (2) and Kazusaka and Howe (4), the NO adsorption sites (Mo^A) in MoO_3/Al_2O_3 catalysts must fulfill the following requirements: (1) Mo^A possesses two anion vacancies and oxygen(s) easily exchangeable with sulfur(s), (2) the concentration of Mo^A is parallel to the anion vacancy concentration on Mo, (3) Mo^A is formed from Mo in tetrahedral coordinations, and (4) Mo^A does not contain H because CO reduction of the catalyst (2) and the decomposition of $Mo(CO)_6/Al_2O_3$ catalysts (4) provide the identical conclusions.

As for the valence state of Mo^A, Mo(VI) and Mo(V) can be eliminated because oxidic catalysts did not adsorb NO and the ESR signal due to Mo(V) in reduced or sulfided catalysts was not affected by the exposure to NO, in agreement with the results by Kazusaka and Howe (4). Mo(III) is also unlikely since neither the Mo(III) ESR signal nor the XPS spectrum was observed under our pretreatment conditions. According to Enemark and Feltham (9), Mo dinitrosyl compounds should contain an even number of d electrons and actually only Mo(II) $(NO)_2$-type species are known. On the basis of the energy correlation diagram for dinitrosyl complexes (9),

however, Mo(IV) $(NO)_2$ also seems possible. In addition, Hall and LoJacono (10) have shown that Mo(III) is produced only at a very high extent of reduction and consequently Mo(II) seems much more difficult to produce under the reduction and sulfiding conditions employed here. Therefore, Mo(IV) might be the most possible species for Mo^A, as suggested by Kazusaka and Howe (4). It is interesting to conjecture a Mo species responsible for NO adsorption on the basis of a reduction mechanism similar to that proposed by Millman and his co-workers (11) (Fig. 3).

In the case of $O^*=O$, paths A, B, and C compete with each other to form Mo^A and Mo^B in certain proportions. Mo^B is generally accepted as an abundant species in reduced catalysts. When $O^*=S$, Mo would be reduced predominantly through path C, since S can be removed much easier than O. This is supported by the fact that Mo is reduced faster in the presence of S, which in incorporated by rapid exchanges between O and S (5, 12). Accordingly, only a small part of Mo would be reduced through path A to form Mo^A having two S atoms. This explains low concentrations of Mo^A in sulfided catalysts in spite of high reduction extents of Mo to Mo(IV). When reduced with CO, reduction of Mo is considered to proceed similarly to H_2 reduction. Mo^A provides two anion vacancies for the formation of dinitrosyl complex. On the basis of the proposed model, it is considered that the amount of adsorbed NO is proportional to the concentration of anion vacancy. Therefore, the species proposed here fulfill the above four requirements on Mo^A. However, the model suggested here for NO
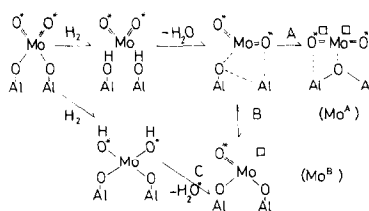

FIG. 3. Possible model.

adsorption sites is rather speculative and requires further verifications.

In summary, it is shown that Mo atoms responsible for NO adsorption in H_2-reduced MoO_3/Al_2O_3 catalysts contain O atoms easily exchangeable with S atoms and that the amount of adsorbed NO depends on the sulfidation degree of Mo regardless of the MoO_3 content.

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YASUAKI OKAMOTO
YUKIHIRO KATOH
YOSHIYUKI MORI
TOSHINOBU IMANAKA
SHIICHIRO TERANISHI

Department of Chemical Engineering
Faculty of Engineering Science
Osaka University
Toyonaka, Osaka 560
Japan