The adsorption characteristics of two Mo sites on a sulfided $MoO_3/\gamma\text{-}Al_2O_3$ surface

Yilu Fu and Fenggang Zhao

Department of Modern Chemistry, Laboratory of Structure Research, University of Science and Technology of China, Hefei, 230026, P.R. China

The surface structure of the oxidized and ammonia dissolved $MoO_3/\gamma\text{-}Al_2O_3$ samples and the adsorption characteristics of the sulfided samples were investigated by Laser Raman Spectroscopy (LRS) and Low Temperature Infrared Spectroscopy (LTIR) techniques.

It was verified that there were two kinds of coordinated unsaturated Mo sites (denoted as Mo_A(CUS) and Mo_B(CUS)) on the surface and the precursors of Mo_A(CUS) and Mo_B(CUS) were Mo(O) and Mo(T), respectively. It was also concluded that Mo_A(CUS) sites could adsorb NO and CO, while Mo_B(CUS) could adsorb CO only. The surface concentration of Mo_A(CUS) might be far smaller than that of Mo_B(CUS).

Keywords: Supported Mo catalysts; NO and CO adsorption; Raman spectroscopy; low temperature IR spectroscopy

1. Introduction

Molybdenum-based catalysts have been used widely in some important catalytic processes and its surface is rather complex. It was investigated by using a lot of surface analytic techniques and had much progress. The $MoO_3/\gamma\text{-}Al_2O_3$ system in the oxidized state has been studied in more detail. It was shown that MoO_3 had monolayer dispersion in Mo(O) and Mo(T) forms on $\gamma\text{-}Al_2O_3$ surface. Bulk MoO_3 and aluminum molybdate were also existent on catalysts with high Mo content [1–5]. Mo(O) could partially dissolve in ammonia water and Mo(T) could not [1,6]. After $MoO_3/\gamma\text{-}Al_2O_3$ was sulfided, the Mo^{+6} quickly reduced to Mo^{+4} and MoS_2 microcrystals were formed gradually. But up to now, whether there was some other valence Mo and what other surface species existed on surface besides MoS_2 was still not clear [2,5,7–11].

The IR spectroscopy of probe molecular adsorption on the $Mo/\gamma\text{-}Al_2O_3$ system has been investigated. It was found that NO was not adsorbed on the oxidized sample; the coordinated unsaturated Mo sites (Mo(CUS)) on reduced or sulfided sample surface had strong adsorption even at room temperature, and

NO was probably adsorbed in twin form, i.e., two NO molecules were coordinated on a Mo(CUS) site [12,13,23]; the NO/Mo ratio was very low at the condition of saturated adsorption and NO was a strong poison to some catalytic reactions [12,14–16]; only some different explanation was given about NO adsorption sites [8,12,17].

There were very few papers concerning IR spectroscopy of CO adsorption on molybdenum catalysts. Knozinger and his co-workers [18] reported that CO could not be adsorbed on oxidized sample and could be adsorbed on reduced or sulfided samples at low temperature.

In our previous report concerning IR study of NO and CO adsorptions on sulfided MoO_3/γ-Al_2O_3 catalyst, it was found that two kinds of Mo(CUS), denoted as Mo_A(CUS) and Mo_B(CUS), had different adsorption abilities. NO was adsorbed on Mo_A(CUS) only while CO could be absorbed on both sites [19]. The goal of the present work is to do more concerning the difference of the adsorption characteristics and the cause of the difference on the two Mo sites.

2. Experimental

1. SAMPLE PREPARATION

Support: the γ-Al_2O_3 support was obtained by calcination of $Al(OH)_3$(Tianjing Chemical Industrial Institute) at 750°C for 16 h in air (S.A. = 270 m^2/g). This material was pressed under the pressure of 200 kg/cm^2, ground and sieved (40–60 mesh).

Calcined samples: the calcined samples were prepared by impregnation with an aqueous solution of ammonium heptamolybdate for 15 min. The MoO_3 loadings were 8.0 wt% or 15.0 wt%. These samples were dried at 70°C and calcined at 500°C for 12 h in air.

Oxidized samples: the calcined samples were oxidized in a flow of O_2(20 ml/min) at 450°C for 2 h.

Ammonia dissolved samples: the 0.3 g oxidized sample was put into 20 ml 3% ammonia water, and dissolved for a certain time, after which the solution was taken off and the samples dried at 70°C.

Sulfided samples: oxidized or ammonia dissolved samples were sulfided in a flow of 8.7% CS_2-H_2 (30 ml/min) at 400°C for 6 h.

2. ADSORPTION GASES

CO gas was produced by Nanjing Analytic Instrument Factory at nominal purity of 99.95%. It was deoxygenated by 401 deoxy agent (Hongguang Chemicals, Dalian) and dehydrated by 5A zeolite. NO was prepared from the reaction of $FeSO_4$ and $NaNO_2$ in concentrated H_2SO_4. The produced gas was purified by KOH and 5A zeolite.

3. MEASUREMENT OF LTIR SPECTROSCOPY

IR spectra were recorded by a Shimadzu IR-435 spectrometer. It can give differential spectra. Self-supported wafers were obtained by pressing the powder at 200 kg/cm^2. They were mounted in a low temperature IR cell (CaF_2 window) which was designed for in situ pretreatment and chemisorption from room temperature to 723 K and for IR measurement from 123 K to room temperature [20]. The sulfided sample wafers were pretreated in a flow of H_2 (20 ml/min) at 450°C for 2 h, evacuated for 30 min at the same temperature and cooled down to room temperature (RT).

4. MEASUREMENT OF LRS

LRS were recorded by a SPEX 1403 spectrometer equipped with holographic grating and a third monochromator. An Ar ion laser was used with 120 mW power from the source of the 514.5 nm line. The wave resolution was ± 2 cm^{-1}. The data were treated by a DMIB system. The self-supported wafers were obtained by pressing the powder at 100 kg/cm^2.

3. Results and discussions

1. SURFACE STRUCTURE OF OXIDIZED AND AMMONIA DISSOLVED SAMPLES

The LRS spectra of oxidized and ammonia dissolved samples of MoO_3 (8.0 wt.%)/γ-Al_2O_3 are shown in fig. 1. For the purpose of assignment of surface species, table 1 lists the main Raman scattering frequencies of surface species in the literature.

On the oxidized sample (fig. 1-a), 219 and 950 cm^{-1} peaks indicate the existence of Mo(O); 325 and 846 cm^{-1} peaks indicate the existence of Mo(T); no other surface species was detected. For ammonia dissolved 0.5 h sample (fig. 1-b) the intensity of Mo(O) peaks decrease and the intensity of Mo(T) peaks are hardly changed. As the length of the dissolution time in ammonia is increased (fig. 1-c–e), the intensity of Mo(O) peaks gradually decrease and that of Mo(T) peaks remained constant. The (4 + 2)h in fig. 1-e expresses that the sample is dissolved by 20 ml ammonia water for 4 h at first, then the solution was taken out and the sample is dissolved by another 20 ml ammonia water for 2 h.

On the MoO_3 (15.0 wt.%)/γ-Al_2O_3 sample, similar phenomena were observed. The different thing is that besides Mo(O) and Mo(T) species, MoO_3 and

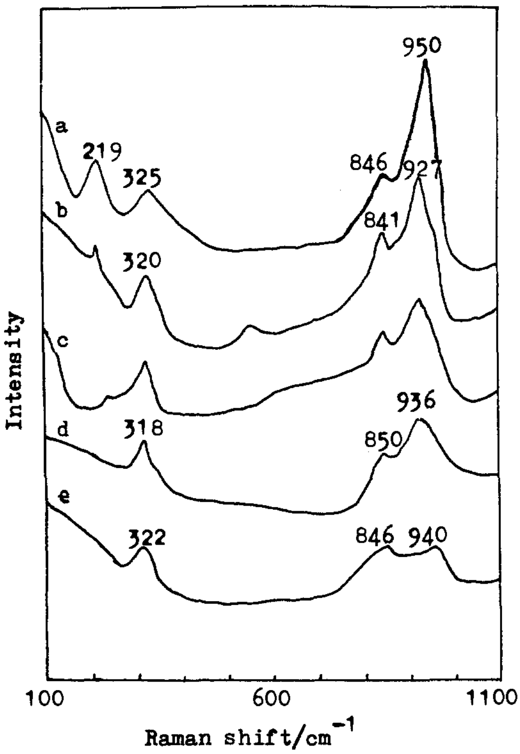

Fig. 1. LRS of ammonia dissolved MoO_3 (8.0 wt.%)/γ-Al_2O_3. Ammonia dissolved time: (a) 0, (b) 0.5 h, (c) 1.5 h, (d) 4.0 h, (e) (4+2) h.

$Al_2(MoO_4)_3$ exist on the surface. 3% ammonia water can dissolve MoO_3 and $Al_2(MoO_4)_3$ completely and with ease. A most part of Mo(O) is also dissolved. Therefore, after full ammonia dissolution, Mo(T) is the chief existing form on the surface.

All of the LRS of ammonia dissolved solution were also measured. There was only one peak at 896 cm^{-1}, which was the character peak of MoO_4^{2-} in solution. It means that Mo ions exist in the unique form of MoO_4^{2-}, although the Mo ions on support surface exist in several states.

Table 1
Main Raman scattering frequency of molybdenum species of MoO_3/γ-Al_2O_3

Surface species	Frequency (cm^{-1})				Refs.
Mo^{6+}(T)	320	791	845	896	[7,11]
Mo^{6+}(O)	213	950			[21]
MoO_3	280	664	818	994	[5]
$Al_2(MoO_4)_3$	386	1004			[5]

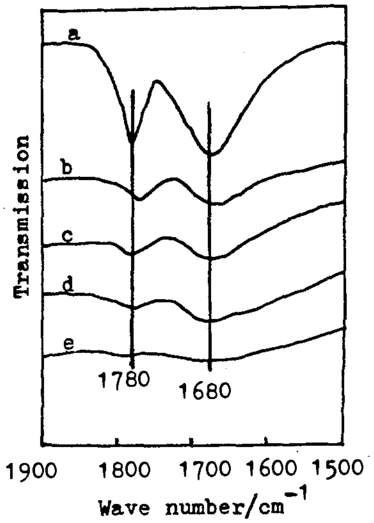

Fig. 2. IR differential spectra of 20 Torr NO adsorption on sulfided MoO_3 (8.0 wt.%)/γ-Al_2O_3 at room temperature. Ammonia dissolved time: (a) 0, (b) 0.5 h, (c) 1.5 h, (d) 4.0 h, (e) (4+2) h.

2. LTIR MEASUREMENT ON SULFIDED SAMPLES

2.1. NO adsorption

The sulfided MoO_3 (8.0 wt.%)/γ-Al_2O_3 samples (with variety of ammonia dissolved time) were exposed to 20 Torr NO for 10 min at room temperature and then the NO was pumped off. The IR differential spectra of NO adsorption and evacuation are exhibited in fig. 2. On the sulfided sample (which is not dissolved by ammonia water) (fig. 2-a), strong double bands of NO adsorption (1780, 1680 cm^{-1}) are observed; after ammonia dissolution for 0.5 h, these double bands of NO adsorption on sulfided sample strikingly decrease (fig. 2-b). As the time of ammonia dissolution is prolonged, the NO adsorption bands are more weakened. Finally, on the sulfided sample with ammonia dissolution for (4 + 2)h (fig. 2-e), the NO adsorption almost vanishes. Similar phenomena were observed in the case on another sulfided sample (15.0 wt.% MoO_3/γ-Al_2O_3). By comparing the results of LRS (fig. 1) with IR differential spectra of NO adsorption, it is clear to see that the tendency of the change of the Mo(O) amount on ammonia dissolved samples coincides with that of the intensity of NO adsorption bands on corresponding sulfided samples. Therefore, we could say that the NO adsorption sites on sulfided samples (denoted as Mo_A(CUS)) should relate with the Mo(O) on corresponding ammonia dissolved samples. In other words, Mo(O) on ammonia dissolved samples must be the precursor of Mo_A(CUS) on corresponding sulfided samples.

2.2. CO adsorption

The Ir differential spectra of 30 Torr CO adsorption at −150°C on ammonia dissolved and sulfided samples of MoO_3(8.0 wt.%)/γ-Al_2O_3 are shown in fig. 3.

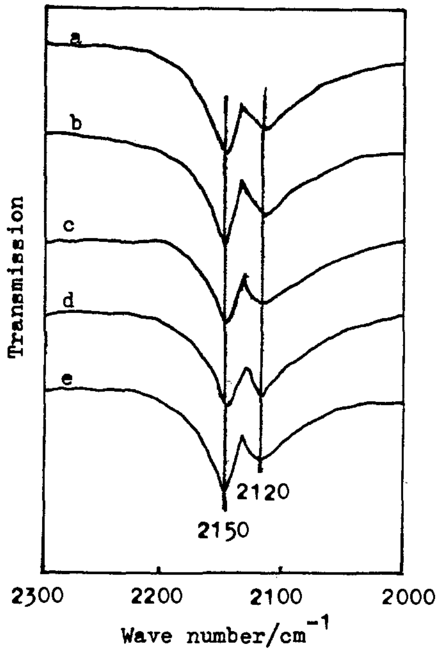

Fig. 3. IR differential spectra of 30 Torr CO adsorption on sulfided MoO_3 (8.0 wt.%)/γ-Al_2O_3 at −150°C. Ammonia dissolved time: (a) 0, (b) 0.5 h, (c) 1.5 h, (d) 4.0 h, (e) (4+2) h.

The 2150 cm^{-1} band is assigned to the CO physical adsorption [20], 2120 cm^{-1} band is the CO chemisorption on Mo(CUS) sites [19]. In spite of the time of ammonia dissolution being different, the intensity of IR bands of CO adsorption does not remarkably change (fig. 3, a–e). The phenomenon is sharply different from NO adsorption. It may imply that surface concentration of Mo_A(CUS) is far smaller than that of Mo_B(CUS). So the IR intensities of CO adsorption have no striking influence after the Mo_A(CUS) sites are dramatically decreased by ammonia dissolution.

2.3. Alternate adsorption of NO and CO

Figs. 4 and 5 exhibit the IR differential spectra of 30 Torr CO adsorption at −150°C on sulfided 8.0 wt% MoO_3/γ-Al_2O_3 samples which are pretreated by 20 Torr NO adsorption at room temperature for 15 min and evacuation to 1×10^{-2} Torr. Because the band intensities of NO adsorption decrease one by one as the time of ammonia dissolution is prolonged, the IR spectra of 0.5 h, 1.5 h and 4.0 h ammonia dissolved and sulfided samples are not shown here.

On the oxidized and sulfided sample, it can be seen from fig. 4 that CO can be adsorbed after preadsorption of NO, meanwhile the NO adsorption bands do not change. Comparing with the situation of only CO adsorption (fig. 3-a), the intensity of CO adsorption on Mo(CUS) (2120 cm^{-1}) is almost the same.

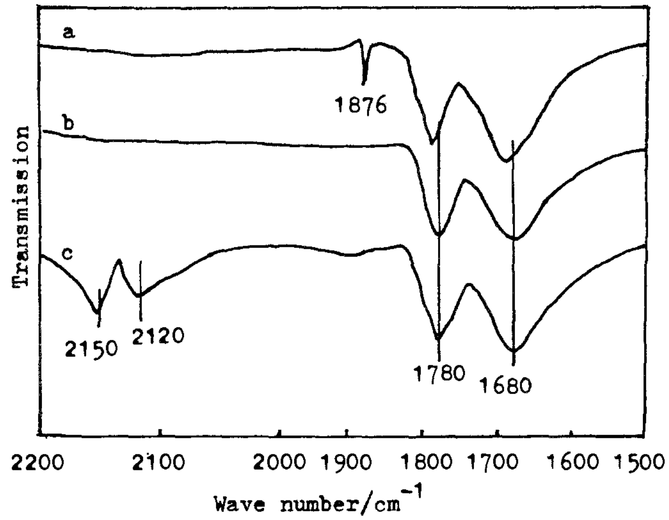

Fig. 4. IR differential spectra of NO, CO alternate adsorption on oxidized and sulfided MoO_3 (8.0 wt.%)/γ-Al_2O_3. (a) RT, 20 Torr NO adsorption for 15 min, (b) evacuation to 1×10^{-2} Torr after step (a), (c) -150°C, 30 Torr CO adsorption for 15 min.

On the ammonia dissolved (with different time) and sulfided samples, the alternate adsorption of NO and CO shows that the intensities of NO adsorbed bands are weakened with ammonia dissolved time. Until ammonia dissolution for (4 + 2)h, the bands of NO adsorption are not detected (fig. 5-a and b). Whereas the intensities of CO adsorption on the Mo(CUS) (2120 cm^{-1}, see fig. 4-c and fig. 5-c) always do not change.

It was known [19] that the surface cannot adsorb NO after CO preadsorption. The experimental facts in figs. 4 and 5 should be caused by the decrease of the Mo_A(CUS) concentration. Because of the prolongation of ammonia dissolved

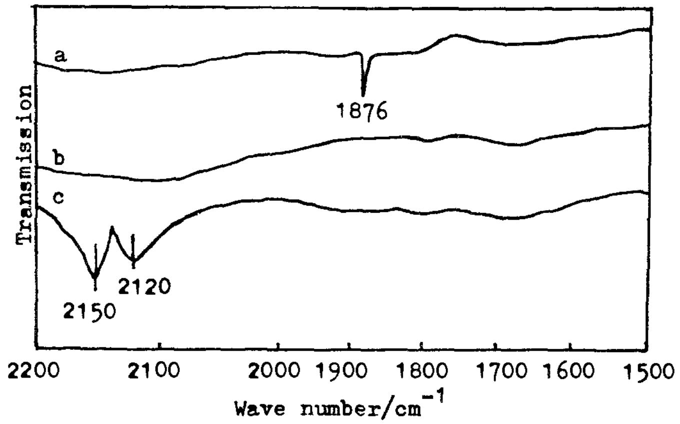

Fig. 5. IR differential spectra of NO, CO alternate adsorption on ammonia dissolved for (4+2) h and sulfided MoO_3 (8.0 wt.%)/γ-Al_2O_3. (a) RT, 20 Torr NO adsorption for 15 min, (b) evacuation to 1×10^{-2} Torr after step (a), (c) -150°C, 30 Torr CO adsorption for 15 min.

time, only the precursor of Mo_A(CUS) is dissolved, whereas the precursor of Mo_B(CUS) is not affected. Moreover, because the surface concentration of Mo_A(CUS) is far smaller than that of Mo_B(CUS), the decrease of Mo_A(CUS) surface concentration only changes the band intensity of NO adsorption and the band intensity of CO adsorption is not affected.

3. A DISCUSSION OF TWO KINDS OF Mo SITES

It was found that adsorbed NO is a strong poison for some catalytic reactions and it was regarded that the edges and corners of MoS_2 microcrystal were the sites of NO adsorption [12,14–16]. But up till now, very few papers discussed what is the precursor of the oxidized state for these adsorbed sites [8,12].

The experimental facts mentioned in this work confirmed that the precursor of Mo_A(CUS) sites is Mo^{6+}(O). After Mo^{6+}(O) sites were sulfided, the MoS_2 mirocrystals were formed [5] and the edges and corners of MoS_2 became the adsorption sites of NO. This view is reasonable and coincides with many publications.

The relation of the adsorption sites between NO and CO at low temperature has not been reported in the literature. Some authors supposed that the adsorption sites both for NO and CO were the same [15,16], others thought they were different [23]. The result in this work shows that the CO adsorption sites are more extensive (including Mo_A(CUS) and Mo_B(CUS)) whereas the NO adsorption sites are only a small part in it (only Mo_A(CUS)).

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