In situ probing of surface sites on supported molybdenum nitride catalyst by CO adsorption

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Both molybdenum and nitrogen sites on fresh Mo_2N/Al_2O_3 are probed by adsorbed CO giving two characteristic IR bands at 2045 and 2200 cm^{-1}, respectively.

Molybdenum nitride has unique physical and chemical properties, such as, electronic, magnetic and catalytic properties, which are similar to noble metals in many aspects. During the last decade, molybdenum nitride has attracted much attention because of its excellent catalytic activity in a number of hydrogenation reactions,[1] such as NH_3 synthesis, hydrotreating, hydrogenolysis and hydrogenation. Specifically supported molybdenum nitrides with high surface areas have been prepared and used in hydrotreating reactions[2–5] and show high potential in industrial applications.

Although molybdenum nitride exhibits a very good catalytic performance, the nature of the surface-active catalytic sites is not well understood. After exposure to air molybdenum nitride is partially oxidized, particularly at the surface,[6] and its surface is very difficult to reduce even with hydrogen at high temperatures, and in most cases, the surface is in an oxynitrided form. In this work, we investigated freshly prepared molybdenum nitride in order to characterize its surface.

A MoO_3/Al_2O_3 (10 mass% Mo) sample was prepared by the incipient wetness impregnation technique contacting γ-Al_2O_3 (S_{BET} = 230 m^2 g^{-1}) with an aqueous solution of $(NH_4)_6Mo_7O_{24}$, followed by drying at 393 K overnight and calcination at 773 K for 4 h. The nitrided Mo/Al_2O_3 catalyst was prepared by temperature programmed reaction of MoO_3/Al_2O_3 with ammonia. The temperature was increased from room temp. to 573 K over 30 min and from 573 to 973 K for 7 h; then the temperature was maintained at 973 K for 2 h. The nitrided sample was cooled to room temperature in flowing ammonia and then passivated in a stream of 1% O_2–N_2 so as to avoid substantial oxidation. The as-prepared sample is denoted passivated Mo_2N/Al_2O_3. The passivated sample was pressed into a self-supporting wafer of mass *ca.* 15 mg. The wafer was placed in a quartz IR cell equipped with CaF_2 windows, and nitrided again in the IR cell in flowing ammonia at given temperatures for 1 h. Samples nitrided in the IR cell are denoted as freshly nitrided or renitrided samples, while the passivated Mo_2N/Al_2O_3 reduced with H_2 at 873 K is denoted reduced passivated sample. The sample was then held *in vacuo* at 773 K for 1 h. Subsequently, the sample was cooled to room temp. and exposed to 10 Torr CO for IR study. All IR spectra were collected at room temp. on a Fourier transform IR spectrometer (Bio-Rad FTS 65A) with a resolution of 4 cm^{-1}.

Fig. 1 shows the IR spectra of CO adsorbed on fresh Mo_2N/Al_2O_3 at different temperatures [Fig. 1(*b*)–(*f*)] and the IR spectrum of CO adsorbed on reduced passivated Mo_2N/Al_2O_3 for comparison [Fig. 1(*a*)]. A broad band at 2180 cm^{-1} and two weak bands at 2100 and 2034 cm^{-1} are observed for the adsorbed CO on reduced passivated Mo_2N/Al_2O_3. For the sample renitrided at 573 K, only a weak band appears at 2184 cm^{-1} as a result of CO adsorption. This band shifts only slightly from 2184 to 2173 cm^{-1} for the sample renitrided at 673 K. However, when the passivated Mo_2N/Al_2O_3 was renitrided at 723 K, the IR spectrum of the adsorbed CO shows a dramatic change [Fig. 1(*d*)]: four IR bands are observed at 2200, 2157, 2110 and 2045 cm^{-1}. For the sample renitrided at 773 K, these four IR bands appear at 2200, 2140, 2090 and 2045 cm^{-1}. The two bands at 2140 and 2090 cm^{-1} decline in intensity while the two bands at 2200 and 2045 cm^{-1} grow significantly.

For passivated Mo_2N/Al_2O_3 renitrided at 873 K, two IR bands can be seen for the adsorbed CO: a strong band at 2200 cm^{-1} and a broad band at 2045 cm^{-1}, and their intensities increase considerably compared with those for Mo_2N/Al_2O_3 renitrided at 723 K. The IR intensities of the two bands scarcely decrease under evacuation at room temperature indicating that the adsorbed species are very stable. Both the bands at 2200 and 2045 cm^{-1} can be still observed under evacuation up to 373 K. When the sample is heated to 423 K under vacuum, the band at 2045 cm^{-1} diminishes while the band at 2200 cm^{-1} can still be seen even the temperature is raised to 673 K and disappears only when the temperature is increased to 773 K. This result suggests that the two bands represent two different types of species formed from the CO adsorption on the fresh Mo_2N/Al_2O_3.

A study[7] of CO adsorption on reduced MoO_3/Al_2O_3 concluded that mainly Mo^{4+} cations were produced when MoO_3/Al_2O_3 was reduced at temperatures in the range of 573–773 K. No adsorbed CO on Mo^0 was detected for MoO_3/Al_2O_3 reduced at temperatures below 973 K. A significant exposure of fully reduced Mo atoms on MoO_3/Al_2O_3 was seen

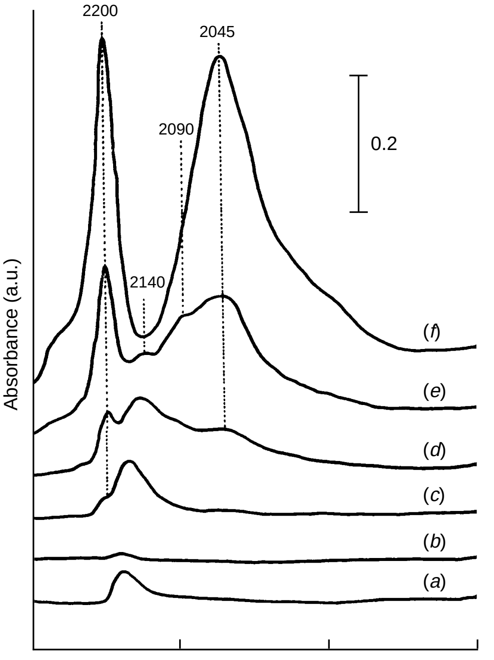

Fig. 1 IR spectra of CO adsorbed on passivated Mo_2N/Al_2O_3 reduced at 873 K (*a*) and on passivated Mo_2N/Al_2O_3 renitrided at 573 (*b*), 673 (*c*), 723 (*d*), 773 (*e*) and 873 K (*f*)

only after a reduction above 973 K.[8] In Fig. 1(*a*), the IR band at 2180 cm^{-1} indicates that CO is adsorbed mainly on Mo^{4+} for the reduced passivated Mo_2N/Al_2O_3. The IR spectrum is similar to that for MoO_3/Al_2O_3 reduced at 873 K but totally different from those of CO adsorbed on the fresh Mo_2N/Al_2O_3 samples [Fig. 1(*b*)–(*f*)]. This leads us to conclude that the surface of reduced passivated Mo_2N/Al_2O_3 is in highly oxidic form, *i.e.* the surface exists mainly as the oxynitride.

The two characteristic bands at 2045 and 2200 cm^{-1} appear only when the sample is renitrided at temperatures at and above 723 K, and their intensities are enhanced significantly with increase in nitriding temperature. It is obvious that these two bands are related to adsorbed CO on molybdenum nitride. The IR band at 2045 cm^{-1} can be safely assigned to the linearly adsorbed CO on surface molybdenum atoms of fresh Mo_2N/Al_2O_3. From the band position and the chemical state of the nitride, the surface molybdenum atom may be partially positively charged.[9–11] By contrast, adsorbed CO on a reduced passivated sample shows IR bands at wavenumbers >2100 cm^{-1}, indicating that the surface molybdenum atom is in a high valence state characteristic of the oxynitride or oxide form even at a reduction temperature as high as 873 K.

It is also interesting that the strong stable band at 2200 cm^{-1} is observed for fresh Mo_2N/Al_2O_3. This band cannot be attributed to CO adsorbed on any molybdenum cation sites since adsorbed CO on molybdenum cations at such a high frequency is easily removed by evacuation even at room temperature. From its vibrational frequency and its high stability,[12] we assign this band to NCO species formed when CO reacts with surface active nitrogen atoms created by *in situ* nitridation. A separate experiment established that the band intensity of the 2200 cm^{-1} band decreased considerably while the band at 2045 cm^{-1} remained unchanged when the fresh catalyst was treated with hydrogen at 773 K. The result is consistent with our assignment of the band at 2200 cm^{-1} to NCO formed *via* reaction between CO and surface nitrogen atoms. Treatment with hydrogen at high temperatures can remove some of the surface active nitrogen atoms; as a result, the band intensity of NCO species is reduced. This result also suggests that a considerable amount of nitrogen atoms are present on the surface of molybdenum nitride, and that they are highly active which may play an important role in catalytic behaviour.

In summary, CO is strongly adsorbed on fresh Mo_2N/Al_2O_3 catalyst leading to two IR bands at 2045 and 2200 cm^{-1} which can be assigned to linearly adsorbed CO on molybdenum and nitrogen sites, respectively when the catalyst is nitrided at temperatures above 723 K. Unlike CO adsorbed on reduced passivated Mo_2N/Al_2O_3, adsorbed CO on molybdenum nitride is very stable and behaves very similarly to that of group 8 metals. This study proves that fully nitrided molybdenum resembles noble metals; also, its surface nitrogen atoms are in a highly active form and readily react with CO to form surface NCO species. Our results also suggest that *in situ* studies of fresh nitrides are very important in the understanding of the real surface of the fresh nitride, while studies on passivated nitrides can not give correct information for the nitride, but rather, give information for the oxynitride or oxygen covered nitride.

Footnote

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