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Adsorption and Reaction of CO on Mo(100)-c(2×2)-N Surface Studied by HREELS

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Abstract: High resolution electron energy loss spectroscopy (HREELS) has been used to investigate the adsorption and reaction of CO on the Mo(100)-c(2×2)N surface. CO directly adsorbed on the N atoms from the c(2×2) layer to form isocyanate (NCO) surface species was found in addition to CO adsorbed on the molybdenum atoms at 120 K, indicating that both Mo and N atoms of the Mo(100)-c(2×2)-N surface are of high reactivities for CO adsorption.

Keywords: HREELS, adsorption, reaction, Mo(100)-c(2×2)-N, CO.

Molybdenum nitrides have attracted significant attention recently due to their unique physical and chemical properties. Many studies have shown that Mo_2N is an active catalyst for CO hydrogenation. The fundamental understanding concerning the reaction mechanisms over Mo_2N, however, is not well established. The powerful surface science techniques may provide an insight into the surface structure and properties of such an important catalytic material. In previous paper[1], we described the results of the adsorption and reaction of ^{15}NO on the Mo(100)-c(2×2)-N surface. In the present work, we further use CO as a probe molecule to investigate the reactive properties of Mo(100)-c(2×2)-N surface.

Details of the instrument, the cleaning of the Mo(100) sample and the preparation of the Mo(100)-c(2×2)-N surface have been described previously[1].

Figure 1 shows the HREEL spectra of CO adsorbed on the Mo(100)-c(2×2)-N surface at 120 K. On the clean Mo(100)-c(2×2)-N surface (**Figure 1** a), a distinct loss peak centered at 512 cm^{-1} could be assigned to the Mo-N stretching mode[1]. When the surface was exposed to 0.1 L CO, five new vibrational features were observed at 1168, 1344, 1660, 1992 and 2240 cm^{-1}, which was accompanied by the decrease in intensity of the peak at 512 cm^{-1}. Further increase in CO exposure caused the following spectroscopic changes: (1) The loss peak at 512 cm^{-1} further weakened and a new vibrational mode at 280 cm^{-1} appeared at the CO exposure of 0.6 L (**Figure 1** d). (2) The 1992 cm^{-1} feature gradually intensified and shifted to 2064 cm^{-1}. (3) The 1168, 1344, 1660 and 2240 cm^{-1} features slightly increased in intensity with remaining rather constant in frequency up to the saturation CO exposure of 2.0 L. (4) A new faint loss peak at 776 cm^{-1} could be observed at higher CO exposures (5.0 L).

By comparing with the CO-adsorbed Mo(100) surface[2], two marked differences could be observed on the present surface. Firstly, the introduction of CO on Mo(100)-c(2×2)-N surface led to the appearance of four new vibrational modes at 2240, 1344, 776 and 1660 cm^{-1}, indicating a formation of new surface species. Since the frequencies of the loss peaks at 2240, 1344 and 776 cm^{-1} are very close to those of the ν_a(NCO) (2274 cm^{-1}), ν_s(NCO) (1327 cm^{-1}) and δ(NCO) (794 cm^{-1}) of gas-phase HNCO[3], respectively, we thus conclude that an NCO species forms on Mo(100)-c(2×2)-N probably through CO directly adsorbed on the N atoms of the c(2×2) layer, *i.e.* $CO(g)+N(ads)\rightarrow NCO(ads)$. This finding, together with our previous results of ^{15}NO adsorption on Mo(100)-c(2×2)-N[1], indicates that the surface N atoms of Mo(100)-c(2×2)-N overlayer demonstrate high reactivity, which is very similar to the observation on the real Mo_2N/Al_2O_3 catalyst as recently reported by Yang *et al*[4]. Although there are other two bending modes at 572 and 670 cm^{-1} of gas-phase HNCO[3], we did not observe these two modes at present. The possible reasons may be that the intensities of the two peaks are too low and are immersed by the $\nu_{Mo\text{-}N}$ peak around 520 cm^{-1}. The intensity of 1344 cm^{-1} peak is much lower than that of ν_a(NCO) at 2240 cm^{-1},

Figure 1 HREEL spectra of CO adsorbed on Mo(100)-c(2×2)N surface at 120 K for different exposure of CO: (a) 0.0 L, (b) 0.1 L, (c) 0.3 L, (d) 0.6 L, (e) 1.0 L, (f) 2.0 L and (g) 5.0 L.

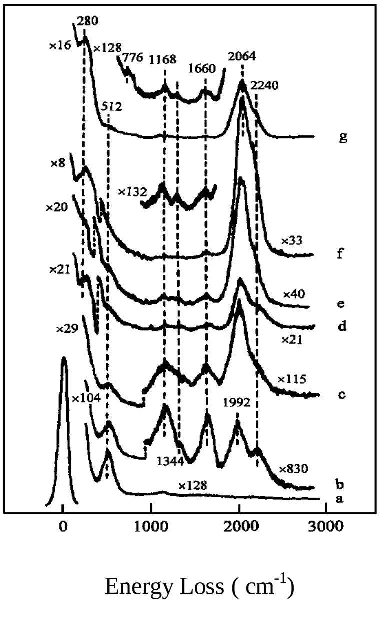
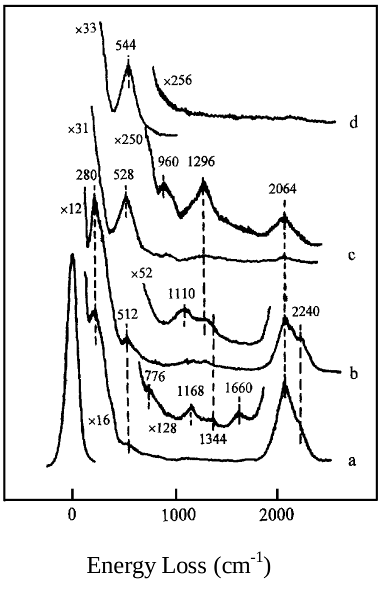


Figure 2 HREEL spectra of CO/Mo(100) -c(2×2)N surface with 5.0 L exposure recorded after heating to various temperatures: (a) 120 K, (b) 250 K, (c) 400 K and (d) 700 K. All spectra were recorded at 120 K.



which is consistent with the observations in isocyanate complexes of transition metals[5] and gas-phase HNCO[3].

The 1660 cm^{-1} CO species can be considered as an inclined CO species bonded to a Mo atom and further coordinated to another Mo atom *via* a π-CO interaction, which is similar to the assignment of ~1500 cm^{-1} CO species observed in the CO adsorbed on oxygen modified Mo(110) surface[6,7] where Colaianni *et al* found that preadsorption of a saturation coverage of oxygen preferentially inhibited the CO-dissociation channel by hindering the formation of the inclined CO with a ν_{CO} of 1345 cm^{-1} and through a ~1500 cm^{-1} CO intermediate in the conversion of the inclined CO to the terminal bonded CO. By comparing the present results with those of clean Mo(100) surface with the same CO coverage[2], we found that the intensity of low-frequency CO species (1168 cm^{-1}) greatly weakened and at the same time a new 1660 cm^{-1} CO species appeared, indicating that the influence of electronegative N atoms on the Mo(100) surface partly resemble that of oxygen on the Mo(110) surface.

The other difference between CO adsorbed on the Mo(100) and Mo(100)-c(2×2)-N surfaces is that the presence of N atoms in the nitride layer induced a blue shift of the peak at 1085 to 1168 cm^{-1}, while the 1984-2050 cm^{-1} peak remained rather constant in frequency. This may be due to the different electron-withdrawing effects of precovered N atoms on different types of CO species. As for the Mo(100)-c(2×2)-N surface, the loss peaks at 1992-2064 and 280 cm^{-1} can be readily assigned to the $\nu_{C\text{-}O}$ and $\nu_{Mo\text{-}CO}$ modes of CO terminally bonded on atop sites, respectively. The frequency shift of the $\nu_{C\text{-}O}$ mode from 1992 to 2064 cm^{-1} may result from CO-CO dipole coupling interactions. The 1168 cm^{-1} feature is assigned to a CO species bonded in an inclined, multiply-coordinated structure. Since N atoms occupied half of four-fold hollow sites of Mo(100) on the Mo(100)-c(2×2)-N surface[8], the 1168 cm^{-1} CO would most likely occupy the rest hollow sites[9]. Compared to the 1085 cm^{-1} CO species observed on CO/Mo(100) surface[2], the 1168 cm^{-1} CO has a less tilted CO bond and thus less overlaps between the 2π* orbital of CO and the d-electron density of the molybdenum surface.

HREEL spectra obtained during the period of heating the CO-saturated Mo(100)-c(2×2)-N overlayer are shown in **Figure 2**. The CO/Mo(100)-c(2×2)-N layer was heated to the desired temperature and then cooled down to 120 K to record the EELS spectra. Heating the surface to 300 K caused the disappearance of the losses at 1168 and 1660 cm^{-1} and a slight decrease in intensity of the peak at 2064 cm^{-1}. At the same time, two new vibrational peaks presented at 1110 and 1296 cm^{-1}. The disappearance of the 1168 and 1660 cm^{-1} modes and the growth of the new losses at 1110 and 1296 cm^{-1} imply that 1168 and 1660 cm^{-1} CO species may dissociate upon heating through the 1110 and 1296 cm^{-1} CO intermediates respectively, resembling the behavior of the 1345 cm^{-1} CO observed during heating the low-coverage CO/Mo(110) overlayer[6,7]. The 1110 cm^{-1} CO species has a more tilted CO bond and more overlap between the CO 2π* orbital and the substrate d-electron density than the 1168 cm^{-1} CO species. And so does the 1296 cm^{-1} CO compared with 1660 cm^{-1} CO species. The slight decrease in intensity of the 2064 cm^{-1} peak indicates that a small amount of terminal bonded CO starts to desorb from the surface, which is also evidenced by the TDS measurements (not shown). On the other hand, almost no change in intensity of the 2240 and 1344 cm^{-1} peaks of NCO species was found, indicating that the NCO species is thermally stable below 300 K.

Heating the surface to 400 K removed the 280, 1100, 2240 and 1344 cm^{-1} modes and substantially decreased the intensity of the 2064 cm^{-1} peak, and simultaneously induced the growth of two new losses at 960 and 528 cm^{-1} (**Figure 2 c**). After further heating to 700 K, only one loss peak at 544 cm^{-1} can be observed. TDS measurements for a CO-saturated surface at 120 K showed that a molecular and two recombinative CO desorption peaks were detected at 319 K and above 800 K, respectively. Besides CO (m/z=28), NO (m/z=30), CN (m/z=26) and NCO (m/z=42) as desorption products had never been found. From the HREELS and TDS results, we could conclude that the NCO surface species decomposed, probably through the route of $NCO(ads) \rightarrow N(ads)+CO(ads$ or g), as the temperature was raised to 400 K. Upon heating, a part of the adsorbed CO (mainly the terminally bonded CO) underwent the intact desorption before 400 K, while the rest dissociated at higher temperature. According to the EELS observation on CO adsorbed on Mo(100)[2] and Mo(110)[6,7], the frequencies of $\nu_{Mo\text{-}O}$ and $\nu_{Mo\text{-}C}$ are all located in the range of 400-550 cm^{-1}. Therefore, the observed loss peak at ~530 cm^{-1} above 400 K may contain the contributions of both the $\nu_{Mo\text{-}O}$ and $\nu_{Mo\text{-}C}$ peaks produced by the CO dissociation. Additionally, the contribution of $\nu_{Mo\text{-}N}$ to the ~530 cm^{-1} peak also must be considered for the surface N atoms of the c(2×2) layer still existed below 1000 K. Between 400 K and 700 K, the observed 960 cm^{-1} loss peak could be assigned to the stretching vibration mode of Mo=O, which is generally observed during the oxidation of Mo(100) surface[10].

In summary, CO can adsorb molecularly on the Mo and N atoms of Mo(100)-c(2×2)-N surface at 120 K simultaneously and form the NCO species. Upon heating the surface, both the desorption and dissociation of adsorbed CO occur. The NCO surface species is rather stable below 300 K and decomposes between 300 and 400 K.

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References

1. J. F. Zhu, S. X. Zhuang, J. C. Guo, *et al*, *Chin. Chem. Lett.*, **1998**, *9*(7), 667.
2. F. Zaera, E. Kollin and J. L. Gland, *Chem. Phys. Lett.*, **1985**, *121*, 464.
3. C. J. Reid, *J. Chem. Phys.*, **1950**, *18*, 1544.
4. S. Yang, C. Li, J. Xu, *et al*, *J. Chem. Soc, Chem, Commun.*, **1997**, 1247.
5. K. Nakamoto, *In Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley & Sons, London, **1986**, p288-289.
6. J. G. Chen, M. L. Colaianni, W. H. Weinberg, *et al*, *Chem. Phys. Lett.*, **1991**, *177*, 113.
7. M. L. Colaianni, J. G. Chen, W. H. Weinberg, *et al*, *J. Am. Chem. Soc.*, **1992**, *114*, 3735.
8. R. Bafrali and A. T. Bell, *Surf. Sci.*, **1992**, *278*, 353.
9. J. P. Fulmer, F. Zaera and W. T. Tysoe, *J. Chem. Phys.*, **1987**, *87*(12), 7265.
10. S.Z.Ren, R.S.Zhai, J.C.Guo, *et al*, *Chinese J. Catal.*, **1998**, *19*(1), 3.

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