ChemComm

A novel reaction on a Mo_2N/γ-Al_2O_3 catalyst: low-temperature isomerization of but-1-ene

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Received (in Cambridge, UK) 17th January 2001, Accepted 9th February 2001
First published as an Advance Article on the web 26th March 2001

An Mo_2N/γ-Al_2O_3 catalyst is found to catalyze the double-bond migration (DBM) of adsorbed but-1-ene below 201 K by *in situ* FT-IR spectroscopy, resembling the behavior of Group VIII metals in the isomerization of butenes.

Recently, molybdenum nitrides have attracted much attention because they show catalytic properties resembling Group VIII metals in a number of reactions involving hydrogen,[1] such as hydrotreating (HDS and HDN), hydrogenolysis, hydrogenation and NH_3 synthesis. However, these studies were concentrated on passivated nitride catalysts. It is known that the passivation procedure causes a dramatic change in the nitride surface, *i.e.* from nitride to oxygen-covered nitride. Therefore, the surface of the passivated catalyst has been modified by the oxygen and it does not reflect the case of the fresh nitride catalyst. Recent study[2] has shown that the reduced, passivated and nitrided Mo_2N/γ-Al_2O_3 catalysts show very different IR spectra of adsorbed CO, indicating quite different properties of the surface sites of the two catalysts. It is therefore reasonable to deduce that the fresh molybdenum nitride may show different catalytic behaviour in some reactions compared with the reduced, passivated one. Here, such an example is presented: the double-bond migration (DBM) of but-1-ene is found, by *in situ* FT-IR spectroscopy, to proceed on an Mo_2N/γ-Al_2O_3 catalyst below 201 K, but not on a reduced, passivated one even at room temperature (RT).

The preparation of the passivated Mo_2N/γ-Al_2O_3 (10 mass% Mo) catalyst is described elsewhere.[3,4] XPS data show that Mo^{6+}, Mo^{4+} and $Mo^{\delta+}$ ($0 < \delta < 4$) cations, with a binding energy of Mo $3d_{5/2}$ at 232.6, 230.7 and 229.0 eV, respectively, are present for the passivated sample. This is consistent with the unsupported Mo nitrides,[4] indicating the formation of the Mo_2N phase on the γ-Al_2O_3 support. Previous XRD results[5] also show that the Mo_2N phase is formed and well dispersed on the support of the Mo_2N/γ-Al_2O_3 catalysts with low Mo loading.

For the IR study, a passivated sample was renitrided in a quartz IR cell in flowing NH_3. The sample renitrided in the IR cell is denoted Mo_2N/γ-Al_2O_3 or nitrided sample, whereas the passivated sample treated with H_2 at 773 K for 2 h is denoted as reduced, passivated Mo_2N/γ-Al_2O_3. Haddix *et al.*[6] have reported that an air-exposed γ-Mo_2N sample can be renitrided by simply treating it in flowing NH_3 at 973 K, and that the procedure did not affect the BET surface area, the crystal structure and the H_2 uptake characteristics. So it can be deduced that the surface of our nitrided sample is in the Mo_2N form. IR spectra were collected on a Fourier transform infrared spectrometer (Nicolet Impact 410) with a resolution of 4 cm^{-1}.

Fig. 1(a)–(e) shows the IR spectra recorded from the adsorption and reaction of but-1-ene on the Mo_2N/γ-Al_2O_3 catalyst below RT. Shown in Fig. 1(a), the IR spectra of adsorbed but-1-ene at 150 K are characterized by bands of ν(CH) at 3070 cm^{-1}, ν(C=C) at 1631 cm^{-1} and CH vibrations in the 3000 and 1400 cm^{-1} regions. The band at 1631 cm^{-1} is attributed to weakly π-adsorbed but-1-ene on the support of the Mo_2N/γ-Al_2O_3 sample. Another band of ν(C=C) at 1597 cm^{-1} can be attributed to σ-bonded but-1-ene on the Mo sites,[7] indicating some chemical changes of adsorbed butenes on the surface of Mo_2N/γ-Al_2O_3 even at quite low temperature. With increased temperatures, the following spectra changes are observed.

(1) At 181 K, the decrease in the amount of adsorbed but-1-ene is evidenced by the decrease in the ν(CH) band at 3070 cm^{-1}, which is accompanied by the appearance of a new band at 3005 cm^{-1}. The change in the ν(C=C) region is also obvious. The intensity ratio of the two bands at 1631 and 1597 cm^{-1} is smaller than that in Fig. 1(a), namely, more σ-bonded but-1-ene is formed with the decrease of π-adsorbed but-1-ene on the surface. Meanwhile, an additional small band at 1619 cm^{-1} appears.

(2) Further increase of the temperature to 201 K causes substantial changes in the IR spectra, where all the characteristic bands of the adsorbed but-1-ene disappear: bands at 3070 and 1631 cm^{-1} disappear and the band at 1597 cm^{-1} decreases in intensity. Concomitantly, new bands appear and increase in intensity: one ν(CH) band at 3005 cm^{-1}, two bands in ν(C=C) region at 1619 and 1614 cm^{-1}, indicating the formation of new adsorbed species from but-1-ene.

(3) At 256 K, shown in Fig. 1(e), the band at 1619 cm^{-1} becomes dominant in the ν(C=C) region and the band at 1597 cm^{-1} is very weak. This IR spectrum is completely different from that of the adsorbed but-1-ene [Fig. 1(a)], suggesting that a reaction of but-1-ene on the Mo_2N/γ-Al_2O_3 catalyst occurs.

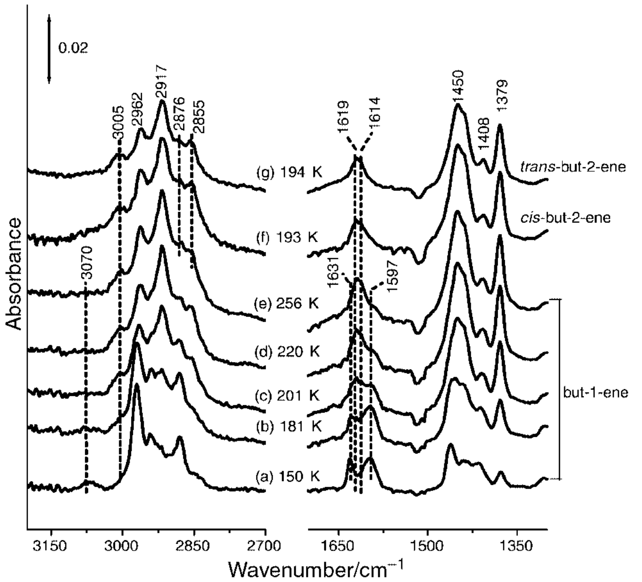

Fig. 1 IR spectra of but-1-enes and but-2-enes adsorbed on to a Mo_2N/γ-Al_2O_3 catalyst at 145 K and recorded at elevated temperatures: but-1-ene at (a) 150 K; (b) 181 K; (c) 201 K; (d) 220 K; (e) 256 K; *cis*-but-2-ene at (f) 193 K; *trans*-but-2-ene at (g) 194 K. In the IR study, the passivated sample was heated from RT to 623 K in 30 min, then to 723 K in 100 min, further from 723 K to 873 K in 75 min, and finally held for 60 min. The renitrided sample was then evacuated at 773 K for 60 min and subsequently cooled to 145 K, a small amount of but-1-ene (*ca.* 0.05 Torr) was introduced and then the temperature was gradually increased to RT.

DOI: 10.1039/b100642h

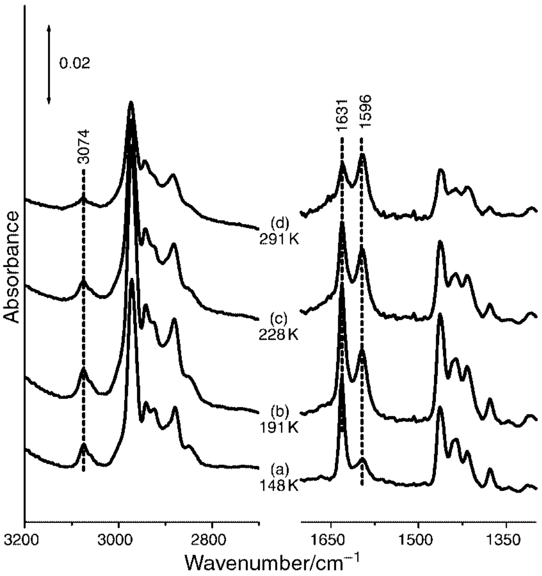

Fig. 2 IR spectra of but-1-ene adsorbed on to a reduced, passivated Mo_2N/γ-Al_2O_3 catalyst initially at (a) 145 K and then increased to (b) 192 K, (c) 231 K and (d) 291 K. The IR procedure for the reduced, passivated sample is similar to that of the nitrided sample.

A similar experiment of but-1-ene adsorption on nitrided γ-Al_2O_3 shows no evident changes in the IR spectra, confirming that the changes in but-1-ene adsorbed on the Mo_2N/γ-Al_2O_3 catalyst are mainly associated with the surface of Mo_2N.

The most likely products formed from the reaction of but-1-ene on the Mo_2N/γ-Al_2O_3 catalyst at such low temperatures are regarded as being the isomers *cis*- and *trans*-but-2-ene. IR spectra of the adsorbed *cis*- and *trans*-but-2-ene on the Mo_2N/γ-Al_2O_3 catalyst at about 193 K are shown respectively in Fig. 1(f) and 1(g) for a comparison with those of the reaction products from the adsorption of but-1-ene [Fig. 1(e)]. In the ν(CH), ν(C=C) and δ(CH) regions, the three spectra show similar contours to each other, implying similar surface species. Hence, it is clear that the adsorbed species produced from the reaction of but-1-ene on the Mo_2N/γ-Al_2O_3 catalyst are a mixture of *cis*- and *trans*-but-2-ene.

The adsorption of but-1-ene was also carried out on the reduced, passivated Mo_2N/γ-Al_2O_3 catalyst. As exhibited in Fig. 2, IR spectra of adsorbed but-1-ene at 145 K [Fig. 2(a)] presents similar contours to those from the Mo_2N/γ-Al_2O_3 catalyst at 150 K [Fig. 1(a)]. However, a further increase of temperatures does not cause changes in the spectra: IR bands at 3074, 1631 and 1596 cm^{-1}, characteristic bands of adsorbed but-1-ene, are still evident even at 291 K and no new bands appear. It is obvious that adsorbed but-1-ene does not convert to its isomers on the reduced, passivated Mo_2N/γ-Al_2O_3 catalyst.

The DBM of butenes has been widely investigated on a variety of catalysts, including solid acid catalysts,[8] base catalysts[9] and noble metal catalysts.[10,11] Only a few studies[12] reported the isomerization properties of reduced, passivated nitride catalysts, and there is no such study on fresh nitrides. Until now, this is the first study reporting the low-temperature isomerization of but-1-ene on a nitrided Mo catalyst. For the Mo_2N/γ-Al_2O_3 catalyst, the surface oxygen sites have been eliminated during the renitridation procedure and the surface Mo sites are in a low valence state (*ca*. 0–2).[2] It can be deduced[13] that the acidity of the nitrided Mo catalyst is quite weak. Therefore, the DBM of but-1-ene may not proceed *via* the same mechanism as that on reduced, passivated nitrides where the activity is attributed to the surface oxide sites as a consequence of the passivation procedure.[12]

A separate coadsorption experiment of CO with but-1-ene on the Mo_2N/γ-Al_2O_3 catalyst showed that preadsorbed CO greatly inhibits the isomerization of but-1-ene, and also that adsorbed but-1-ene significantly influences CO adsorption on Mo sites,[3] suggesting that the DBM of but-1-ene takes place on the same surface sites as for CO adsorption, mostly the $Mo^{\delta+}$ ($0 < \delta < 2$) cus (coordinatively unsaturated sites). Hence, it is likely that the Mo_2N/γ-Al_2O_3 catalyst behaves in a similar way to noble metal catalysts where but-1-ene isomerization also takes place on metal sites. The mechanism of the reaction can be referred from the literature[10] where the paths for an addition–abstraction (AD–AB) mechanism (alkyl–reversal) and an abstraction–addition (AB–AD) mechanism (π-allylic intermediate) are reported. Rooney and Webb[10] suggested that, in the isomerization of *n*-butenes on metal catalysts, the alkyl intermediates prevail at low temperatures whereas allylic intermediates participate to a greater extent in the surface processes as temperature is increased. Therefore, for low-temperature DBM of but-1-ene on the Mo_2N/γ-Al_2O_3 catalyst, it is reasonable to deduce that the mechanism of this reaction resembles one of the two mechanisms proposed on noble metal catalysts, most possibly the AD–AB mechanism (alkyl intermediate).

In conclusion, a novel reaction, low-temperature isomerization of but-1-ene, is found on the Mo_2N/γ-Al_2O_3 catalyst using IR spectroscopy. The reduced, passivated Mo_2N/γ-Al_2O_3 catalyst does not catalyze this reaction even at RT. The isomerization reaction is proposed to proceed *via* an alkyl intermediate on the surface $Mo^{\delta+}$ ($0 < \delta < 2$) cus on the nitrided Mo sample. This mechanism is quite different from that of the passivated nitride catalyst in isomerization reactions but is similar to that of Group VIII metals. The results manifest the unique catalytic properties of fresh nitride catalysts and urge more attention to be focussed on fresh nitrides, which may catalyze some new reactions.

This work was supported financially by the National Nature Science Foundation of China (NSFC, No. 29625305).

Notes and references

1 S. T. Oyama, *Catal. Today*, 1992, **15**, 179.
2 S. Yang, C. Li, J. Xu and Q. Xin, *J. Phys. Chem. B*, 1998, **102**, 6986.
3 Z. Wu, Z. Hao, P. Ying, C. Li and Q. Xin, *J. Phys. Chem. B*, 2000, **104**, 12275.
4 Z. Wu, Y. Chu, S. Yang, Z. Wei, C. Li and Q. Xin, *J. Catal.*, 2000, **194**, 23.
5 C. Sayag, G. Bugli, P. Havil and G. Djéga-Mariadassou, *J. Catal.*, 1997, **167**, 372.
6 G. W. Haddix, J. A. Reimer and A. T. Bell, *J. Catal.*, 1987, **108**, 50.
7 N. Sheppard and C. De La Cruz, *Adv. Catal.*, 1996, **41**, 1.
8 J. N. Kondo, L. Shao, F. Wakabayashi and K. Domen, *J. Phys. Chem.*, 1997, **101**, 9314.
9 M. P. Rosynek, J. S. Fox and J. L. Jensen, *J. Catal.*, 1981, **71**, 64.
10 J. J. Rooney and G. Webb, *J. Catal.*, 1964, **3**, 488.
11 D. Yoon, M. X. Yang and G. A. Somorjai, *J. Catal.*, 1998, **176**, 35.
12 M. K. Neylon, S. Choi, H. Kwon, K. E. Curry and L. T. Thompson, *Appl. Catal., A: General*, 1999, **183**, 253.
13 M. Nagai, Y. Goto, A. Irisawa and S. Omi, *J. Catal.*, 2000, **191**, 128.