

# A novel reaction on a Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> catalyst: low-temperature isomerization of but-1-ene

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**An Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> 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,<sup>1</sup> such as hydrotreating (HDS and HDN), hydrogenolysis, hydrogenation and NH<sub>3</sub> 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<sup>2</sup> has shown that the reduced, passivated and nitrated Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> catalyst below 201 K, but not on a reduced, passivated one even at room temperature (RT).

The preparation of the passivated Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> (10 mass% Mo) catalyst is described elsewhere.<sup>3,4</sup> XPS data show that Mo<sup>6+</sup>, Mo<sup>4+</sup> and Mo<sup>δ+</sup> (0 < δ < 4) cations, with a binding energy of Mo 3d<sub>5/2</sub> at 232.6, 230.7 and 229.0 eV, respectively, are present for the passivated sample. This is consistent with the unsupported Mo nitrides,<sup>4</sup> indicating the formation of the Mo<sub>2</sub>N phase on the γ-Al<sub>2</sub>O<sub>3</sub> support. Previous XRD results<sup>5</sup> also show that the Mo<sub>2</sub>N phase is formed and well dispersed on the support of the Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> catalysts with low Mo loading.

For the IR study, a passivated sample was renitrated in a quartz IR cell in flowing NH<sub>3</sub>. The sample renitrated in the IR cell is denoted Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> or nitrated sample, whereas the passivated sample treated with H<sub>2</sub> at 773 K for 2 h is denoted as reduced, passivated Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub>. Haddix *et al.*<sup>6</sup> have reported that an air-exposed γ-Mo<sub>2</sub>N sample can be renitrated by simply treating it in flowing NH<sub>3</sub> at 973 K, and that the procedure did not affect the BET surface area, the crystal structure and the H<sub>2</sub> uptake characteristics. So it can be deduced that the surface of our nitrated sample is in the Mo<sub>2</sub>N form. IR spectra were collected on a Fourier transform infrared spectrometer (Nicolet Impact 410) with a resolution of 4 cm<sup>-1</sup>.

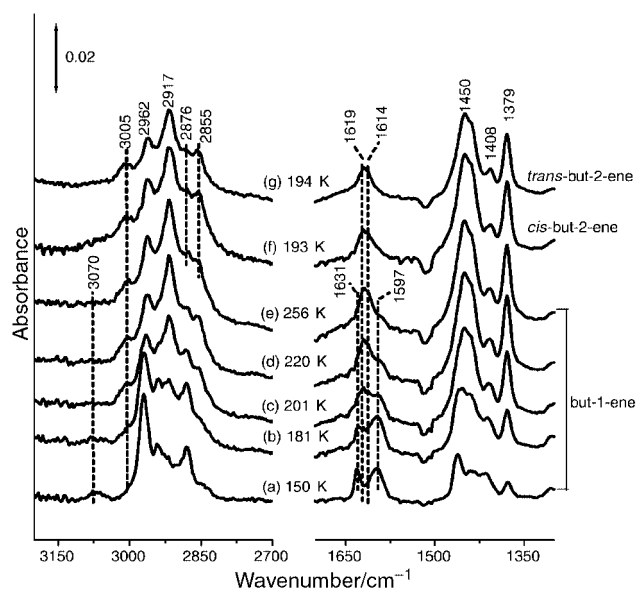
Fig. 1(a)–(e) shows the IR spectra recorded from the adsorption and reaction of but-1-ene on the Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> catalyst below RT. Shown in Fig. 1(a), the IR spectra of adsorbed but-1-ene at 150 K are characterized by bands of ν(CH) at 3070 cm<sup>-1</sup>, ν(C=C) at 1631 cm<sup>-1</sup> and CH vibrations in the 3000 and 1400 cm<sup>-1</sup> regions. The band at 1631 cm<sup>-1</sup> is attributed to weakly π-adsorbed but-1-ene on the support of the Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> sample. Another band of ν(C=C) at 1597 cm<sup>-1</sup> can be attributed to σ-bonded but-1-ene on the Mo sites,<sup>7</sup> indicating some chemical changes of adsorbed butenes on the

surface of Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> even at quite low temperature. With increased temperatures, the following spectra changes are observed.

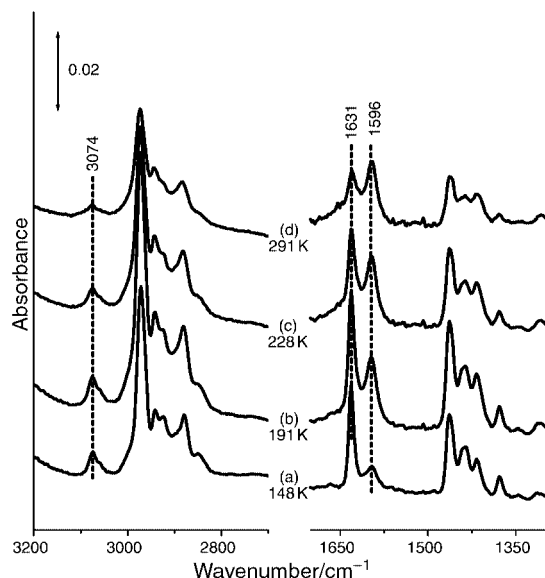
(1) At 181 K, the decrease in the amount of adsorbed but-1-ene is evidenced by the decrease in the ν(CH) band at 3070 cm<sup>-1</sup>, which is accompanied by the appearance of a new band at 3005 cm<sup>-1</sup>. The change in the ν(C=C) region is also obvious. The intensity ratio of the two bands at 1631 and 1597 cm<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> disappear and the band at 1597 cm<sup>-1</sup> decreases in intensity. Concomitantly, new bands appear and increase in intensity: one ν(CH) band at 3005 cm<sup>-1</sup>, two bands in ν(C=C) region at 1619 and 1614 cm<sup>-1</sup>, 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<sup>-1</sup> becomes dominant in the ν(C=C) region and the band at 1597 cm<sup>-1</sup> 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<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> catalyst occurs.



**Fig. 1** IR spectra of but-1-ene and but-2-ene adsorbed on a Mo<sub>2</sub>N/γ-Al<sub>2</sub>O<sub>3</sub> 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 renitrated 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.



**Fig. 2** IR spectra of but-1-ene adsorbed on a reduced, passivated  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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 nitrified sample.

A similar experiment of but-1-ene adsorption on nitrified  $\gamma\text{-Al}_2\text{O}_3$  shows no evident changes in the IR spectra, confirming that the changes in but-1-ene adsorbed on the  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  catalyst are mainly associated with the surface of  $\text{Mo}_2\text{N}$ .

The most likely products formed from the reaction of but-1-ene on the  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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  $\nu(\text{CH})$ ,  $\nu(\text{C}=\text{C})$  and  $\delta(\text{CH})$  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  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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  $\text{cm}^{-1}$ , 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  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  catalyst.

The DBM of butenes has been widely investigated on a variety of catalysts, including solid acid catalysts,<sup>8</sup> base catalysts<sup>9</sup> and noble metal catalysts.<sup>10,11</sup> Only a few studies<sup>12</sup> 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 nitrified Mo catalyst. For the  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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).<sup>2</sup> It can be deduced<sup>13</sup> that the acidity of the nitrified 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.<sup>12</sup>

A separate coadsorption experiment of CO with but-1-ene on the  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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,<sup>3</sup> suggesting that the DBM of but-1-ene takes place on the same surface sites as for CO adsorption, mostly the  $\text{Mo}^{\delta+}$  ( $0 < \delta < 2$ ) cus (coordinatively unsaturated sites). Hence, it is likely that the  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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<sup>10</sup> where the paths for an addition–abstraction (AD–AB) mechanism (alkyl–reversal) and an abstraction–addition (AB–AD) mechanism ( $\pi$ -allylic intermediate) are reported. Rooney and Webb<sup>10</sup> 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  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  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  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  catalyst using IR spectroscopy. The reduced, passivated  $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$  catalyst does not catalyze this reaction even at RT. The isomerization reaction is proposed to proceed *via* an alkyl intermediate on the surface  $\text{Mo}^{\delta+}$  ( $0 < \delta < 2$ ) cus on the nitrified 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.

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