

An IR Study on Selective Hydrogenation of 1,3-Butadiene on Transition Metal Nitrides: 1,3-Butadiene and 1-Butene Adsorption on Mo₂N/ γ -Al₂O₃ Catalyst

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The surface species formed from the adsorption of 1,3-butadiene and 1-butene on Mo₂N/ γ -Al₂O₃ catalyst have been characterized by *in situ* FT-IR spectroscopy with an attempt to get insight into the selective hydrogenation of 1,3-butadiene on transition metal nitride catalysts. 1,3-Butadiene adsorption on the Mo₂N/ γ -Al₂O₃ catalyst forms several kinds of chemisorbed surface species: π -adsorbed butadiene (π_s and π_d); σ -bonded species; dehydrogenated species. π_s - and σ -bonded butene species are present on the surface for 1-butene adsorption and reaction on the nitride catalyst. The presence of the π_d -adsorbed butadiene significantly prevents 1-butene from its adsorption, further hydrogenation, and isomerization on the nitrated catalyst, accordingly resulting in high selectivity in the hydrogenation of 1,3-butadiene to 1-butene. The surface nitrogen atoms weaken the interaction between 1,3-butadiene and the catalyst surface, and result in the high selectivity in the hydrogenation of 1,3-butadiene to 1-butene.

1. Introduction

The selective hydrogenation of dienes in C₄ alkene cuts has received considerable attention since this reaction is of vital importance in manufacturing high-purity alkene streams.¹ The active components of the catalysts for the reaction are usually noble metals such as palladium, platinum, etc.^{2–4} Unfortunately, a certain amount of carbon monoxide or some other poisons have to be added to the feed to inhibit the further hydrogenation of olefins,⁵ because olefins are very easily to be hydrogenated to alkanes on most noble metal catalysts. Therefore, it has been an attractive objective for a long time to develop catalysts, especially non-noble metal catalysts,^{6–8} for the selective hydrogenation of dienes to olefins, particularly for the selective hydrogenation of 1,3-butadiene to butene.

In recent years, transition metal carbides and nitrides have attracted much attention because they show catalytic properties resembling Group VIII metals in a number of hydrogen-involved reactions. For example, they are active in hydrogenation of ethene^{9,10} and carbon monoxide.^{11,12} Very recently, our studies have shown that molybdenum nitride catalyst has mild activity but high selectivity in hydrogenation of ethyne to ethene¹³ and of 1,3-butadiene to 1-butene (selectivity is 85% at the conversion of 30% at 313 K).¹⁴ The results show a promising prospect for the application of transition metal nitride catalysts in the field of selective hydrogenation. However, the mechanism of the selective hydrogenation on nitride catalysts and the role of the incorporated nitrogen atoms in the nitride remain unclear because the selective hydrogenation of dienes on nitride catalysts has not been well investigated before.

IR spectroscopy is a predominant technique in the surface characterization of supported catalysts.^{15–18} Extensive work has been conducted on the selective hydrogenation of 1,3-butadiene on noble metal catalysts;^{19–23} meanwhile much IR work has been carried out on the adsorption of 1,3-butadiene^{24–30} and

some other C₄ hydrocarbons on single crystals of metals and supported metal catalysts.^{31–38} To our knowledge, no IR study has been done on the selective hydrogenation of dienes on transition metal nitride catalysts so far.

The objective of this paper is to detect the surface species derived from the adsorption of 1,3-butadiene and 1-butene on Mo₂N/ γ -Al₂O₃ and then to elucidate the relationship between the surface adsorbed species and the selectivity in the hydrogenation of 1,3-butadiene on molybdenum nitride catalyst. *In situ* FT-IR study was performed on the Mo₂N/ γ -Al₂O₃ catalyst that was prepared from a renitridation of the passivated nitride as described in previous papers.^{39,40} Our results show that the high selectivity of 1,3-butadiene hydrogenation to 1-butene is mainly due to the competitive adsorption of the surface species; namely, the π_d -adsorbed butadiene strongly prevents 1-butene from its adsorption and further hydrogenation. The nitrogen atoms of the molybdenum nitride are found to be important in improving the selectivity in the hydrogenation of 1,3-butadiene to 1-butene.

2. Experimental Section

2.1. Catalyst Preparation. MoO₃/ γ -Al₂O₃ sample with Mo loading of 10 wt % was prepared by incipient wetness impregnation of γ -Al₂O₃ (S_{BET} = 172 m²/g) with an aqueous solution of (NH₄)₆Mo₇O₂₄, followed by drying at 393 K overnight and calcination at 773 K for 4 h. The Mo₂N/ γ -Al₂O₃ catalyst, i.e., nitrated catalyst, was prepared by the temperature-programmed reaction of MoO₃/ γ -Al₂O₃ with ammonia as following procedures: The temperature was increased from room temperature (RT) to 623 K in 1 h and from 623 to 973 K in 6 h, and then the temperature was maintained at 973 K for another 2 h. Passivated Mo₂N/ γ -Al₂O₃ sample was prepared from the nitrated sample which was passivated at RT in a stream of 1% O₂/N₂ so as to avoid the violent oxidation of the freshly prepared nitride.

2.2. FT-IR Studies. A passivated Mo₂N/ γ -Al₂O₃ sample was pressed into a self-supporting wafer (ca. 15 mg/cm²) and

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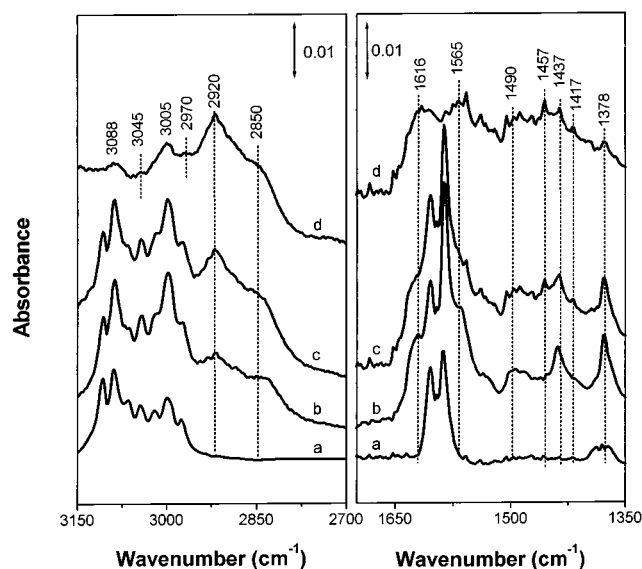


Figure 1. IR spectra of 1,3-butadiene adsorbed on (a) nitrided γ - Al_2O_3 , (b) $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 catalyst for 1 min, (c) $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 catalyst for 30 min, and (d) outgassing of (c) at RT.

renitrided in flowing ammonia in a quartz IR cell with CaF_2 windows. The sample was heated from RT to 623 K in 30 min, then to 723 K in 100 min, further from 723 to 873 K in 75 min, and finally held at this temperature for 60 min. The sample renitrided in the IR cell is called $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ or nitrided sample. Identical IR spectra of adsorbed CO were obtained for CO adsorption on the samples either from the nitridation of MoO_3/γ - Al_2O_3 or from the renitridation of passivated $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 . To save time, passivated $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 instead of MoO_3/γ - Al_2O_3 was used as the starting sample in the IR cell; otherwise it takes long time to nitride MoO_3/γ - Al_2O_3 sample. Haddix et al.⁴¹ have also reported that air-exposed γ - Mo_2N sample can be renitrided by simply treating it in flowing ammonia at 973 K, and the procedure did not affect the BET surface area, the crystal structure, and the H_2 uptake characteristics.

The as-prepared sample was evacuated at 773 K for 60 min and subsequently cooled to RT. Then following different IR experiments were carried out: (1) About 1 Torr (1 Torr = 133.33 Pa) 1,3-butadiene was introduced into the IR cell for adsorption experiment. (2) About 5 Torr 1-butene was introduced into the IR cell for adsorption experiment. (3) The 1 Torr 1,3-butadiene was first contacted with the sample and outgassed at RT, and then 5 Torr 1-butene was introduced. (4) The catalyst sample was exposed to 10 Torr CO and 10 Torr 1,3-butadiene or 1-butene in the IR cell for coadsorption experiment.

All infrared spectra were collected at RT on a Fourier transform infrared spectrometer (Nicolet Impact 410) with a resolution of 4 cm^{-1} and 64 scans in the region 4000 – 1000 cm^{-1} .

3. Results and Spectra Interpretation

3.1. Adsorption of 1,3-Butadiene on $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 Catalyst. **3.1.1. Adsorption of 1,3-Butadiene.** Figure 1 shows the IR spectra of 1,3-butadiene adsorbed on nitrided γ - Al_2O_3 and $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 catalyst. In the 3150 – 1350 cm^{-1} region, shown in Figure 1a, adsorbed butadiene on γ - Al_2O_3 gives IR bands similar to that of 1,3-butadiene in the gas phase, indicating that the 1,3-butadiene is weakly or physically adsorbed on the support. Figure 1b,c exhibits the IR spectra of adsorbed butadiene on $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 catalyst for different adsorption

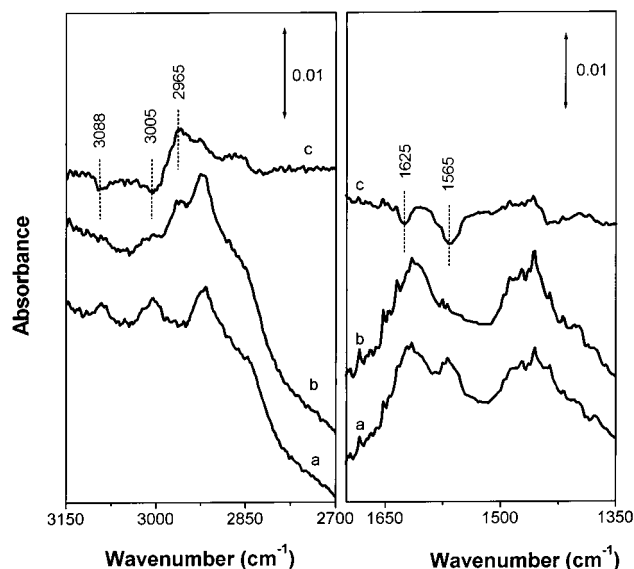


Figure 2. IR spectra of 1,3-butadiene adsorbed on $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 catalyst: (a) outgassed at RT; (b) followed by hydrogen addition at RT; (c) the subtraction result of (b) – (a).

times. When 1,3-butadiene was introduced onto the $\text{Mo}_2\text{N}/\gamma$ - Al_2O_3 sample, IR bands at 2920, 2850, 1623, 1564, 1490, 1457, 1437, 1417, and 1378 cm^{-1} appear together with the bands due to gas phase 1,3-butadiene. The differences among parts a–c of Figure 1 manifest the chemical changes of the adsorbed butadiene on Mo_2N surface.

With the adsorption time, the following changes are observed in Figure 1: (a) In the $\nu(\text{CH})$ region, the bands at 2920 and 2850 cm^{-1} , corresponding to $\nu(\text{CH}_2)_{\text{as}}$ and $\nu(\text{CH}_2)_{\text{s}}$, respectively, become stronger in intensity. (b) In the 1700 – 1300 cm^{-1} region, the bands at 1490, 1437, and 1378 cm^{-1} do not show evident change in intensity while the bands at 1457 and 1417 cm^{-1} grow in intensity.

Figure 1d shows the IR spectrum recorded after an outgassing at RT of the gas phase 1,3-butadiene. The IR bands of gas phase 1,3-butadiene disappear after the outgassing. The $\nu(\text{CH})$ region exhibits absorbances at 3088, 3005, 2920, and 2850 cm^{-1} , which do not decrease in intensity with further evacuation at RT. Additional bands with weaker intensity are observed at 3045 and 2970 cm^{-1} . Absorbance features are also observed at 1616, 1565, 1490, 1457, 1437, 1417, and 1378 cm^{-1} in the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH})$ regions.

The bands at 3088 and 3005 cm^{-1} are due to the stretching modes of unsaturated C–H groups and could be ascribed to π -adsorbed species. The bands at 1616, 1565, and 1490 cm^{-1} can be ascribed to C=C stretching modes. For C=C groups with only σ -type metal substitution, $\nu(\text{C}=\text{C})$ is observed at lowered frequencies: 1650 – 1550 cm^{-1} ; with π -bonding only, 1600 – 1460 cm^{-1} .³⁸ So the band at 1616 cm^{-1} could be attributed to σ -bonded species and the band at 1565 cm^{-1} to single π -adsorbed butadiene (π_s). The 1490-cm^{-1} band is probably due to di- π -adsorbed butadiene (π_d) according to the IR results of the $\text{Fe}(\text{CO})_3\text{C}_4\text{H}_6$ complex: 1479 cm^{-1} for $\nu(\text{C}=\text{C})$.⁴²

Figure 2a,b shows the IR spectra of adsorbed butadiene before and after H_2 addition, respectively. After H_2 treatment at RT, exhibited in Figure 2b, the bands at 3088 and 3005 cm^{-1} diminish considerably with the appearance of an IR band at 2965 cm^{-1} . The band at 1565 cm^{-1} disappears while the band at 1490 cm^{-1} shows no apparent change. The subtraction spectrum (b – a), Figure 2c, shows these changes more clearly.

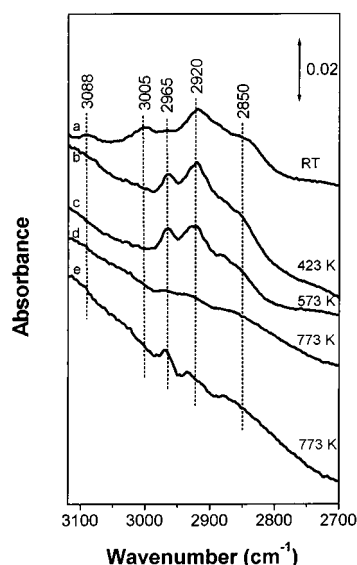


Figure 3. IR spectra of 1,3-butadiene adsorbed on Mo₂N/γ-Al₂O₃ catalyst outgassed at different temperatures: (a) RT; (b) 423 K; (c) 573 K; (d) 773 K; (e) hydrogenation at 773 K.

Several negative bands at 3088, 3005, 1625, and 1565 cm⁻¹ are clearly observed. It demonstrates that the π_s species is less stable than the π_d species and can be easily hydrogenated, being consistent with the report of Soma.²⁷ The negative band at 1625 cm⁻¹ can be attributed to the free ν(C=C) of the π_s adsorbed butadiene, which is overlapped by the IR band at 1616 cm⁻¹ in Figure 2a. No change of the 1616-cm⁻¹ band is observed, suggesting that the σ-bonded species cannot be hydrogenated at RT.

The strong absorbance at 2920 cm⁻¹ and the medium absorbance at 1437 and 1417 cm⁻¹ are also the evidence for the presence of σ-bonded species. The IR bands at 1437 and 1417 cm⁻¹ are suggested to be related to M-CH₂- or M-CH-group.^{28,37} These bands can be ascribed to the ν(CH₂) and δ-(CH) modes of σ-bonded C₄H₆ species, respectively. These assignments are in agreement with those by Soma²⁷ for di-σ-C₄H₆ on Ni/Al₂O₃ and by Sheppard³⁰ for the same structure on Pt(111). Therefore, the σ-bonded species is possibly di-σ-adsorbed C₄H₆ on the Mo₂N/γ-Al₂O₃ catalyst. In an investigation of the adsorption and decomposition of 1,3-butadiene on clean and carbide-modified vanadium (110) surfaces, Chen²⁴ suggested that the bonding geometry of the submonolayer C₄H₆ on the carbide-modified surface is most likely in the di-σ-species, MoCH₂-MoCHCH=CH₂.

3.1.2. Desorption and Hydrogenation of the Adsorbed Butadiene Species. Figure 3 shows the IR spectra of 1,3-butadiene adsorbed on Mo₂N/γ-Al₂O₃ catalyst and after a subsequent heating in a vacuum at different temperatures. The evacuation at higher temperature produces an obvious IR band at 2965 cm⁻¹, characteristic of ν(CH₃)_{as}. The IR bands at 2965, 2920, and 2850 cm⁻¹ remain even after outgassing at 573 K, indicating the presence of very stable species derived from 1,3-butadiene adsorption. The increase of the intensities of these IR bands owes possibly to the hydrogenation of some dehydrogenated species at high temperatures. Although no strong IR bands are observed after outgassing at 773 K (Figure 3d), a subsequent hydrogenation at the same temperature produces again some distinct bands at 2967, 2935, and 2880 cm⁻¹ in the ν(CH) region, corresponding to ν(CH₃) (Figure 3e). This implies that there are some severely dehydrogenated species formed on the catalyst surface after a high temperature evacuation. These

TABLE 1: Assignment of the Observed IR Bands from 1,3-Butadiene Adsorbed on Mo₂N/γ-Al₂O₃ Catalyst^a

IR band (cm ⁻¹)	assgmt	
	vibration mode	surf species
3088 (m)	ν(HC=) _{as}	I/II
3045 (vw), 3005 (m)	ν(HC=)	I/II
2970 (vw)	ν(CH ₃) _{as}	II
2920 (s)	ν(CH ₂) _{as}	II/III
2850 (sh)	ν(CH ₂) _s	II/III
1616 (s)	ν(C=C)	I-1/II
1564 (m)	ν(C=C)	I-1
1490 (b)	ν(C=C)	I-2
1457 (s)	δ(CH ₃) _{as} /δ(CH ₂) _{as}	II
1437 (w)	δ(CH ₂) _s	II
1417 (w)	δ(CH ₂) _s	II/III
1378 (vw)	δ(CH ₃)/δ(CH ₂)	II

^a Key: (s) strong; (m) medium; (w) weak; (vw) very weak; (sh) shoulder; (b) broad; I, π-complex; I-1, π_s-adsorbed butadiene; I-2, π_d-adsorbed butadiene; II, σ-bonded species; III, severely dehydrogenated species.

dehydrogenated species possibly cause the catalyst deactivation in the hydrogenation of 1,3-butadiene.

In summary, there are several kinds of species derived from the adsorption of 1,3-butadiene on the Mo₂N/γ-Al₂O₃ catalyst: π (π_s and π_d) adsorbed butadiene; σ-bonded species possibly in di-σ-form; dehydrogenated species. A tentative assignment for the IR bands is given in Table 1.

3.1.3. Adsorption of 1,3-Butadiene on Mo₂N_x/γ-Al₂O₃ (x < 1) Catalyst. In a previously study,⁴⁰ two surface sites, N and Mo sites, of the Mo₂N/γ-Al₂O₃ catalyst were probed by CO adsorption. The fact that a transition metal nitride shows catalytic behaviors different from those of its corresponding metal and metal oxide is mainly due to the insertion of nitrogen atoms into the lattice of the metal; so it is worthwhile to investigate the role of the N site of Mo₂N/γ-Al₂O₃ played in the selective hydrogenation of 1,3-butadiene.

As confirmed by TPD and FT-IR techniques,^{40,43} the surface nitrogen atoms in the Mo₂N lattice can be partly removed by a treatment with H₂ at high temperatures. To figure out the function of the surface N sites, the Mo₂N/γ-Al₂O₃ sample was reduced by H₂ at 903 K and then evacuated at the same temperature. Some nitrogen atoms could be eliminated in this way; thus, the treated sample is denoted as the Mo₂N_x/γ-Al₂O₃ (x < 1) catalyst. Then the adsorption of 1,3-butadiene on this N-deficient sample was conducted.

Figure 4 shows the IR spectra of 1,3-butadiene adsorbed on differently pretreated Mo₂N/γ-Al₂O₃ catalysts. The IR spectrum of 1,3-butadiene adsorbed on Mo₂N_x/γ-Al₂O₃ (x < 1) catalyst, given in Figure 4a, exhibits a contour similar to that of adsorbed butadiene on Mo₂N/γ-Al₂O₃ sample (Figure 1b); namely, IR bands at 2920, 2850, 1623, 1564, 1490, 1457, 1437, 1417, and 1378 cm⁻¹ appear together with the bands due to gas phase 1,3-butadiene. But it is notable that the band at ca. 1490 cm⁻¹, characteristic of ν(C=C) of π_d-bonded butadiene species, is weaker than that in Figure 1a. Figure 4b,c compares the IR spectra of 1,3-butadiene adsorbed on differently treated catalysts after outgassing at RT. The absorbance features in the ν(CH) (3088, 3005, 2965, 2920, and 2850 cm⁻¹), ν(C=C) (1616, 1565, and 1490 cm⁻¹), and δ(C-H) (1457, 1437, 1417, and 1378 cm⁻¹) regions of the two spectra are similar in positions, indicating similar species formed on the two catalysts; namely, π (π_s and π_d) adsorbed butadiene, σ-bonded species, and severely dehydrogenated species are present on the surface of the Mo₂N_x/γ-Al₂O₃ (x < 1) catalyst. But some of the bands are quite different in intensity. As shown in Figure 4b, the bands

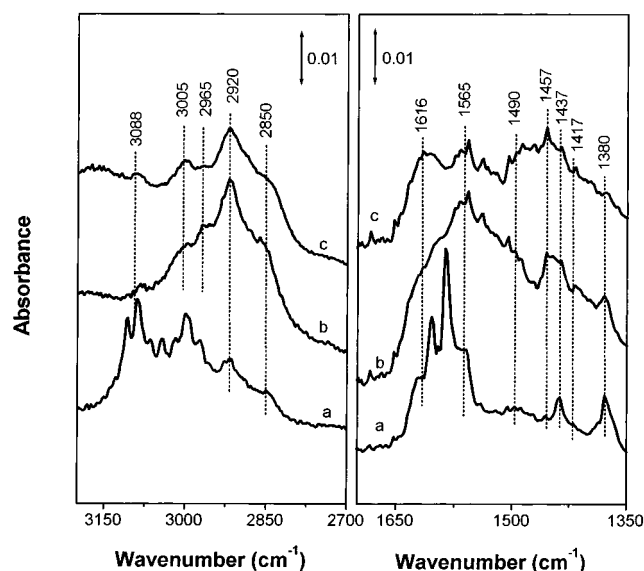


Figure 4. IR spectra of 1,3-butadiene adsorbed on (a) $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ ($x < 1$) catalyst for 1 min, (b) outgassed after 30-min adsorption, and (c) $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

at 2920 and 1565 cm^{-1} are extremely strong, and the band at 2965 cm^{-1} is apparent. The strong bands at 2920 and 2965 cm^{-1} suggest more σ -bonded species present on the surface of $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ ($x < 1$) catalyst. While the strong band at 1565 cm^{-1} and the weak band at 1490 cm^{-1} indicate that more π_s butadiene species is formed on the N-deficient catalyst than that of the normally treated catalyst. These differences suggest that most of the adsorbed butadiene interacts strongly with the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ ($x < 1$) catalyst and undergoes dramatic changes in bonding modes with the surface.

3.2. Adsorption of 1-Butene on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ Catalyst.

Our reaction results show that 1,3-butadiene can be selectively hydrogenated to 1-butene on $\gamma\text{-Mo}_2\text{N}$ catalyst.¹⁴ For example, the selectivity to 1-butene is 85% at the conversion of 30% of 1,3-butadiene at 313 K. It is interesting why 1-butene is the main product. Therefore, the adsorption of 1-butene was compared with that of 1,3-butadiene to get an insight into the surface mechanism of selective hydrogenation of 1,3-butadiene on molybdenum nitride catalyst.

Figure 5 exhibits the IR spectra of 1-butene adsorbed on $\gamma\text{-Al}_2\text{O}_3$ and $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalysts at RT. The spectrum contour of 1-butene adsorbed on $\gamma\text{-Al}_2\text{O}_3$ (Figure 5a) is quite similar to that of gas phase 1-butene, suggesting that 1-butene adsorption on Al_2O_3 is negligible at RT. Figure 5b,c shows the changes of IR bands of 1-butene adsorbed on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst with adsorption time. The IR band at 3090 cm^{-1} , characteristic of $\nu(\text{=CH}_2)$ of 1-butene, disappears after 10-min adsorption (Figure 5c), accompanying with the appearance of an IR band at 3010 cm^{-1} assigned to $\nu(\text{=CH})$ of 2-butenes. Other IR bands in the $\nu(\text{CH})$, $\nu(\text{C=C})$, and $\delta(\text{CH})$ regions in Figure 5c are also different from those of 1-butene, indicating that 1-butene has reacted with the surface of the nitrated sample. Deduced from the IR bands, the most possible products for the reaction of 1-butene on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst at RT are the isomers *cis*- and *trans*-2-butenes.

Figure 5d gives the IR spectrum recorded after an outgassing at RT of the sample. IR bands at 3010, 2965, 2920, 2880, and 2850 cm^{-1} in the $\nu(\text{CH})$ region and bands at 1615, 1452, 1408, and 1380 cm^{-1} are still observed. The band at 3010 cm^{-1} is due to π -adsorbed butene, consistent with that of 1-butene adsorption on Pt/SiO_2 .³³ Similar to that of 1,3-butadiene, the

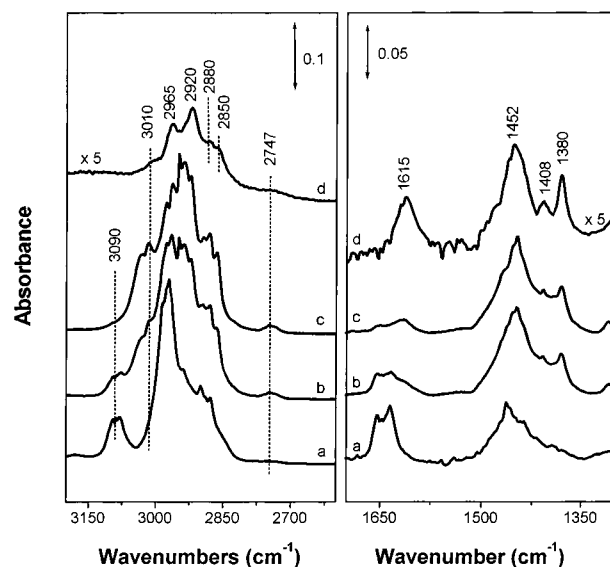


Figure 5. IR spectra of 1-butene adsorbed on (a) nitrided $\gamma\text{-Al}_2\text{O}_3$ for 2 h, (b) $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst for 1 min, (c) $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst for 10 min, and (d) outgassing of (c).

TABLE 2: Assignment of the Observed IR Bands from 1-Butene Adsorbed on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ Catalyst^a

bands (cm^{-1})	assgmt	
	vibration	surf species
3010 (m)	$\nu(\text{HC=})$	I
2965 (m)	$\nu(\text{CH}_3)_{\text{as}}$	II
2920 (s)	$\nu(\text{CH}_2)_{\text{as}}$	II
2880 (w)	$\nu(\text{CH}_3)_s$	II
2857 (sh)	$\nu(\text{CH}_2)_s$	II
1615 (s)	$\nu(\text{C=C})$	II
1452 (s)	$\delta(\text{CH}_3)_{\text{as}}/\delta(\text{CH}_2)_{\text{as}}$	II
1408 (w)	$\delta(\text{CH}_2)_s$	II
1380 (s)	$\delta(\text{CH}_3)/\delta(\text{CH}_2)$	II

^a Key: (s) strong; (m) medium; (w) weak; (sh) shoulder; I, π -complex; II, σ -species.

band at 1615 cm^{-1} , stable for hydrogenation at RT, can be attributed to $\nu(\text{C=C})$ of the σ -allyl butene species. The bands at 2965, 2920, 1452, 1408, and 1380 cm^{-1} are evidence for the presence of σ -allyl species.^{33,37} In conclusion, $\pi(\pi_s)$ adsorbed butene and σ -allyl butene species are produced by 1-butene adsorption and reaction on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst. An assignment for these IR bands is listed in Table 2.

The effect of 1,3-butadiene on the adsorption of 1-butene on the catalyst is shown in Figure 6. 1,3-Butadiene was adsorbed on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst first and outgassed (Figure 6a) and then followed by the adsorption of 1-butene. Interestingly, the major contours of Figure 6b,c are similar to that of gas 1-butene, which is quite different from those in Figure 5b,c. No evident IR bands of 2-butenes are observed even after 2-h adsorption, implying that preadsorbed butadiene simply prevents 1-butene from its adsorption and reaction on the catalyst surface. The major feature of Figure 6d collected after evacuation of the sample is similar to that of Figure 6a. It indicates that most 1,3-butadiene is still adsorbed on the catalyst. Meanwhile, some small differences between the spectra of parts a and d of Figure 6 can be summarized as the following: (a) Absorbance features at 2965, 1616, and 1457 cm^{-1} increase in intensity slightly, which are similar to those of adsorbed butene species (Figure 5d). (b) Concomitantly, bands at 3088, 3005, and 1565 cm^{-1} decrease in intensity slightly, which are due to adsorbed butadiene on the catalyst. The two different trends show that

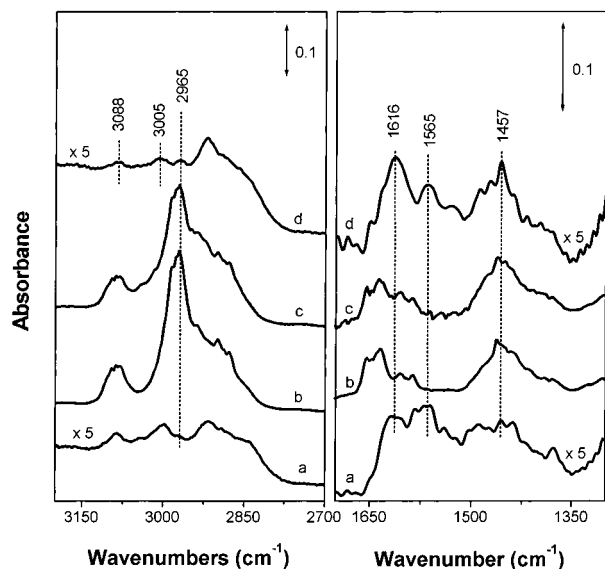


Figure 6. IR spectra of (a) 1,3-butadiene preadsorbed on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst, (b) 1-butene adsorbed on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst, (c) 1-butene preadsorbed with 1,3-butadiene for 1 min and (d) evacuation of (c).

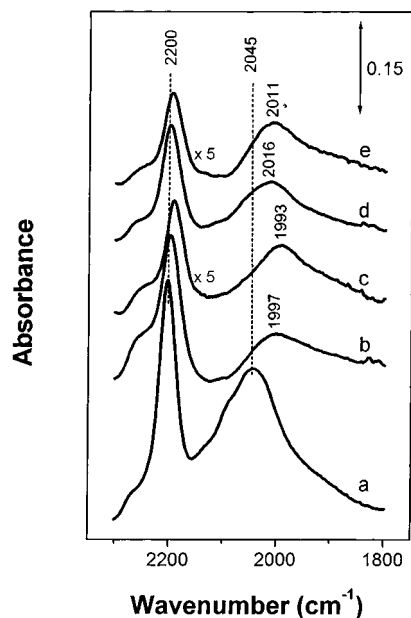


Figure 7. IR spectra in the $\nu(\text{CO})$ region of adsorbed CO on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst (a) CO adsorbed alone, (b) first CO and then 1,3-butadiene, (c) first 1,3-butadiene and then CO, (d) first CO and then 1-butene, and (e) first 1-butene and then CO.

only a small portion of 1-butene can adsorb on the nitride catalyst with preadsorbed butadiene.

3.3. Coadsorption of 1,3-Butadiene/1-Butene with CO.

Figure 7 shows the IR spectra of coadsorbed CO with 1,3-butadiene/1-butene on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst. All spectra were obtained after an outgassing of the gas-phase CO at RT. CO adsorption on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ gives two characteristic IR bands at 2045 and 2200 cm^{-1} , corresponding to the adsorbed CO on the Mo and N sites, respectively, forming linearly adsorbed CO and NCO species.⁴⁰ After CO was adsorbed on the catalyst for 30 min and outgassed, 1,3-butadiene was introduced to the sample. Both bands at 2200 and 2045 cm^{-1} shift to lower frequencies at 2197 and 2000 cm^{-1} , respectively, accompanied with a decrease in intensity (Figure 7b). Similarly, shown in Figure 7c, when 1,3-butadiene was preadsorbed, the 2200- cm^{-1}

band shifts to 2193 cm^{-1} and 2045 cm^{-1} to 1991 cm^{-1} . At the same time, their intensities are greatly weakened.

When CO was preadsorbed on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst, subsequently adsorbed 1-butene also has a strong influence on the IR bands of adsorbed CO. As exhibited in Figure 7d, the band at 2200 cm^{-1} shifts to 2198 cm^{-1} and 2045 cm^{-1} to 2016 cm^{-1} . When 1-butene was preadsorbed, shown in Figure 7e, adsorbed CO gives two weak bands at 2195 and 2011 cm^{-1} .

Obviously, the presence of either preadsorbed 1,3-butadiene or 1-butene cannot only significantly influence the frequency of CO vibration but also strongly suppress the adsorption of CO on the nitrated sample, especially on the Mo sites. It is indicated that both 1,3-butadiene and 1-butene are adsorbed mainly on the surface Mo sites of $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst and have both electronic and blocking effects on the surface sites. The low-frequency shift of $\nu(\text{CO})$ led by coadsorption of 1,3-butadiene or 1-butene can be interpreted in terms of the electronic effects of π -donation of 1,3-butadiene or 1-butene. This is indirect evidence for the presence of π -bonded species of 1,3-butadiene or 1-butene on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst. It should be noted that the shift of CO frequency caused by 1,3-butadiene is larger than that of 1-butene, suggesting a stronger interaction of π -bonded butadiene with the nitride catalyst than that of π -bonded 1-butene.

4. Discussion

4.1. Selectivity of the Hydrogenation of 1,3-Butadiene. Our catalytic reaction test shows that the 1,3-butadiene hydrogenation on $\gamma\text{-Mo}_2\text{N}$ catalyst produces mainly 1-butene together with small portion of 2-butenes and butane.¹⁴ The high selectivity in 1-butene can be explained by comparing the interaction modes of 1,3-butadiene and 1-butene with the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Adsorption of 1,3-butadiene and 1-butene on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst results in both π - and σ -bonded species. π -Adsorbed species is considered to be the dominant intermediate in olefin hydrogenation as confirmed by recent sum frequency generation (SFG) studies.^{44–46} The σ -bonded species may play a role in side reactions and in catalyst deactivation.⁴⁷ Therefore, a comparison of the configuration of π -adsorbed species of the two molecules is necessary for the explanation of the selectivity.

The interaction modes of the π -adsorbed species on the surface of $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst are different for 1,3-butadiene and 1-butene. Both π_d - and π_s -adsorbed species are formed from 1,3-butadiene adsorption while adsorption of 1-butene gives only π_s -adsorbed species. For π_d -adsorbed butadiene, its heat of adsorption is about twice the heat of π_s -adsorbed butene.²⁶ As shown in Figure 6, preadsorbed butadiene can strongly inhibit 1-butene from its adsorption and isomerization on the nitride catalyst. The IR results of their coadsorption with CO also indicate that π -adsorbed butadiene interacts with the catalyst surface more strongly than that of π -bonded butene. As a consequence, the 1-butene formed by hydrogenation is less easily to be adsorbed on the catalyst and is difficult to replace the adsorbed butadiene, consistent with the IR results shown in Figures 6. This is similar to the case of Pd catalyst in the selective hydrogenation of 1,3-butadiene. Bertolini et al.^{25,26} concluded that 1,3-butadiene is di- π -bonded while 1-butene is π -bonded to Pd(111) and explained the high selectivity by competitive adsorption of the two molecules.

Therefore, the high selectivity of unsupported $\gamma\text{-Mo}_2\text{N}$ catalyst in the selective hydrogenation of 1,3-butadiene can be attributed to the stronger adsorption of 1,3-butadiene than 1-butene. The 1-butene desorbs once it is formed by the hydrogenation of adsorbed butadiene; as a consequence, the

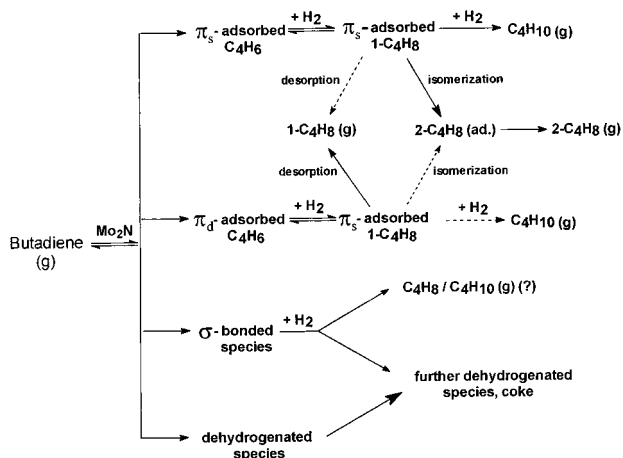


Figure 8. Proposed scheme for adsorption and hydrogenation 1,3-butadiene on γ - Mo_2N catalyst. (g) indicates the gas phase; lines of dots mean a lower possibility along the arrow than solid lines.

possibility of further hydrogenation of 1-butene to butane and conversion to 2-butenes is much less, resulting in high selectivity to 1-butene. A scheme of 1,3-butadiene hydrogenation on molybdenum nitride catalyst is proposed in Figure 8.

It is worth noting that a portion of the π -adsorbed butadiene is in single π mode, similar to that of 1-butene on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Their adsorption strength is comparable, and therefore, the formation of a small part of butane and 2-butenes is possible in the hydrogenation reaction.

4.2. Catalytic Function of the Incorporated N Atoms in the Nitride. The unique catalytic properties of molybdenum nitride catalyst are generally considered to be related to the incorporated N atoms. When the surface N atoms are partly removed by H_2 treatment and evacuation at high temperatures, the IR results show that more σ -bonded and π_s -bonded species are formed on the catalyst. These surface species have great influences on both the selectivity and stability of the nitride catalyst in the hydrogenation of 1,3-butadiene.

As discussed above, the selectivity in the hydrogenation of 1,3-butadiene on $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst is mainly due to the competitive adsorption of π_d -adsorbed butadiene and π_s -adsorbed 1-butene. In the case of the N-deficient nitride catalyst, more π_s -adsorbed butadiene and less molecularly π_d -adsorbed butadiene are present on the surface. So the adsorption strengths of the π -adsorbed 1-butene and butadiene are comparable and the further hydrogenation of 1-butene becomes easier, which would inevitably lead to a lower selectivity in 1-butene for the N-deficient nitride catalyst compared with the normal nitride catalyst.

The σ -bonded species is considered to play a role in side reactions and the catalyst deactivation,⁴⁷ so the nitride catalyst lacking surface N atoms is deactivated more rapidly because of more σ -adsorbed species on the surface. The interaction of 1,3-butadiene with the differently treated $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst can be explained by the different electronic properties of the catalyst surfaces. The activation of $\text{C}=\text{C}$ bond involves the donation of metal d-electrons to the antibonding $\text{p}\pi^*$ -orbitals of the unsaturated hydrocarbons.⁴⁸ It is generally accepted that the formation of carbide and nitride narrows the filled portion of the metal d-band,⁴⁹ which would result in a less efficient $\text{d}-\text{p}\pi^*$ overlapping between the nitride catalyst and the $\text{C}=\text{C}$ bonds of the adsorbate than between the nitride catalyst after removing part of its surface nitrogen atoms. This is consistent with our observation of much less σ -bonded species on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst than on the catalyst short of nitrogen.

In other words, the presence of incorporated nitrogen atoms reduces the degree of interaction between the unsaturated hydrocarbons and the catalyst surface; namely, it leads to a proper interaction between 1,3-butadiene and the catalyst. This contributes to the mild activity, high selectivity, and stable life of the nitride catalyst in the selective hydrogenation of 1,3-butadiene.

5. Conclusions

(1) There are at least three kinds of adsorbed species formed from the adsorption of 1,3-butadiene on the $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst: π_s - and π_d -adsorbed butadiene; σ -adsorbed species possibly in di- σ -form; dehydrogenated species. The adsorption and reaction of 1-butene on the nitride catalyst produces two types of surface species: π_s - and σ -bonded butene species. These species are adsorbed mainly on the surface Mo sites as studied by CO coadsorption.

(2) The high selectivity in 1-butene for the hydrogenation of 1,3-butadiene on $\gamma\text{-Mo}_2\text{N}$ catalyst is explained in term of competitive adsorption; namely, the π_d -adsorbed butadiene strongly inhibits the adsorption of 1-butene and blocks its further hydrogenation and isomerization.

(3) On the $\text{Mo}_2\text{N}_x/\gamma\text{-Al}_2\text{O}_3$ ($x < 1$) catalyst, adsorption of 1,3-butadiene results in more π_s -adsorbed butadiene and σ -bonded surface species, leading to lower selectivity and easier deactivation of the catalyst. These imply that the incorporated N atoms weaken the interaction between the olefin and molybdenum nitride and thus improve the selectivity and stability of the catalyst in the hydrogenation of 1,3-butadiene.

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