

Selective liquid hydrogenation of long chain linear alkadienes on molybdenum nitride and carbide modified by oxygen

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Abstract

The as-synthesized molybdenum nitrides and carbide has higher conversion of alkadienes and selectivity of alkenes for selective hydrogenation of longer chain alkadienes (C₁₀–C₁₃) than the supported palladium catalyst used in industry at higher temperature and pressure. The introduction of oxygen element to the surface of molybdenum nitride or carbide is favorable to improvement of selectivity of alkenes. The passivated molybdenum nitride or carbide catalyst pretreated in H₂ at 450 °C has higher yield of alkenes than corresponding unpassivated and passivated molybdenum nitride or carbide, respectively. It was proved by XPS that the modification of molybdenum nitride or carbide by oxygen results in the change of oxidation states of molybdenum and their content. Decreasing of Mo⁰ content and improvement of Mo²⁺ and Mo³⁺ are favorable to the elevation of selectivity of alkenes.

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1. Introduction

Olefin stream produced in the plant for producing the feedstock of detergent-linear alkyl benzene by dehydrogenation of C₁₀–C₁₃ paraffins contains 1–3% of alkadienes. The presence of these alkadienes will cause a lot of side reactions in the subsequent alkylation, resulting in a decrease of the yield and quality of alkyl benzene [1]. Therefore, it is of both scientific and industrial significance to make an investigation on the selective hydrogenation of alkadienes to alkenes. Palladium catalysts have by far be proved to be the most active and selective for selective hydrogenation of alkadienes and alkynes to alkenes. However, they are less effective (with lower selectivity of alkenes) at higher temperature and pressure, which is required by this industrial process to avoid using huge cooling system. In addition, palladium catalysts are easy to be poisoned by sulfur compound. Therefore, it is of significance to find an alternative non-noble metal catalyst for hydrogenation instead of expensive noble metals catalyst.

Recently, molybdenum nitrides and carbides have attracted much attention because they show excellent catalytic properties resembling expensive noble metals in a number of

hydrogen involved reactions, such as NH₃ synthesis, ethane hydrogenolysis, hydrogenation of benzene and CO, selective hydrogenation of ethyne, hydrodenitrogenation, hydrodesulfurization, and hydrocarbon isomerization [2–14]. Usually, molybdenum nitride was prepared by nitriding MoO₃ with NH₃ in a temperature program [15]. Molybdenum carbide catalyst was prepared by carburization of MoO₃ with a mixture of H₂ and CH₄ in a temperature program developed by Boudart and co-workers [16]. The molybdenum nitride or carbide synthesized by temperature-programmed nitriding or carburization of MoO₃, respectively, is pyrophoric, and a passivation step is required to prevent the bulk oxidation of these materials on exposure to air. A treatment with 1 vol.% O₂/Ar or He, or N₂ at room temperature leads to oxynitride or oxycarbide surface layers, and the O atoms in this oxynitride or oxycarbide were very difficult to be completely removed [17]. Therefore, the real catalytic active phase of passivated molybdenum nitride or carbide as catalyst in the catalytic reaction is molybdenum oxynitride or oxycarbide phase instead of pure molybdenum nitride or carbide phase. Sayag et al. [18] made a detailed investigation on the surface properties of passivated molybdenum oxynitride. Miga et al. [19] proposed a model of a dual site for MoO_xN_y, and studied the effect of this dual site on HDN of indole. Xiao et al. [20] suggested that the hydrogenation/dehydrogenation sites were Mo and the cracking

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sites were related to N atoms. In our previous work, we synthesized molybdenum oxynitrides by hydrazine reduction of MoO_3 at moderate temperature, it was discovered that some of these molybdenum oxynitrides were very efficient for selective hydrogenation of longer chain alkadienes, and exhibited good resistance to poisoning of H_2S [21]. Bouchy et al. [22] studied the microstructure and characterized molybdenum oxycarbide prepared by treating MoO_3 or a hydrogen bronze of molybdenum oxide in the flow of H_2 and n -heptane at 350°C , they found this molybdenum oxycarbide was a highly selective catalyst for the isomerization of alkanes. However, it was discovered by Boudart and Leclercq that when heated above 400°C in the presence of a carbon source, this molybdenum oxycarbide transferred into another oxycarbide, which was not selective for alkane isomerization [23]. So it is important to make a systematic investigation of the electronic modification of molybdenum nitride and carbide by oxygen, and its effect on the catalytic activities of these materials [24]. To our best knowledge, up to now, there have been no reports of selective hydrogenation of long chain alkadienes on molybdenum nitride or carbide catalyst. In this work, we made an investigation on electronic modification of molybdenum nitride and carbide by oxygen, by using CO chemisorption and in situ XPS, and applied these catalysts in the selective hydrogenation of longer chain linear alkadienes (C_{10} – C_{13}). It was found that the as-synthesized molybdenum nitrides and carbide has higher conversion of alkadienes and selectivity of alkenes than the supported palladium catalyst used in industry at higher temperature and pressure, and the electronic modification of molybdenum carbide or nitride by an appropriate amount of oxygen results in obvious improvement of their catalytic performance for selective hydrogenation of longer chain alkadienes.

2. Experimental

2.1. Preparation of catalysts

The unsupported γ - Mo_2N was prepared by temperature-programmed nitriding of MoO_3 in a flow of 12 vol.% N_2/NH_3 in a quartz tube reactor (30 mm i.d. \times 800 mm). The loading of MoO_3 precursor was 7 g and the flowing of 12 vol.% N_2/NH_3 was 660 ml/min. After a rapid heat up of the MoO_3 sample to 300°C in 30 min, the sample was heated up to 700°C at a rate of $1^\circ\text{C}/\text{min}$ and kept at the final temperature for 12 h. The synthesized catalyst was then rapidly cooled down to room temperature in a flow of 12 vol.% N_2/NH_3 , and flushed in N_2 for 0.5 h. This obtained unpassivated catalyst was denoted as γ - $\text{Mo}_2\text{N}(\text{in situ})$. The $\text{MoN}_x\text{O}_y(2)$ catalyst was prepared by passivating γ - $\text{Mo}_2\text{N}(\text{in situ})$ with 40 ml (STP)/min of 1% O_2/Ar for 12 h. The $\text{MoN}_x\text{O}_y(1)$ catalyst was prepared by reducing the $\text{MoN}_x\text{O}_y(2)$ catalyst with 40 ml (STP)/min of H_2 for 1 h at 450°C .

The unsupported molybdenum carbide was prepared by temperature-programmed carburization of MoO_3 in a flow of 16 vol.% CH_4/H_2 in a quartz tube reactor (30 mm i.d. \times 800 mm). The loading of MoO_3 precursor was 7.2 g and the flowing rate of 16 vol.% CH_4/H_2 was 670 ml (STP)/min. After a rapid heat up of the MoO_3 sample to 350°C in 25 min, the sample was heated up to 700°C at a rate of $0.5^\circ\text{C}/\text{min}$ and kept at the final temperature for 2 h. The synthesized catalyst was then rapidly cooled down to room temperature in a flow of 16 vol.% CH_4/H_2 , and flushed in H_2 for 0.5 h. This obtained unpassivated catalyst was denoted as $\text{Mo}_2\text{C}(\text{in situ})$. The $\text{MoC}_x\text{O}_y(2)$ catalyst was prepared by passivating $\text{Mo}_2\text{C}(\text{in situ})$ with 40 ml (STP)/min of 1% O_2/Ar for 12 h. The $\text{MoC}_x\text{O}_y(1)$ catalyst was prepared by reducing the $\text{MoC}_x\text{O}_y(2)$ catalyst with 40 ml (STP)/min of H_2 for 1 h at 450°C .

2.2. Characterization of catalysts

BET surface area of the catalysts was measured using a MICROMERITICS ASAP-2000 adsorption analyzer using nitrogen as adsorbate. Powder X-ray diffraction analysis was performed with Ni-filtered $\text{Cu K}\alpha$ radiation on a Shimadzu XD-3A X-ray diffractometer. The working voltage of 35 kV and the electronic current of 25 mA were employed.

The surface species of the as-synthesized catalysts were analyzed by a ESCALab MK2 X-ray photoelectron spectrometer. $\text{Mg K}\alpha$ radiation was selected as X-ray source. The catalysts were prepared in situ by using same condition mentioned in Section 2.1, and transferred from the quartz tube reactor used for preparation of catalyst to a small beaker with *iso*-octane [25] in the flowing H_2 deoxygenated by MnO/SiO_2 to protect the catalyst from air oxidation, then mounted on a double-sided adhesive tape, and placed in a UHV chamber from XPS analysis, and out-gassed. After the residual pressure in this chamber was below 10^{-9} Pa, the spectra of catalyst were collected and corrected by referencing the binding energy to carbon ($\text{C}_1 = 284.6$ eV). The spectra were de-convoluted using a special software program.

Pulsed chemisorption technique [8] was employed to measure the amount of irreversibly chemisorbed CO on the prepared catalysts. $\text{Mo}_2\text{N}(\text{in situ})$ or $\text{Mo}_2\text{C}(\text{in situ})$ was prepared in situ by using same condition mentioned in Section 2.1, respectively, then flushed by He (99.999%) at a rate of 40 ml (STP)/min at 450°C for 1 h, finally, cooled to room temperature for CO pulsed chemisorption. To measure the amount of irreversibly chemisorbed CO on $\text{MoN}_x\text{O}_y(2)$ catalyst or $\text{MoC}_x\text{O}_y(2)$ catalyst, the catalyst was flushed by He (99.999%) at a rate of 40 ml (STP)/min at 450°C for 1 h before CO pulsed chemisorption at room temperature. To measure the amount of irreversibly chemisorbed CO on $\text{MoN}_x\text{O}_y(1)$ catalyst or $\text{MoC}_x\text{O}_y(1)$ catalyst, before CO pulsed chemisorption at room temperature, $\text{MoN}_x\text{O}_y(2)$ catalyst or $\text{MoC}_x\text{O}_y(2)$ catalyst was pretreated in H_2 at a rate of 40 ml (STP)/min under atmospheric pressure at 450°C for 1 h, then flushed by He (99.999%) at a rate of 40 ml

(STP)/min at 450 °C for 1 h. Pulse of a known quantity (1.96 μmol) of CO (99.95%) deoxygenated by MnO/SiO₂ were injected every 5 min on the sample at room temperature in flowing He (99.999%) purified by an oxygen trap (MnO/SiO₂). The injection was continued until probe molecules saturated the surface. After each injection, the quantity of probe molecules not chemisorbed was measured using a conventional device equipped with a TCD.

2.3. Catalytic activity measurement

The measurement of reaction of catalysts for selective hydrogenation of longer chain alkadienes were accomplished on homemade apparatus by using a technical process of hydrogenation of feedstock saturated by hydrogen, which is similar to industrial process [1]. The feedstock composed of 84.38% alkanes, 10.40% alkenes, 1.26% alkadienes, and 3.96% aromatic hydrocarbons were firstly saturated by hydrogen in a 2 l autoclave at 100 °C and 17 atm. Then the feedstock saturated by hydrogen was delivered into a fixed-bed micro-reactor of 20 mm i.d. \times 400 mm stainless tube from the autoclave by a valve for hydrogenation under different reaction conditions (e.g. 160 °C, 14 atm, H₂/alkadienes (molar ratio) = 1.28, LSV = 8.0 ml g⁻¹ catalyst h⁻¹). The details of the reaction conditions and method of product analysis were reported in our previous work [21].

3. Result and discussion

3.1. Properties and structure of catalysts

The XRD profiles of as-synthesized catalysts are showed in Fig. 1. The molybdenum nitride prepared by temperature-programmed reduction of MoO₃ with NH₃ and N₂ exhibits a characteristic pattern of γ -Mo₂N without

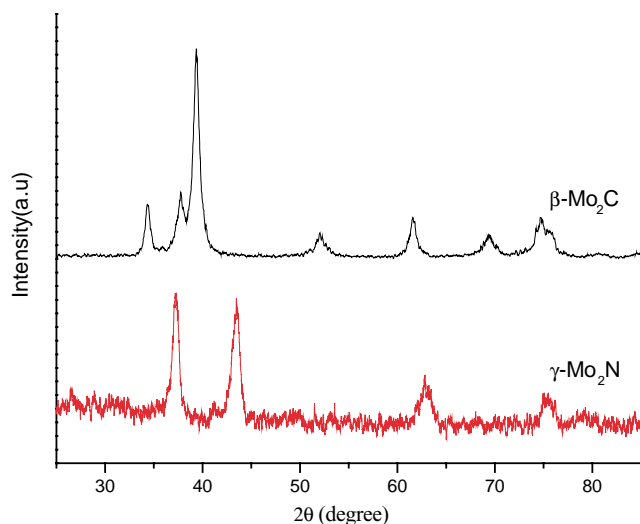


Fig. 1. XRD patterns of catalysts.

Table 1
Properties of catalysts

Catalyst	Surface area (m ² g ⁻¹)	CO ($\mu\text{mol g}^{-1}$)	n_{CO} ($\times 10^{13} \text{ cm}^{-2}$)
Mo ₂ N(in situ)	4.4	563.4	771.2
MoN _x O _y (1)	4.4	57.1	78.2
MoN _x O _y (2)	4.4	8.4	11.5
Mo ₂ C(in situ)	6.7	57.7	51.9
MoN _x O _y (1)	6.7	21.5	19.3
MoN _x O _y (2)	6.7	2.7	2.4

evidence of any other phase. The molybdenum carbide prepared by carburization of MoO₃ with CH₄ and H₂ exhibits a characteristic pattern of β -Mo₂C without any other phase. Passivation and reduction procedure have no effect on the bulk crystalline structure of molybdenum carbide and nitride

Table 1 shows the CO chemisorption on the catalysts. The number density of CO (n_{CO}) is calculated as the amount of gas uptake per unit surface area. The number density of CO (n_{CO}) on unpassivated molybdenum nitride (Mo₂N(in situ)) is as high as $771.2 \times 10^{13} \text{ cm}^{-2}$. But the passivated molybdenum nitride catalyst (MoN_xO_y(2)) only has a number density of $11.5 \times 10^{13} \text{ cm}^{-2}$. The reduction of this passivated molybdenum nitride by H₂ at 450 °C results in the elevation of n_{CO} from 11.5×10^{13} to $78.2 \times 10^{13} \text{ cm}^{-2}$ (MoN_xO_y(1)). Yang et al. [26] reported that CO was strongly absorbed on fresh Mo₂N/Al₂O₃ catalyst leading to two IR bands at 2045 and 2200 cm⁻¹. They assigned these bands to linearly absorbed CO on molybdenum and nitrogen sites to form MoCO and NCO surface species, respectively. Therefore, the very high n_{CO} of unpassivated molybdenum nitride is reasonably attributed to the presence of two absorbed sites of molybdenum and nitrogen sites. The number density of CO (n_{CO}) on unpassivated molybdenum carbide (Mo₂C(in situ)) is $51.9 \times 10^{13} \text{ cm}^{-2}$. But the passivation in 1% O₂/Ar of Mo₂C(in situ) leads to rapidly decreasing of n_{CO} from 51.9×10^{13} to $2.4 \times 10^{13} \text{ cm}^{-2}$ (MoC_xO_y(2)). The reduction of this passivated molybdenum carbide by H₂ at 450 °C results in the elevation of n_{CO} from 2.4×10^{13} to $19.2 \times 10^{13} \text{ cm}^{-2}$ (MoC_xO_y(1)).

X-ray photoelectron spectral of Mo 3d profiles of as-synthesized catalysts is shown in Fig. 2. The passivated molybdenum carbide (MoC_xO_y(2)) has different XPS spectral pattern from unpassivated molybdenum carbide (Mo₂C(in situ)) and H₂ reduced molybdenum carbide (MoC_xO_y(1)), which have very similar XPS spectral pattern and same peak binding energy (227.86 eV) of Mo 3d situated below 229.9 eV. Compared with MoC_xO_y(2), the peak binding energy of Mo 3d situated below 229.9 eV for the Mo₂C(in situ) and MoC_xO_y(1) shifts to lower binding energy (from 228.65 to 227.86 eV). The similar situation was observed for Mo₂N samples with different oxygen content, but compared with MoC_xO_y(2), there is only a small shoulder peak situated below 229.9 eV for passivated molybdenum nitride (MoN_xO_y(2)), which shows that Mo

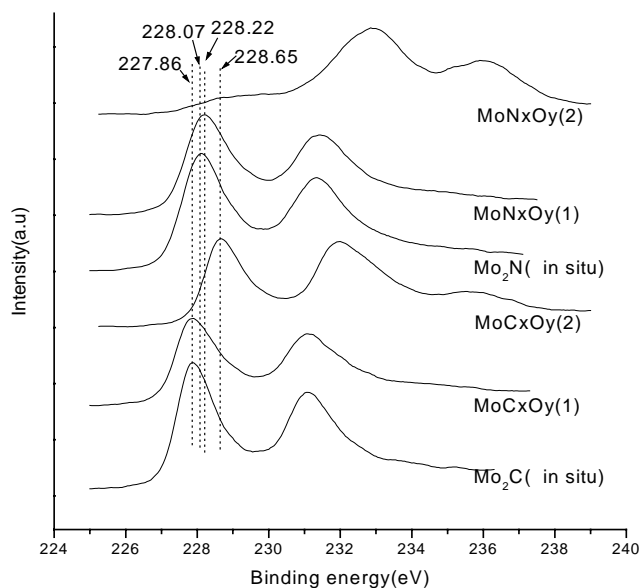


Fig. 2. Mo 3d XPS spectra of as-synthesized catalysts.

species with lower oxidation state in molybdenum nitride is more easily oxidized to higher oxidation state than in molybdenum carbide. As MoO_2 (Mo^{4+}) has no activity for the hydrogenation of alkadienes and alkenes under our experimental condition, it could be reasonably concluded that the active species for the hydrogenation of alkadienes and alkenes are $\text{Mo}^{\delta+}$ ($0 \leq \delta$) species on the surface of as-synthesized catalysts. Therefore, we mainly concentrate on the distribution and abundance of $\text{Mo}^{\delta+}$ ($0 \leq \delta < 4$) species with a binding energy of Mo 3d lower than 229.9 eV on as-synthesized catalysts. The binding energy of $\text{Mo } 3d_{5/2}^0$, $\text{Mo } 3d_{5/2}^{2+}$, $\text{Mo } 3d_{5/2}^{3+}$, $\text{Mo } 3d_{5/2}^{4+}$, $\text{Mo } 3d_{5/2}^{5+}$, and $\text{Mo } 3d_{5/2}^{6+}$ are 227.8, 229.0, 229.9, 231.8, and 233.1 eV, respectively [14]. Using a special software program deconvoluted the spectral of XPS Mo 3d for the as-synthesized catalysts. The XPS results of the as-synthesized catalysts were tabulated in Table 2. There is no Mo^0 species on the surface of the passivated molybdenum carbide or nitride. The abundance of Mo^{2+} and Mo^{3+} is 16.2 and 28.8%, respectively, for the $\text{MoC}_x\text{O}_y(2)$ catalyst, but the $\text{MoN}_x\text{O}_y(2)$ catalyst only has 4.4% Mo^{2+} and 6.8% Mo^{3+} . The reduction of the passivated molybdenum carbide or nitride at 450 °C by H_2 leads to the appearance of Mo^0 species and the rapid

Table 2
XPS analysis of catalysts

Catalyst	Distribution (%)					
	Mo^0	Mo^{2+}	Mo^{3+}	Mo^{4+}	Mo^{5+}	Mo^{6+}
$\text{Mo}_2\text{N}(\text{in situ})$	22.1	27.6	18.5	8.7	13.5	9.6
$\text{MoN}_x\text{O}_y(1)$	16.7	24.4	18.0	11.6	15.1	14.2
$\text{MoN}_x\text{O}_y(2)$	0	4.4	6.8	6.8	16.5	65.5
$\text{Mo}_2\text{C}(\text{in situ})$	27.6	26.2	21.8	9.3	10.5	4.6
$\text{MoCC}_x\text{O}_y(1)$	23.9	26.5	16.4	11.5	9.9	11.8
$\text{MoC}_x\text{O}_y(2)$	0	16.2	28.8	12.7	14.8	27.5

elevation of their surface $\text{Mo}^{\delta+}$ ($0 \leq \delta < 4$) species content, especially for the $\text{MoN}_x\text{O}_y(2)$ catalyst. Compared with $\text{MoN}_x\text{O}_y(1)$, the $\text{Mo}_2\text{N}(\text{in situ})$ has higher Mo^0 species and $\text{Mo}^{\delta+}$ ($0 \leq \delta < 4$) species content. The abundance of $\text{Mo}^{\delta+}$ ($0 \leq \delta < 4$) species is 59.1 and 68.2%, respectively, for $\text{MoN}_x\text{O}_y(1)$ and $\text{Mo}_2\text{N}(\text{in situ})$. The $\text{Mo}_2\text{C}(\text{in situ})$ has higher Mo^0 species and $\text{Mo}^{\delta+}$ ($0 \leq \delta < 4$) species content than $\text{MoC}_x\text{O}_y(1)$. The abundance of $\text{Mo}^{\delta+}$ ($0 \leq \delta < 4$) species is 66.8 and 75.6%, respectively, for $\text{MoC}_x\text{O}_y(1)$ and $\text{Mo}_2\text{C}(\text{in situ})$. Based on the above observation, it is concluded that the introduction of oxygen on the surface of molybdenum carbide or nitride could modify electronic properties of surface Mo species, and change the relative distribution of different Mo species.

3.2. Catalytic characteristics of catalysts

Fig. 3 showed the changes of conversion and selectivity of alkadienes hydrogenation with reaction time on $\text{Mo}_2\text{N}(\text{in situ})$ catalyst at 160 °C, 14 atm, $\text{H}_2/\text{alkadienes}$ (molar ratio) = 1.28, $\text{LSV} = 8.0 \text{ ml g}^{-1} \text{ catalyst h}^{-1}$. It can be seen from the figure that the $\text{Mo}_2\text{N}(\text{in situ})$ catalyst reached steady state after experienced some deactivation during the first 3 h. The other catalysts had similar situation. The conversion and selectivity of as-synthesized catalysts were summarized in Table 3 (the data was an average value of the results after hydrogenation reached steady state). Palladium catalysts have by far proved to be the most active and selective for selective hydrogenation of alkadienes and alkynes to alkenes. However, from Table 3, it can be seen that 0.3% Pd/ Al_2O_3 catalyst has only 53.8% conversion of alkadienes and -24.1% selectivity of alkenes at 160 °C, 14 atm, $8.0 \text{ ml g}^{-1} \text{ catalyst h}^{-1}$ and $\text{H}_2/\text{alkadienes}$ (molar ratio) = 1.28. The negative selectivity of alkenes shows that there is a net alkenes content loss after hydrogenation. This noble metal catalyst is much less effective than the as-synthesized molybdenum nitrides and carbide at higher

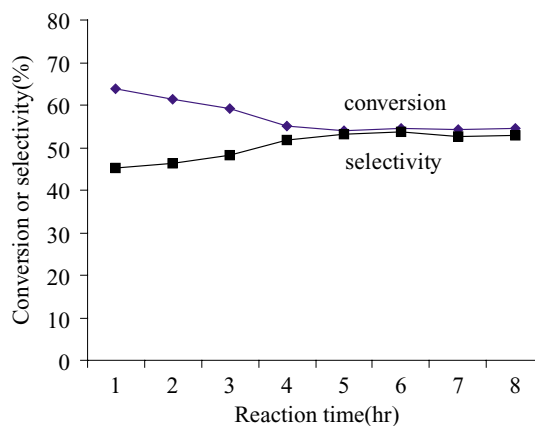


Fig. 3. Conversion and selectivity changes of alkadienes hydrogenation with reaction time on $\text{Mo}_2\text{N}(\text{in situ})$ catalyst at 160 °C, 14 atm, $\text{H}_2/\text{alkadienes}$ (molar ratio) = 1.28, $\text{LSV} = 8.0 \text{ ml g}^{-1} \text{ catalyst h}^{-1}$.

Table 3

Activity and selectivity of catalysts at 160 °C, 14 atm, H₂/alkadienes (molar ratio) = 1.28, LSV = 8.0 ml g⁻¹ catalyst h⁻¹

Catalyst	Conversion of alkadienes (%)	Selectivity of alkenes (%)	Yield of alkenes (%)	Change of alkanes content after hydrogenation (%) ^a	Change of alkenes content after hydrogenation (%) ^b
Mo ₂ N(in situ)	54.3	52.9	28.7	0.32	0.36
MoN _x O _y (1)	84.4	71.4	60.3	0.30	0.76
MoN _x O _y (2)	32.9	100	32.9	0.00	0.41
Mo ₂ C(in situ)	73.6	56.5	41.6	0.40	0.52
MoC _x O _y (1)	69.3	87.8	60.8	0.11	0.77
MoC _x O _y (2)	65.0	89.4	58.1	0.09	0.73
0.3% Pd/Al ₂ O ₃	53.8	-24.1	-13.0	0.84	-0.16

^a Content of alkanes in product—content of alkanes in feedstock.^b Content of alkenes in product—content of alkenes in feedstock.

temperature and pressure. Unpassivated molybdenum nitride (Mo₂N(in situ)) only has 54.3% of conversion of alkadienes and 52.9% of selectivity of alkenes. The introduction of oxygen element to the surface of molybdenum nitride is favorable to the increasing of selectivity of alkenes. The selectivity of alkenes increases rapidly from 52.9% for unpassivated molybdenum nitride (Mo₂N(in situ)) to 71.4% for passivated molybdenum nitride catalyst pretreated in H₂ (Mo₂N_xO_y(1)), and to 100% for passivated molybdenum nitride catalyst (Mo₂N_xO_y(2)). The passivated molybdenum nitride (Mo₂N_xO_y(2)) has lowest activity of hydrogenation. Compared with Mo₂N(in situ) and MoN_xO_y(2), the passivated molybdenum nitride catalyst pretreated in H₂ (MoN_xO_y(1)) with higher yield of alkenes is more effective for selective hydrogenation of longer chain alkadienes. The molybdenum carbide has similar situation. Unpassivated molybdenum carbide (Mo₂C(in situ)) has 73.6% of conversion of alkadienes and 56.5% of selectivity of alkenes. The introduction of oxygen element to the surface of molybdenum carbide is favorable to the increasing of selectivity of alkenes. The selectivity of alkenes increases rapidly from 56.5% for unpassivated molybdenum carbide (Mo₂C(in situ)) to 87.8% for passivated molybdenum carbide catalyst pretreated in H₂ (MoC_xO_y(1)), and to 89.4% for passivated molybdenum carbide catalyst (MoC_xO_y(2)). No matter how the reaction conditions (e.g. reaction temperature, pressure, liquid space velocity, etc.) are changed, the above-mentioned trends in which the introduction of oxygen element to the surface of molybdenum nitride or carbide is favorable to the increasing of selectivity of alkenes keep unchanged. It is concluded that the passivated molybdenum nitride or carbide catalyst pretreated in H₂ are more effective than corresponding unpassivated and passivated molybdenum nitride or carbide because of their highest yield of alkenes.

The effect of reaction temperature on the activity and selectivity of longer chain alkadienes hydrogenation on as-synthesized catalysts was showed in Fig. 4. For MoN_xO_y(1) catalyst, with the elevation of reaction temperature from 120 to 200 °C, the conversion of alkadienes increases from 61.5 to 86.8% and selectivity of alkenes decreases from 83.7 to 67.3%. For MoC_xO_y(1) catalyst, increasing reaction temperature from 120 to 200 °C leads

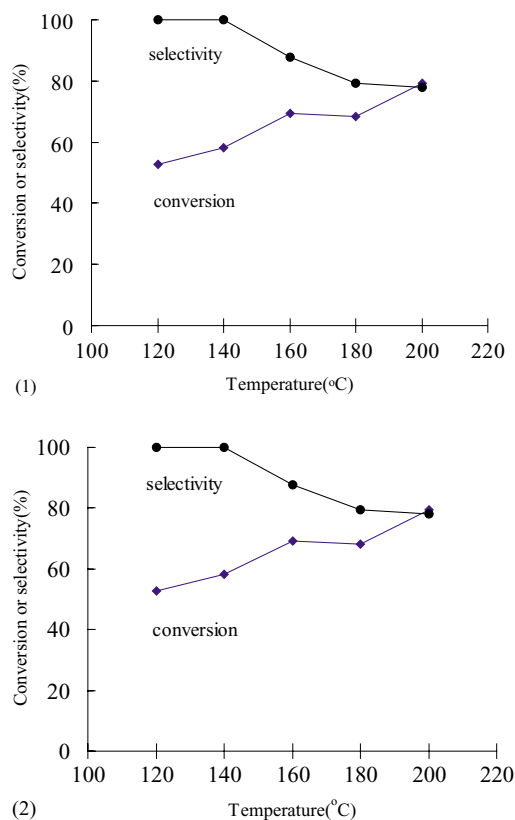


Fig. 4. Conversion and selectivity alkadienes hydrogenation on some of as-synthesized catalysts at different reaction temperatures, 14 atm, H₂/alkadienes (molar ratio) = 1.28, LSV = 8.0 ml g⁻¹ catalyst h⁻¹: (1) MoC_xO_y(1) and (2) MoN_xO_y (1).

to the increasing of conversion of alkadienes from 52.7 to 79.4% and decreasing of selectivity from 100 to 78.0%. These results show that molybdenum nitride and carbide have good reaction temperature tolerance, which is requested by industrial process of selective hydrogenation of long chain alkadienes (C₁₀–C₁₃) [1].

It was reported by Nagai et al. [27] that the activity of Mo species for hydrogenation of carbazole increased in order as follows: Mo metal β-Mo₂N_{0.78} > γ-Mo₂N > MoO₂. This result showed that Mo species with lower oxidation state had a higher activity than Mo species with higher

oxidation state. The higher activity of Mo species with lower oxidation state inevitably results in a lower selectivity of alkenes as the excessive hydrogenation of alkenes to alkanes is more easily proceeding on the Mo species with higher activity than on the Mo species with lower activity. Based on the results of XPS analysis, it is reasonably inferred that the lower selectivity of alkenes and higher conversion of alkadienes for Mo₂C(in situ) or Mo₂N(in situ) than passivated molybdenum carbide or nitride, respectively, is attributed to the presence of Mo⁰, and the much higher total abundance of Mo^{δ+} (0 ≤ δ < 4) species. The more Mo⁰ species content and higher total abundance of Mo^{δ+} (0 ≤ δ < 4) species for Mo₂C(in situ) than H₂ reduced molybdenum carbide leads to the higher selectivity of alkenes and lower conversion of alkadienes of H₂ reduced molybdenum carbide than Mo₂C(in situ). It can be seen that the total abundance of Mo^{δ+} (0 ≤ δ < 4) species (68.2%) of Mo₂N(in situ) is higher than one of H₂ reduced molybdenum nitride (59.1%), but why does Mo₂N(in situ) have lower conversion of alkadienes than H₂ reduced molybdenum nitride? We suggest that the lower conversion of alkadienes for the Mo₂N(in situ) than H₂ reduced molybdenum nitride might have some relationship with the presence of two absorbed sites of molybdenum and nitrogen sites on the surface of Mo₂N(in situ) and its unusually high *n*_{CO}, which results in much stronger absorption of both alkadienes and alkenes on Mo₂N(in situ) than on H₂ reduced molybdenum nitride so that it is difficult for the replacement of alkenes by a small amount of alkadienes in feedstock and hereafter hydrogenation of alkadienes. At the same time, a higher coverage of both alkadienes and alkenes on the surface of the catalyst might lead to the lower coverage of surface activated hydrogen atom, which results in the lower activity of this catalyst.

Miga et al. [19] reported that the molybdenum oxynitride prepared by passivating unpassivated molybdenum nitride in 1% O₂/He are bifunctional catalyst with metallic and acidic sites active in the hydrodenitrogenation (HDN). Our results show that the introduction of oxygen element to the surface of molybdenum nitride or carbide not only results in bifunctional sites (metallic and acidic sites) but also in electronic modification of molybdenum nitride or carbide. The oxidation states and its relative content of molybdenum on the surface of molybdenum nitride or carbide are changed by such electronic modification by oxygen, which play decisive role on the change of selectivity and activity for selective hydrogenation of longer chain alkadienes.

4. Conclusion

In summary, molybdenum nitride or carbide catalyst has much better catalytic performance than industrial used supported palladium catalyst at higher reaction temperature and pressure. The passivated molybdenum nitride or carbide

catalyst pretreated in H₂ at 450 °C has higher yield of alkenes than corresponding unpassivated and passivated molybdenum nitride or carbide. The oxidation states and its relative content of Mo species on the surface of molybdenum nitride or carbide could be changed by this electronic modification by oxygen, which play decisive role on the change of selectivity and activity for selective hydrogenation of longer chain alkadienes. Decreasing of Mo⁰ content and improvement of Mo²⁺ and Mo³⁺ are favorable to the elevation of selectivity of alkenes.

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