The preparation of molybdenum oxynitride by hydrazine reduction of MoO_3 at moderate temperature and its application in the selective hydrogenation of long-chain linear alkadienes

Yuanzhi Li [a,b], Yining Fan [a,*], and Yi Chen [a]

[a] *Department of Chemistry, Laboratory of Mesoscopic Materials and Molecular Engineering, Nanjing University, Nanjing, Jiangsu 210093, P.R. China*
[b] *Department of Chemistry, Three Gorges University, Hubei, Yichang 443000, P.R. China*

Received 15 January 2002; accepted 23 April 2002

Molybdenum oxynitride was prepared by hydrazine reduction of MoO_3 at moderate temperatures. The anhydrous condition was favorable to production of amorphous molybdenum oxynitride, and the presence of hydrogen favored the reduction of Mo^{6+} and Mo^{4+} species to $Mo^{\delta+}$ $(0 < \delta < 4)$ species. These molybdenum oxynitrides exhibited activity for hydrogenation which depended on the amount of $Mo^{\delta+}$ $(0 < \delta < 4)$ species produced under reaction conditions. The amorphous molybdenum oxynitride $MoO_{1.83}N_{0.36}$ catalyst showed a good catalytic activity, selectivity, and resistance to poisoning of H_2S for liquid-phase hydrogenation of longer-chain alkadienes.

KEY WORDS: molybdenum oxynitride; hydrazine reduction of MoO_3; selective hydrogenation; long-chain linear alkadienes (C_{10}–C_{13}); palladium; H_2S poisoning.

1. Introduction

Palladium catalysts have by far proved to be the most active and selective for selective hydrogenation of alkadienes and alkynes to alkenes. However, they are less effective at higher temperature and pressure, which is required by some industrial process to avoid using a huge cooling system, such as selective hydrogenation of undesirable longer-chain alkadienes (C_{10}–C_{13}) to alkenes used in the linear alkyl benzene production process. In addition, palladium catalysts are easily poisoned by sulfur compounds. Therefore, it is of significance to find an alternative non-noble metal catalyst for hydrogenation instead of expensive noble metal catalysts.

Recently, molybdenum nitrides have attracted much attention because they show excellent catalytic properties resembling expensive noble metals in a number of hydrogen-involved reactions, such as NH_3 synthesis [1], ethane hydrogenolysis [2], CO hydrogenation [3], HDN of uinoline, carbazole and pyridine [4], and HDS of dibenzothiophene and thiophene [5]. Hao *et al.* [6] reported that molybdenum nitride had a good selectivity for hydrogenation of ethyne to ethene. Usually, molybdenum nitride was prepared by nitriding MoO_3 with NH_3 in a temperature program. It is of significance and interesting to find an alternative method of preparation of molybdenum nitride. Wise and Markel [7] reported a new method for the synthesis of molybdenum nitride by temperature-programmed reaction of MoO_3 with a mixture of H_2 and N_2. Marchand *et al.* [8] prepared molybdenum nitride δ-MoN by temperature-programmed ammonolysis of MoS_2. Chiu *et al.* [9] developed a low-temperature solution route to amorphous molybdenum nitride by employing a mixture of Na_2MoO_4, $(Me_3Si)_2NH$, Me_3SiCl and NEt_3 in refluxing DME. The molybdenum nitride synthesized by temperature-programmed nitriding of MoO_3 was pyrophoric, and a passivation step was required to prevent the bulk oxidation of these materials on exposure to air. A treatment with 1 vol% O_2/Ar or He, or N_2 at room temperature led to oxynitride surface layers, and the N and O atoms in this oxynitride were very difficult to completely remove even by reducing with H_2 at 500 °C [10]. Therefore, the real catalytic active phase of passivated molybdenum nitride as catalyst in the catalytic reaction was molybdenum oxynitride phase instead of pure molybdenum nitride phase. Miga *et al.* [11] made a series of investigations into this oxynitride, and proposed a model of a dual site for MoO_xN_y. It is important to make a systematic investigation of the electronic modification of nitrides by oxygen and its effect on the catalytic activities of these materials [12]. In this work, we present a novel route to the synthesis of molybdenum oxynitrides by hydrazine reduction of MoO_3 at moderate temperature and apply these molybdenum oxynitrides in the selective hydrogenation of longer-chain linear alkadienes (C_{10}–C_{13}), an important petrochemical industrial reaction for the production of alkyl benzene. It was discovered that these molybdenum oxynitrides exhibited a good catalytic activity and selectivity for alkenes.

---

[*] To whom correspondence should be addressed.
E-mail: chem612@nju.edu.cn

1011-372X/02/0900-0111

2. Experimental

2.1. Preparation of catalysts

Hydrazine hydrate ($NH_2–NH_2·H_2O$) in the amount of 0.25–0.66 mol was slowly added to 14.4 g MoO_3 (0.1 mol) in a small beaker. After the violent reaction ended, the small beaker was transferred into a 1L autoclave with 140 g CaO at the bottom of the autoclave, the autoclave was purged by N_2, then the pressure in the autoclave was adjusted to 0–15 atm by flowing H_2 into the autoclave. The autoclave was heated from room temperature to 300 °C and kept at 300 °C for 24 h. After the reaction, the autoclave was cooled down to ambient temperature, and the gases were let out. Finally, the product was passivated by allowing a mixture of 1% O_2/N_2 to diffuse into the autoclave at a flow rate of 40 ml (STP)/min for 12 h to prevent the product from violently oxidizing if exposed to air immediately following the reaction. The detailed reaction conditions such as the dosage of hydrazine hydrate, the pressure of H_2 in the autoclave, and dosage of CaO are presented in table 1. The unsupported γ-MO_2N was prepared by temperature-programmed reductive nitriding of MoO_3 in a flow of 12 vol% N_2/NH_3 in a quartz tube reactor (30 mm i.d. × 800 mm). The loading of MoO_3 precursor was 18 g and the flowing of 12 vol% N_2/NH_3 was 1700 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 °C/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. Finally, the catalyst was passivated with 40 ml (STP)/min of 1% O_2/N_2 for 12 h.

2.2. Characterization of catalysts

The composition of the as-synthesized catalyst was determined according to the procedure as follows: the content of N was measured on a Perkin-Elmer 240C; the content of Mo was determined by induced-coupled plasma (ICP) on a Jarrell-Ash100. The content of O was the remnant mass of the sample apart from the total content of N and Mo. BET surface area of the catalysts was measured using a Micromeritics ASAP-200 adsorption analyzer using nitrogen as adsorbate. Powder X-ray diffraction analysis was performed with Ni-filtered Cu K_α radiation with a Shimadzu XD-3A X-ray diffractometer. A working voltage of 35 kV and an electronic current of 25 mA were employed. The surface species of the as-synthesized catalysts were analyzed by an ESCALab Mk II X-ray photoelectron spectrometer. Mg K_α radiation was selected as the X-ray source. The catalyst was pressed into a self-supported wafer and fixed on a holder, then the catalyst was out-gassed. The residual pressure in the analysis chamber was maintained below 10^{-9} Torr. The spectra of catalysts were collected and corrected by referencing the binding energy to carbon (C(1s) = 284.6 eV). The spectra were deconvoluted using a special software program.

Temperature-programmed reduction (TPR) experiments were carried out in 5% H_2 in Ar (by volume) with a flow rate of 40 ml (STP)/min and a temperature ramping of 10 °C/min from room temperature to 1000 °C.

2.3. Catalytic activity measurement

The measurement of reaction of catalysts for selective hydrogenation of longer-chain alkadienes was accomplished on a homemade apparatus by using a technical process of hydrogenation of feedstock saturated by H_2 hydrogen [13]. The feedstock, composed of 83.05% alkanes, 9.69% alkenes, 1.60% alkadienes, and 5.66% aromatic hydrocarbons, was first saturated by hydrogen in a 2L autoclave at 100 °C and 17.5 atm. The solubility of H_2 in the feedstock was measured according to the reported procedure [13], and it was proved that the mole percent content of H_2 in the feedstock at 100 °C and 17.5 atm was 1.65%, which was in good agreement with the result calculated by $x = (P - P^0)/(-777.3 + 683045.4/T)$ (x is the mole percent content of hydrogen in the dehydrogenated oil composed of longer-chain alkanes, alkenes and alkadienes (C_{10}–C_{13}); P is the pressure of hydrogen; P^0 is the saturated vapor pressure of the dehydrogenated oil (C_{10}–C_{13}); T is the temperature) [13]. Next, the feedstock saturated by hydrogen was delivered by a valve from the autoclave into a fixed-bed microreactor of 20 mm i.d. × 400 mm stainless tube for hydrogenation.

Table 1
Preparation condition and properties

No.	Dosage of $NH_2–NH_2·H_2O$ (mol)	Pressure of H_2 (atm)	Dosage of CaO (g)	Component	Surface area ($m^2\,g^{-1}$)
1	–	–	–	γ-Mo_2N	4.4
2	0.25	15	140	$MoO_{1.83}N_{0.36}$	10.7
3	0.41	15	140	$MoO_{1.49}N_{0.39}$	8.7
4	0.66	15	140	$MoO_{1.34}N_{0.28}$	12.3
5	0.66	0	140	$MoO_{2.23}N_{0.49}$	13.4
6	0.25	0	0	MoO_2	2.74

A total of 6 g of catalyst was loaded in this reactor. Every catalyst was pretreated in H_2 at a rate of 80 ml (STP)/min under atmospheric pressure at 400 °C for 1 h except for 0.075% Pd/Al_2O_3 (200 °C). The poisoning test of H_2S on the catalyst was performed as follows: after the catalyst reached the steady state, 6.8×10^{-4} mol of H_2S was added to the reactor in 30 min by shutting off the supply of feedstock, then the supply of feedstock was restored. The feedstock and products were analyzed by a Waters 510 high-pressure liquid chromatograph equipped with a Waters 410 differential detector, and with a 3.9×300 μPorasil™ and a 3.9×150 Nova-Pak® silica column for separations, using trimethylpentane as mobile phase. The mole percent contents of alkadienes, alkenes, alkanes and aromatic hydrocarbons were calculated according to a normalization calculation method. The mole corrected coefficients of alkadienes, alkenes, alkanes and aromatic hydrocarbons were determined by using corresponding standard samples provided by the Institute of Jinling Petrochemical Co. Ltd. (note: this procedure and method of measuring mole content of alkadienes, alkenes, alkanes and aromatic hydrocarbons in feedstock or product has been used by the Institute for industrial analysis and monitoring of the industrial process of hydrogenation of longer-chain alkadienes for a long time). The conversion of alkadienes and selectivity of alkenes were defined as follows:

Conversion of alkadienes

$$= \frac{\begin{array}{c}\text{content of alkadienes in the feedstock}\\ -\text{ content of alkadienes in product}\end{array}}{\text{content of alkadienes in the feedstock}} \times 100\%$$

Selectivity of alkenes

$$= \frac{\begin{array}{c}\text{content of alkenes in product}\\ -\text{ content of alkenes in feedstock}\end{array}}{\begin{array}{c}\text{content of alkadienes in feedstock}\\ -\text{ content of alkadienes in product}\end{array}} \times 100\%$$

3. Results and discussion

3.1. Composition and structure of catalysts

The preparation condition and properties of the as-synthesized catalysts are summarized in table 1. It can be seen that MoO_2 was obtained in the absence of CaO at the bottom of the autoclave, and molybdenum oxynitrides were synthesized if excessive CaO existed at the bottom of the autoclave.

The chemical equations of these reactions were as follows:

$$MoO_3 + NH_2{-}NH_2 \longrightarrow MoN_xO_y + (3-y)H_2O + (y-1)H_2 + (1-0.5x)N_2 \quad (1)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (2)$$

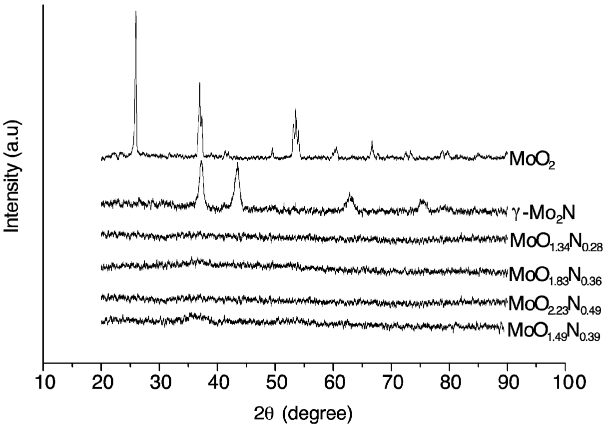

Figure 1. XRD patterns of catalysts.

Loading excessive CaO at the bottom of the autoclave was aimed at removing water contained in $NH_2{-}NH_2{\cdot}H_2O$ and produced in the process of reaction of MoO_3 with $NH_2{-}NH_2$ in order to make the reaction of MoO_3 with $NH_2{-}NH_2$ proceed under an almost anhydrous condition, which was favorable to making reaction (1) move to right. The composition of molybdenum oxynitrides could be adjusted to a certain range by changing synthesizing conditions such as the mole ratio of MoO_3 and $NH_2{-}NH_2{\cdot}H_2O$ and the pressure of hydrogen. There was no mass loss of molybdenum in the conversion of MoO_3 reduced by hydrazine to molybdenum oxinitride.

The XRD profiles of as-synthesized catalysts are shown in figure 1. Molybdenum nitride prepared by temperature-programmed reduction of MoO_3 with NH_3 and N_2 exhibited a characteristic pattern of γ-Mo_2N without evidence of any other phase. Molybdenum dioxide prepared by hydrazine reduction of MoO_3 without the existence of CaO at the bottom of the autoclave exhibited a characteristic pattern of crystalline MoO_2 with f.c.c structure. Molybdenum oxynitrides synthesized by hydrazine reduction of MoO_3 with the existence of excessive CaO at the bottom of the autoclave had no diffraction peak, indicating that all these molybdenum oxynitrides were amorphous. It was observed that the as-synthesized molybdenum oxynitrides still remained amorphous after they were used as catalysts for the hydrogenation of long-chain alkadienes for a long time.

In table 2 the XPS results of the as-synthesized molybdenum oxynitrides are tabulated. A binding energy of 229.0 eV or so was assigned to $Mo^{\delta+}$ ($0 < \delta < 4$) since this binding energy is situated midway between those of Mo^{4+} ($3d_{5/2} = 230.2$ eV) and Mo^0 ($3d_{5/2} = 227.8$ eV) [10]. It can be found that Mo^{6+}, Mo^{4+} and $Mo^{\delta+}$ ($0 < \delta < 4$) were present for the as-synthesized oxynitrides, and the ratio of Mo^{6+}, Mo^{4+} and $Mo^{\delta+}$ ($0 < \delta < 4$) contents was dependent on the preparation conditions. The molybdenum oxynitride ($MoO_{2.23}N_{0.49}$) prepared in the absence of hydrogen in the autoclave had no $Mo^{\delta+}$ ($0 < \delta < 4$) species, but

Table 2
XPS analysis of catalysts

Catalyst	Temperature of reduction (°C)	Ratio of atoms		Binding energy (eV)		Binding energy of $Mo3d_{5/2}$ (eV) and content of percent (%)		
		N/Mo	O/Mo	N(1s)	O(1s)	Mo^{6+}	Mo^{4+}	$Mo^{\delta+}$ ($0 < \delta < 4$)
$MoO_{1.83}N_{0.36}$	170	2.66	2.46	397.6	530.3	232.7 (29.8)	230.6 (65.4)	229.0 (4.8)
$MoO_{1.83}N_{0.36}$	400	2.40	2.34	397.5	530.3	232.7 (27.6)	230.4 (38.4)	229.4 (34.0)
$MoO_{2.23}N_{0.49}$	170	2.85	2.50	397.9	530.4	232.7 (74.7)	230.6 (25.3)	229.5 (0)
γ-Mo_2N [10]	200	0.51	0.70	397.1	530.3	232.5 (33)	230.1 (21)	228.6 (46)

$Mo^{\delta+}$ ($0 < \delta < 4$) species appeared in the molybdenum oxynitride ($MoO_{1.83}N_{0.36}$) prepared in the presence of hydrogen in the autoclave. It was inferred that the presence of hydrogen was favorable to the reduction of Mo^{6+} and Mo^{4+} species to $Mo^{\delta+}$ ($0 < \delta < 4$) species. As can be seen in table 2, with elevation of reduction temperature from 170 to 400 °C, the content of Mo^{6+} and Mo^{4+}species decreased, and the content of $Mo^{\delta+}$ ($0 < \delta < 4$) species on the surface of $MoO_{1.833}N_{0.36}$ catalyst was increased from 4.8 to 34.0%. The as-synthesized $MoO_{1.83}N_{0.36}$ catalyst activated by hydrogen at 400 °C had a composition of Mo^{6+}, Mo^{4+}, and $Mo^{\delta+}$ ($0 < \delta < 4$) species similar to γ-Mo_2N.

3.2. TPR of catalysts

Figure 2 shows the H_2-TPR of the as-synthesized catalysts. It can be seen that passivated γ-Mo_2N has an H_2 consumption peak in the range of 400–500 °C which was caused by reduction of different surface oxynitride species and/or surface molybdenum oxides created during passivation [10]. No H_2 consumption peak appeared below 600 °C for MoO_3 and MoO_2, but the as-synthesized molybdenum oxynitrides all had reduction peaks in the range 350–480 °C. XPS results substantiated that MoO_2 reduced at 400 °C in hydrogen had no $Mo^{\delta+}$ ($0 < \delta < 4$) species, but $Mo^{\delta+}$ ($0 < \delta < 4$) species appeared after the as-synthesized molybdenum oxynitrides were reduced at 400 °C in hydrogen for 1 h. These results showed that the H_2 consumption peak appeared in the range 350–480 °C since the as-synthesized molybdenum oxynitrides were not caused by reduction of the molybdenum oxide species, but caused by reduction of oxynitrides containing Mo^{6+} and/or Mo^{4+} to $Mo^{\delta+}$ ($0 < \delta < 4$) species. The reduction peak of MoO_3 between 650 and 800 °C corresponds to the reduction of MoO_3 to MoO_2 [10], and the further elevation of temperature resulted in reduction of MoO_2 to Mo metal [15]. The H_2 consumption peaks for the as-synthesized molybdenum oxynitrides in the range 780–980 °C were proved by XRD to be caused by the transformation of molybdenum oxynitrides to Mo metal as the final products of all as-synthesized molybdenum oxynitrides after TPR were Mo metal.

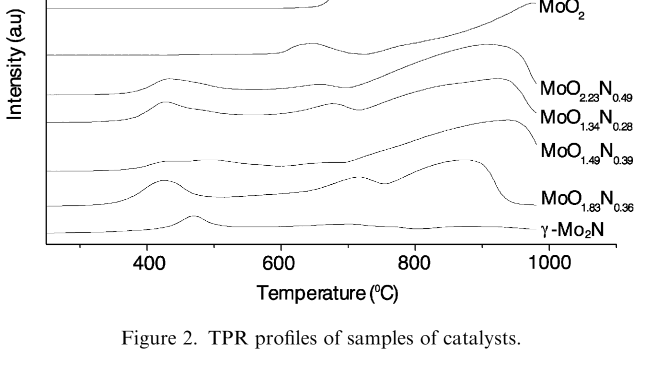

Figure 2. TPR profiles of samples of catalysts.

3.3. Catalytic characteristics of catalysts

The conversion and selectivity of as-synthesized catalysts are summarized in table 3 (the data are an average value of several results after hydrogenation reached the 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 they are much less effective than some as-synthesized molybdenum oxynitrides (such as $MoO_{1.83}N_{0.36}$) at higher temperature and pressure. The $MoO_{1.83}N_{0.36}$ catalyst had a conversion of 83.6% and a very high selectivity of 94.0%; but 0.075% Pd/Al_2O_3 only had a conversion of 50.5% and a selectivity of 30.2% at 100 °C and 14 atm. It can be seen that MoO_2 displayed no activity for the hydrogenation of alkadienes under 200 °C and 12 atm, but the as-synthesized molybdenum oxynitrides all exhibited good catalytic activity, apart from $MoO_{2.23}N_{0.49}$, on which the conversion of alkadienes was only 19.5%. The activity of Mo species for hydrogenation of carbazole increased in order as follows: Mo metal $\gg$ β-$Mo_2N_{0.78}$ > γ-Mo_2N > MoO_2 [14]. This result showed that Mo species with lower valence had a higher activity than Mo species with higher valence. Combined with the results of XPS, it could be found that there was some relationship between activity and amount of $Mo^{\delta+}$ ($0 < \delta < 4$) species. Catalyst with more $Mo^{\delta+}$ ($0 < \delta < 4$) species had higher activity. No activity for the hydrogenation of alkadienes on MoO_2 under 200 °C and 12 atm could be reasonably attributed

Table 3
Activity and selectivity of catalysts at 200 °C, 12 atm, H_2/alkadienes (molar ratio) = 1.03, LSV = 6.67 ml g^{-1}-catalyst h^{-1}

Catalyst	Conversion of alkadienes (%)	Selectivity of alkenes (%)	Change of alkanes content after hydrogenation (%)	Change of alkenes content after hydrogenation (%)
0.075% Pd/Al_2O_3 [a]	50.5	30.2	0.56	0.24
γ-Mo2N	79.6	93.2	0.09	1.18
$MoO_{1.83}N_{0.36}$	83.8	94	0.08	1.26
$MoO_{1.49}N_{0.39}$	84	56.1	0.59	0.75
$MoO_{1.34}N_{0.28}$	92.5	22.3	1.14	0.33
$MoO_{2.23}N_{0.49}$	19.5	81.3	0.06	0.25
MoO_2	0	0	0	0

[a] Reaction conditions: 100 °C, 14 atm, H_2/alkadienes (molar ratio) = 1.28, LSV = 8.87 ml g^{-1}-catalyst h^{-1}.

to no presence of $Mo^{\delta+}$ $(0 < \delta < 4)$ species on the surface of MoO_2. The similar activity and selectivity of the $MoO_{1.83}N_{0.36}$ to those of γ-Mo_2N catalyst could be explained by the fact that the $MoO_{1.83}N_{0.36}$ catalyst activated by hydrogen at 400 °C had a similar surface composition of Mo^{6+}, Mo^{4+} and $Mo^{\delta+}$ $(0 < \delta < 4)$ species to γ-Mo_2N.

The effect of reaction temperature on the activity and selectivity of longer-chain alkadiene hydrogenation is shown in figure 3. A great influence of reaction temperature on the selectivity was observed. When the reaction temperature was elevated from 200 to 280 °C, the conversion of alkadienes increased from 83.8 to 93.8%, and the selectivity of alkenes decreased quickly from 94.0 to −48.0%.

Figures 4 and 5 show the conversion and selectivity of alkadiene hydrogenation over $MoO_{1.83}N_{0.36}$ and 0.075% Pd/Al_2O_3 catalyst as a function of time before and after addition of H_2S, respectively. After addition of H_2S, the catalytic activity of hydrogenation over 0.075% Pd/Al_2O_3 decreased rapidly from 52.2% to only 1% in 30 min, then gradually reached a new steady state with only 12% conversion. The increase of selectivity from 28.5 to 100% indicated that partial poisoning of H_2S could improve the selectivity of the palladium catalyst. On the other hand, after flux of H_2S into reactor, when the hydrogenation reached a new state, the molybdenum oxynitride $MoO_{1.83}N_{0.36}$ catalyst still maintained higher catalytic activity with a conversion of more than 92%. Although the selectivity decreased substantially, this molybdenum oxynitride had 73.0% or so selectivity. These results showed that the molybdenum oxynitride $MoO_{1.83}N_{0.36}$ catalyst exhibited a better resistance to poisoning of H_2S than the palladium catalyst, which was important in the petrochemical industrial process.

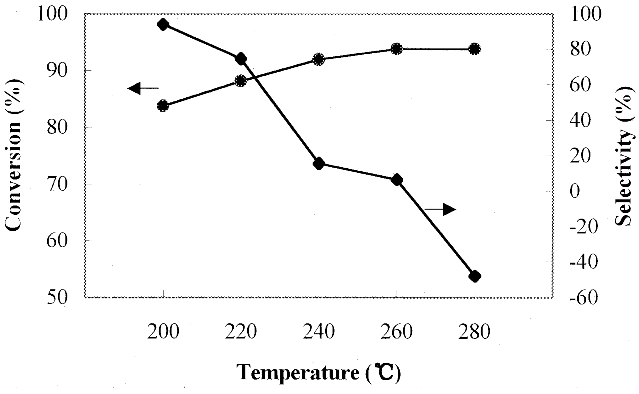

Figure 3. Conversion and selectivity of alkadiene hydrogenation on $MoO_{1.83}N_{0.36}$ catalyst at different reaction temperature, 12 atm, H_2/alkadienes (mole ratio) = 1.03, LSV = 6.67 ml g^{-1}-catalyst h^{-1}.

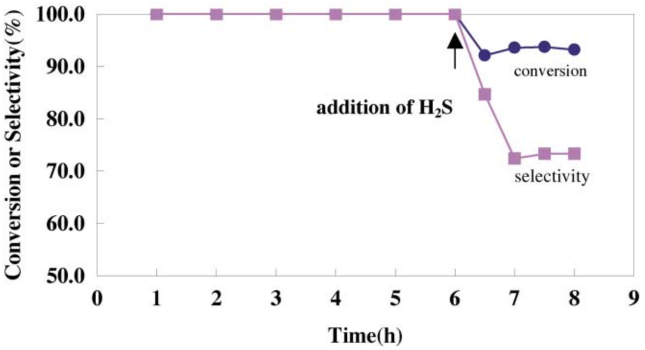

Figure 4. Poisoning of H_2S on $MoO_{1.83}N_{0.36}$. Reaction conditions: 14 atm, 180 °C H_2/alkadienes (mole ratio) = 1.28, LSV = 6.67 ml g^{-1}-catalyst h^{-1}.

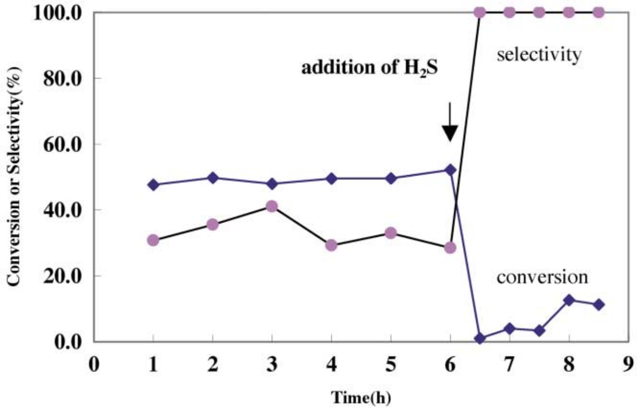

Figure 5. Poisoning of H_2S on 0.075% Pd/Al_2O_3. Reaction conditions: 14 atm, 100 °C H_2/alkadienes (mole ratio) = 1.28, LSV = 8.33 ml g^{-1}-catalyst h^{-1}.

3. Conclusions

Molybdenum oxynitrides were prepared from MoO_3 and hydrazine hydrate at moderate temperature. The anhydrous condition was favorable to production of amorphous molybdenum oxynitride, and the existence of hydrogen favored the reduction of Mo^{6+} and Mo^{4+} species to $Mo^{\delta+}$ $(0 < \delta < 4)$ species. These molybdenum oxynitrides exhibited activity for hydrogenation which depended on the amount of $Mo^{\delta+}$ $(0 < \delta < 4)$ species produced under reaction condition. The amorphous molybdenum oxynitride $MoO_{1.83}N_{0.36}$ catalyst showed a good catalytic activity, selectivity, and resistance to poisoning of the sulfur compound for liquid-phase selective hydrogenation of alkadiene.

Acknowledgments

The authors are grateful to the Institute of Jinling Petrochemical Co. Ltd. for its financial support and help in the analysis of samples.

References

[1] L.Volpe and M. Boudart, J. Phys. Chem. 90 (1986) 4878.
[2] G.S. Ranhotra, A.T. Bell and J.A. Reimer, J. Catal. 108 (1987) 40.
[3] J.C. Schlatter, S.T. Oyama, J.E. Metcalf and J.M. Lambert, Ind. Eng. Chem. Res. 27 (1988) 1648.
[4] U.S. Ozkan, L. Zhang and P.A. Clark, J. Catal. 172 (1997) 294.
[5] E.J. Markel and J.W. Van Zee, J. Catal. 126 (1990) 643.
[6] Z.X. Hao, Z.B. Wei, L.J. Wang, X.H. Li, C. Li, E. Min and Q. Xin, Appl. Catal. 192 (2000) 81.
[7] R.S. Wise and E.J. Markel, J. Catal. 145 (1994) 344.
[8] R. Marchand, F. Tessier and F.J. Disalvo, J. Mater. Chem. 9 (1999) 297.
[9] H.T. Chiu, S.H. Chuang, G.H. Lee and S.M. Peng, Advanced. Mater. 10 (1998) 1475.
[10] Y.J. Zhang, Q. Xin, I. Rodriguez-Ramos and A. Guerrero-Ruiz, Appl. Catal. 180 (1999) 237.
[11] K. Miga, K. Stanczyk, C. Sayag, D. Brodzki and G. Djega-Mariadassou, J. Catal. 183 (1999) 63.
[12] J.G. Chen, Chem. Rev. 96 (1996) 1477.
[13] R.Q. Ma, Chemical Industry for Daily Use 3 (1993) 26.
[14] M. Nagai, Y. Goto, A. Miyata, M. Kiyoshi, K. Hada, K. Oshikawa and S. Omi, J. Catal. 182 (1999) 292.