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Hydrodesulfurization over intrazeolite molybdenum nitride clusters prepared by using hexacarbonyl molybdenum as a precursor

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Abstract

Metal nitride catalysts have received extensive attention because of their potential high performance for hydrodesulfurization (HDS). In the present study, highly dispersed Mo nitride clusters having a composition of Mo_2N are synthesized in zeolite pores by means of a CVD method using $Mo(CO)_6$ as a precursor. The catalytic properties of the molybdenum nitride catalysts for the HDS of thiophene are compared with that of an intrazeolite molybdenum sulfide catalyst. The molybdenum nitride catalyst shows a more stable thiophene HDS activity than the molybdenum sulfide catalyst. Molybdenum nitride clusters are only partially sulfided even after a prolonged HDS reaction.

Keywords: Hydrodesulfurization; Zeolite; CVD; Molybdenum nitride; Hexacarbonyl molybdenum

1. Introduction

Transition metal sulfides form a very important group of materials exhibiting a number of interesting properties. One particular chemical property of several of these sulfides is the ability, in the presence of hydrogen, to catalyze sulfur removal from heterocyclic organic molecules such as thiophene, benzothiophene, and dibenzothiophene. Substantial improvements have been made in Mo sulfide-based hydrodesulfurization (HDS) catalysts since their inception into industrial process nearly 60 years ago [1]. Such improvements have allowed petroleum refineries to reduce sulfur content of transportation fuels in response to environmental regulations implemented in a number of countries. Recently, the US Environmental Protection Agency (EPA) has issued regulations that would lower its allowed sulfur content in diesel fuel from the current 50 to 15 ppm in 2006 [2,3]. There are considerable efforts being expended to develop new catalysts for the production of clean petroleum fuels [4].

Recently, much attention has been paid to metal nitride catalysts [3,5–11] because of their possible high activity and long life for HDS reaction. In the conventional preparation of molybdenum nitride catalysts, molybdenum oxide precursors have to be treated at high temperatures (>973 K) to reduce Mo^{6+} oxide to lower oxidation states. Aggregation of the Mo species results from the high temperature treatment to form larger clusters [12]. However, it is expected that molybdenum nitrides will be easily synthesized at a lower temperature, when $Mo(CO)_6$ is used as a precursor [13–17]. It has been reported that highly dispersed Mo sulfide clusters [18–24], Mo oxide clusters [25–27], and Mo oxycarbide species [28] have been synthesized by use of $Mo(CO)_6$ encaged in zeolite pores as a precursor. In the present study, we tried to, for the first time, prepare highly dispersed molybdenum nitride clusters, Mo_2N, encaged in NaY

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supercages by means of a CVD method using $Mo(CO)_6$. The local structure of Mo_2N incorporated in NaY was studied by mean of Mo K-edge XAFS. The catalytic activity and selectivity of the HDS of thiophene were also examined.

2. Experimental

2.1. Catalyst preparation

Intrazeolite Mo nitride catalysts were prepared by using $Mo(CO)_6$ as a precursor. An NaY zeolite was supplied by the Catalysis Society of Japan as a Reference Catalyst ($Si/Al = 2.8$, JRC-Z-Y5.5). After evacuation at 673 K for 1 h ($<1\times10^{-3}$ Pa), a zeolite sample (0.1 g) was exposed to a vapor of $Mo(CO)_6$ for 16 h at room temperature (RT), followed by evacuation for 10 min at RT to remove physisorbed $Mo(CO)_6$ on the external surface of the zeolite [20–22]. The $Mo(CO)_6$/NaY sample was evacuated, as the temperature was increased from RT to 523 K at a rate of ca. 8.0 K min^{-1}, and was kept isothermal at 523 K for 15 min. This sample is denoted Mo/NaY. 15 kPa of ammonia was introduced to Mo/NaY at 523 K and then the temperature was ramped to 673 K at a rate of 10 K min^{-1} and kept at 673 K for 24 h. The NH_3 gas was exchanged with a fresh NH_3 gas during nitridation at 673 K. After the nitridation, the sample was evacuated at 673 K for 1 h. In order to investigate the effect of NH_3 pressure, Mo/NaY was nitrided with 5 kPa of NH_3. The amounts of H_2 and N_2 produced during the nitridation were analyzed by means of an on-line TCD gas chromatograph (Column packing: Active Carbon). The nitride catalysts prepared in this way are designated as MoN_x/NaY. If necessary, the nitridation temperature and time are followed in parentheses, such as MoN_x/NaY (673–24) for MoN_x/NaY nitrided at 673 K for 24 h. The amount of Mo in MoN_x/NaY was 10 wt.% Mo. An intrazeolite Mo sulfide catalyst, MoS_x/NaY, was prepared according to the previous procedures [20–22], for comparison.

2.2. Benzene adsorption measurement

The pore volumes of NaY, Mo/NaY, MoN_x/NaY and MoS_x/NaY were measured by means of benzene adsorption at 298 K on a BELSORP 18 PLUS (Nippon Bel) as described previously [20]. The obtained isotherms were analyzed to estimate the pore volumes according to a Dubinin–Radushkevich method [29].

2.3. Catalytic reaction

HDS reaction of thiophene was carried out using a closed circulation system [20–22]. Reaction products were analyzed by means of an on-line TCD gas chromatograph (Column packing: Sebaconitrile). The HDS of thiophene was carried out at 623 K and an initial H_2 pressure of 26.6 kPa. The thiophene pressure was kept constant during the reaction by holding a small amount of liquid thiophene at 273 K as a reservoir in the bottom of a U-shaped tube in the circulation system. The reaction gas was replaced with a fresh reaction gas after 1440 min (24 h), and the HDS reaction was subsequently started in the second run. This procedure was repeated in the third run, too.

2.4. Mo K-edge XAFS measurements

The Mo K-edge XAFS spectra of the samples before and after the HDS reaction were measured at BL01B1 of SPring-8 in a transmission mode at RT. The synchrotron radiation was monochromatized by means of a Si(3 1 1) monochromator. An energy calibration was carried out using Mo foil as a reference. The EXAFS data were analyzed by using a program “Rigaku EXAFS(REX)”. The analysis involves pre-edge extrapolation and background removal by a cubic smooting method to obtain EXAFS oscillations, which were Fourier transformed from k-space (2.98–15 nm^{-1}) to R-space. Mo K-edge XANES spectra were normalized by using the edge height.

3. Results and discussion

When Mo/NaY was treated with NH_3, N_2 and H_2 were produced, the amount of H_2 being always greater than that of N_2. Fig. 1 shows the N/Mo atomic ratio, calculated from the amounts of N_2 and H_2 produced during the nitridation, as a function of the treatment time with NH_3. The N/Mo atomic ratio for the sample treated at 673 K was ca. 0.5 after 1440 min (24 h), suggesting the formation of Mo_2N clusters irrespective of the initial NH_3 pressure. The NH_3 pressure during the

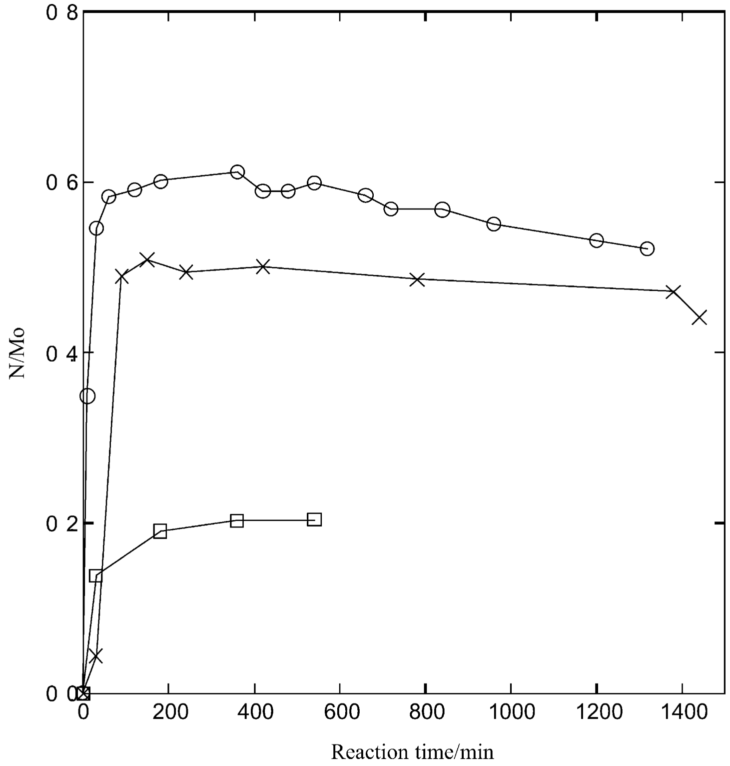

Fig. 1. The atomic ratio of N to Mo for the samples treated at 523 or 673 K by NH_3. Nitrided at: 673 K for ca. 15 kPa NH_3 (○), 523 K for ca. 15 kPa NH_3 (□), 673 K for ca. 5 kPa NH_3 (×).

nitridation reaction, however, showed a pronounced effect on the ratio of N to Mo at 673 K in the initial stage of the nitridation. At the higher NH_3 pressure, the N/Mo atomic ratio first exceeded 0.5 and gradually approached to 0.5. On the other hand, the N/Mo atomic ratio was 0.5 at the lower NH_3 pressure from the initial stage of the nitridation. It is suggested that at the higher NH_3 pressure, an excess amount of nitrogen over the composition of Mo_2N is incorporated in the form of nitride nitrogen or adsorbed NH_x. With the sample treated at 523 K, the N/Mo atomic ratio was ca. 0.2 after 500 min and hardly nitrided further. This fact may be ascribed to a slow rate of nitridation of Mo at 523 K. It is concluded that Mo_2N clusters are formed and stabilized in MoN_x/NaY at 673 K. Table 1 shows the pore volume of the catalyst calculated from benzene adsorption isotherms, according to Dubinin–Radushkevich method [29]. It is obvious that the pore volume of the host zeolite NaY is significantly decreased by the incorporation of Mo_2N clusters, indicating that Mo species are inside the zeolite pores.

The chemical state and local structure of the incorporated Mo atoms were studied by means of the Mo K-edge XAFS. Fig. 2 compares the XANES spectra for MoN_x/NaY (673–24), $Mo(CO)_6$/NaY and Mo metal. It is obvious from the fine structures around 20,000–20,040 eV that the spectrum for MoN_x/NaY (673–24) is distinctly different from those for $Mo(CO)_6$/NaY and Mo metal. Accordingly, it is concluded that $Mo(CO)_6$ is completely decomposed after the nitridation and that nitrogen atoms

Table 1
Pore volumes of NaY, Mo/NaY and MoN_x/NaY (673–24)

Catalyst	Pore volume (ml g^{-1})
NaY	0.275
Mo/NaY	0.213
MoN_x/NaY (673–24)	0.209

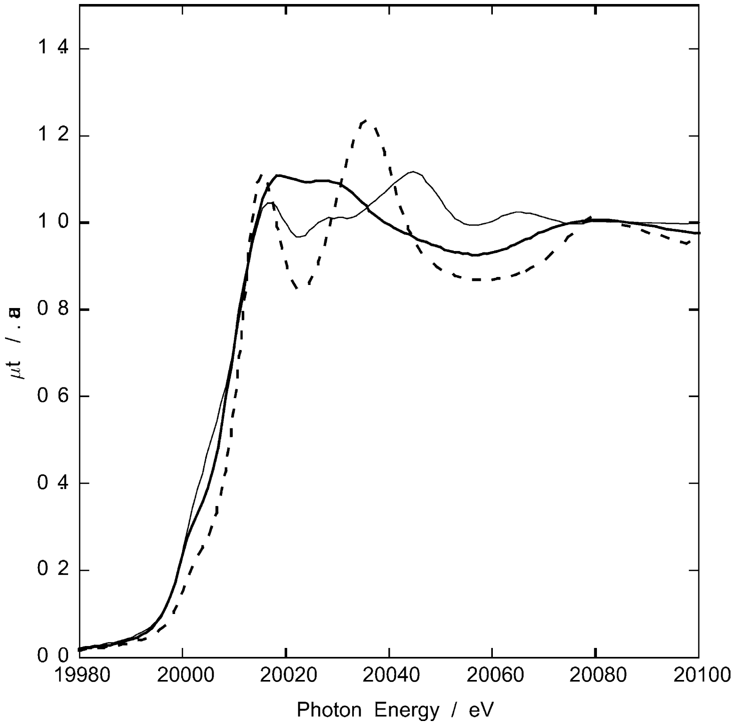

Fig. 2. XANES spectra for $Mo(CO)_6$/NaY (dashed line), MoN_x/NaY nitrided at 673 K for 24 h (thick line), and Mo metal (foil) (thin line).

incorporated into MoN_x/NaY (673–24) bind with the Mo atoms.

Fig. 3 shows the Fourier transforms (FTs) of the k^3-weighted EXAFS oscillations for the MoN_x/NaY (673–24) and $Mo(CO)_6$/NaY. The FT of the nitrided catalyst showed the first shell around 0.2 nm, indicating the presence of light atoms such as C, N and/or O attached to Mo. Assuming a Mo–Mo shell, the coordination number of the second shell for MoN_x/NaY (673–24) was calculated by EXAFS analysis to be about unity (Table 2), indicating the formation of highly dispersed Mo nitride clusters, possibly dimer clusters in the supercage of NaY. The formation of dimer clusters of Mo oxide [25,26], Mo sulfide

Table 2
The structural parameters as derived from Mo K-edge EXAFS analysis of MoN_x/NaY and MoS_x/NaY

Sample name	Atom pair	CN	*R* (nm)	σ (nm)	E_0 (eV)	Rf
MoN_x/NaY (673–24)	Mo–O(N)	1.2	0.201	0.0059	−2.1	3.5
	Mo–O	2.4	0.214	0.0073	−6.8	
	Mo–Mo	1.4	0.281	0.0086	5.1	
MoS_x/NaY	Mo–S	6.2	0.242	0.0108	0.18	1.8
	Mo–Mo	0.9	0.269	0.0086	−8.3	
Reference compounds						
MoS_2	Mo–S	5	0.242	0.0060	0	
	Mo–Mo	6	0.316	0.0060	0	
$Na_2MoO_4 \cdot 2H_2O$	Mo–O	4	0.177	0.0060	0	

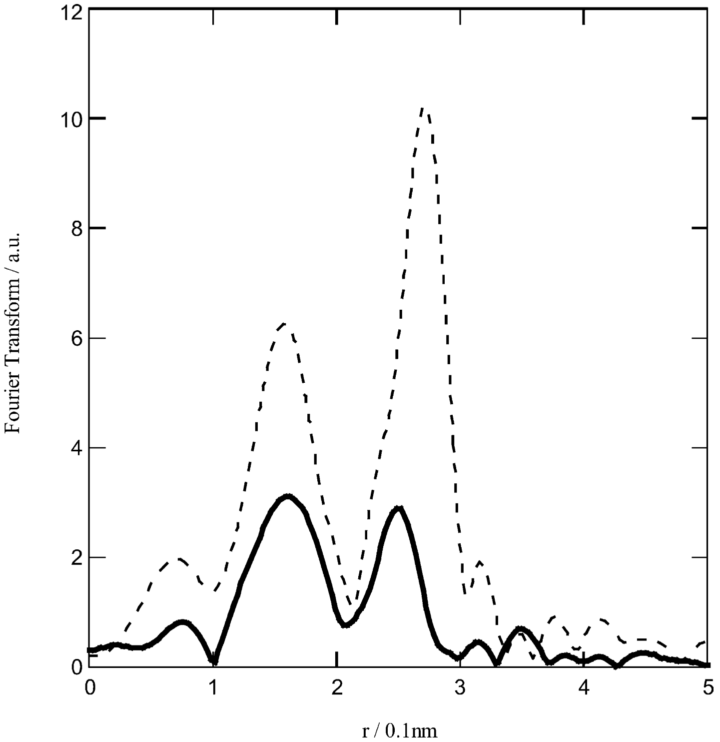

Fig. 3. FTs of k^3-weighted EXAFS oscillations of Mo K-edge for $Mo(CO)_6$/NaY (dashed line) and MoN_x/NaY nitrided at 673 K for 24 h (thick line).

[18–23] and Mo oxycarbide [28] have been reported for the oxidation, sulfidation and decomposition of $Mo(CO)_6$ encaged in NaY, respectively.

The reaction products of the HDS of thiophene over MoN_x/NaY and MoS_x/NaY were butane and butenes in addition to H_2S. Fig. 4 shows the HDS activity of MoN_x/NaY (673–24) and MoS_x/NaY. With MoN_x/NaY (673–24), the amount of butenes increased as the reaction time and reached a maximum, followed by a gradual decrease, accompanying a steady increase in the amount of butane. The amount of H_2S increased steadily with increasing the reaction time. The amounts of C_4-products and H_2S were not changed very much in the second and third runs, after replacing the reaction gas. It is shown that MoN_x/NaY (673–24) is highly resistant to deactivation under the present reaction conditions. With MoS_x/NaY, the production amounts of the C_4 compounds were significantly low compared to those for MoN_x/NaY, although the amount of H_2S production was higher over MoS_x/NaY than MoN_x/NaY. The amount of the reaction products, H_2S and C_4, of MoS_x/NaY decreased by about 25% in the second run, suggesting a considerable deactivation of the catalyst after 1440 min (24 h).

It is significant that the amounts of C_4 compounds are much less than that of H_2S over MoS_x/NaY. In order to clarify this point, a H_2S/C_4 ratio was calculated on the basis of the results in Fig. 4. Fig. 5 shows the H_2S/C_4 ratios for MoN_x/NaY and MoS_x/NaY as a function of reaction time. With MoS_x/NaY, the H_2S/C_4 mole ratio was close to unity at the initial stage of the reaction as reported previously [20,30]. However, it increased with increasing reaction time. A similar behavior was also observed in the second run, but to a smaller extent. MoS_x/NaY was prepared by a sulfidation in a stream of H_2S/H_2 at 673 K. The previous XPS results showed that $Mo(CO)_6$ was completely sulfided to MoS_2, $S/Mo = 2.0$ [20–22]. Furthermore, it is hard to consider that sulfur is evolved from MoS_x/NaY during the reaction. Hence, it is deduced that a considerable fraction of the C_4

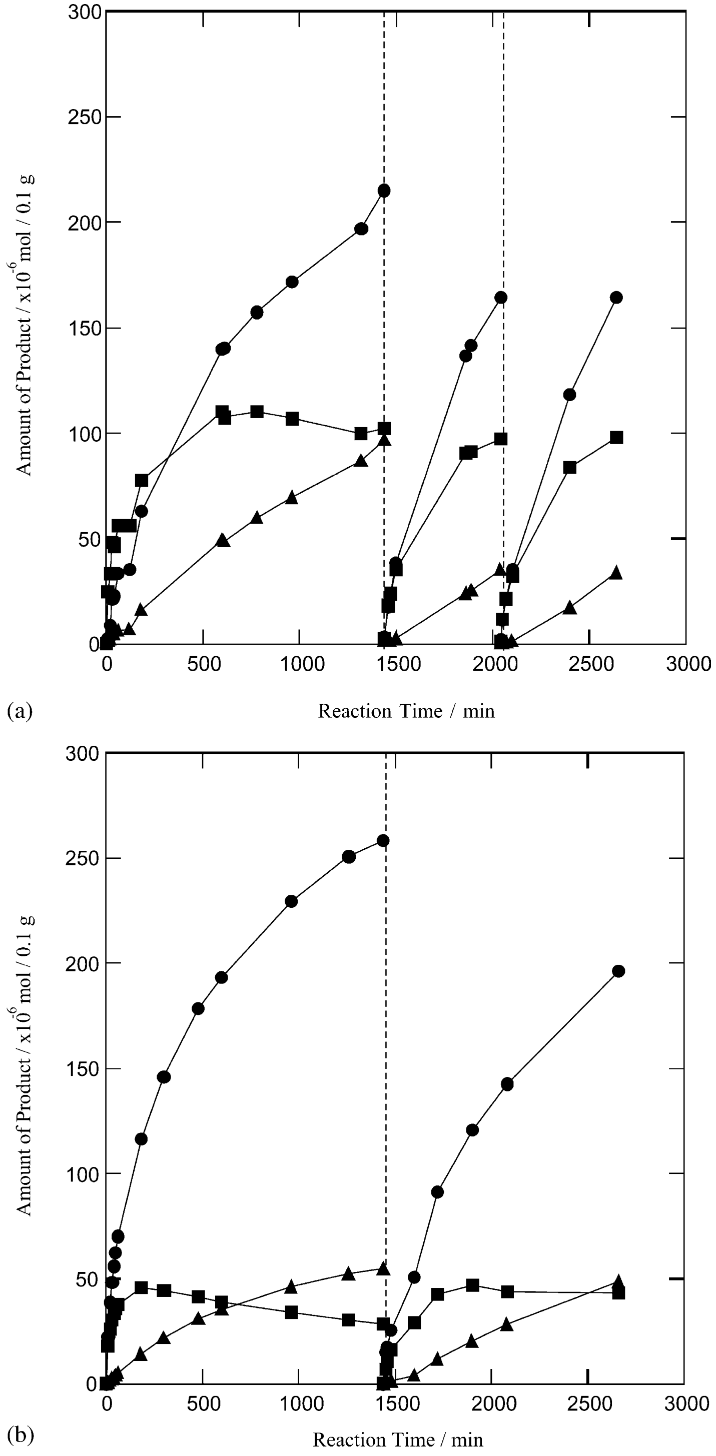

Fig. 4. Thiophene HDS activities of MoN_x/NaY (a) and MoS_x/NaY (b) as a function of reaction time. The reaction gas was replaced at the reaction time indicated by the dotted line. Butane (▲), the sum of the amounts of 1-, *cis*- and *trans*-2-butenes (■) and hydrogen sulfide (●).

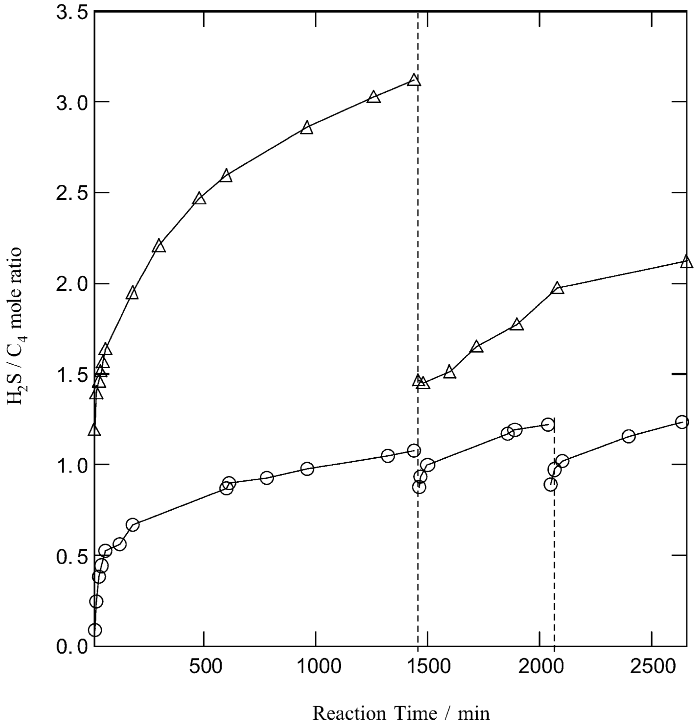

Fig. 5. H_2S/C_4 mole ratio as a function of reaction time. The reaction gas was replaced at the reaction time indicated by the dotted line. MoN_x/NaY (673–24) (○) and MoS_x/NaY (△).

compounds are accumulated inside or outside of the zeolite pores by polymerization reactions. Acidic sites may be generated on MoS_x/NaY due to the formation of Mo–SH groups [31,32].

On the other hand, as presented in Fig. 5, the H_2S/C_4 mole ratio was considerably low over MoN_x/NaY (673–24) at the initial stage of the HDS reaction and increased gradually to the ratio expected for the reaction stoichiometry ($H_2S/C_4 = 1.0$). This fact evidently shows that H_2S is consumed in the initial stage of the reaction. In the second and third runs, the H_2S/C_4 mole ratios were close to unity from the beginning of the reaction. Slight increases in the ratio were observed as the reaction proceeded but to a much lesser extent than that observed for MoS_x/NaY. It is considered that MoN_x/NaY is sulfided only in the initial stage of the HDS reaction. However, it is worthy of note that the catalytic behaviors of MoN_x/NaY in the second and third runs are still very close to those in the first run and that these behaviors are completely different from those for MoS_x/NaY. These results clearly suggest that MoN_x/NaY is not completely sulfided during the reaction and that no significant polymerization of butanes takes place in contrast to MoS_x/NaY.

The Mo K-edge XAFS spectra were measured for MoN_x/NaY (673–24) before and after the HDS reaction at 673 K for 24 h to examine the chemical state of Mo nitride species. Fig. 6 compares the XANES spectra for MoN_x/NaY (673–24) before the HDS reaction, MoN_x/NaY (673–24) after the HDS reaction and MoS_x/NaY. After the HDS reaction, the edge energy of XANES for MoN_x/NaY decreased by 1 eV and the XANES structure slightly changed by the reaction. However, the XANES spectrum for MoN_x/NaY after the reaction was still completely different from that for MoS_x/NaY, indicating that MoN_x/NaY (673–24) was only partially sulfided. Fig. 7 shows the FT of Mo K-edge EXAFS oscillation. A weak peak assigned to Mo–S appeared at 0.2 nm in the FT for MoN_x/NaY (673–24) after the HDS reaction, indicating that Mo is slightly sulfided. The peak at 0.25 nm due to Mo–Mo contribution became weaker, suggesting that the structure of the cluster, Mo_2N, is slightly disordered.

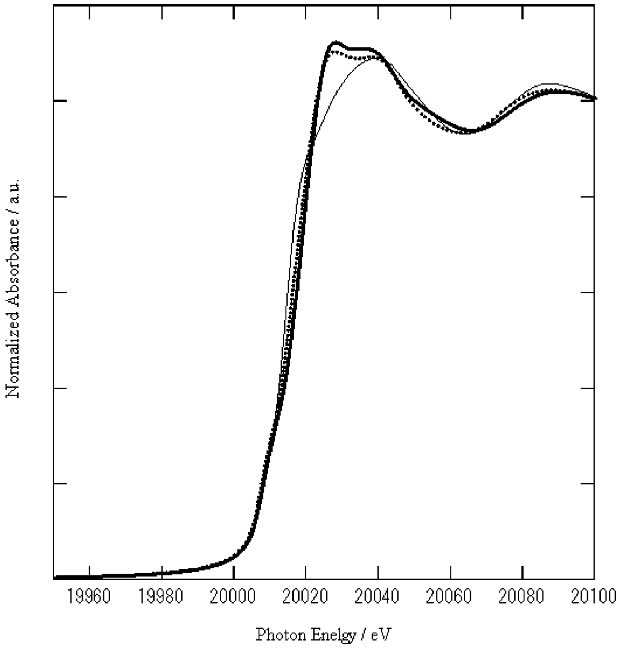

Fig. 6. XANES spectra of the Mo K-edge for MoN_x/NaY nitrided at 673 K for 24 h before (thick line) and after (dotted line) the HDS of thiophene at 623 K for 24 h and MoS_x/NaY (thin line).

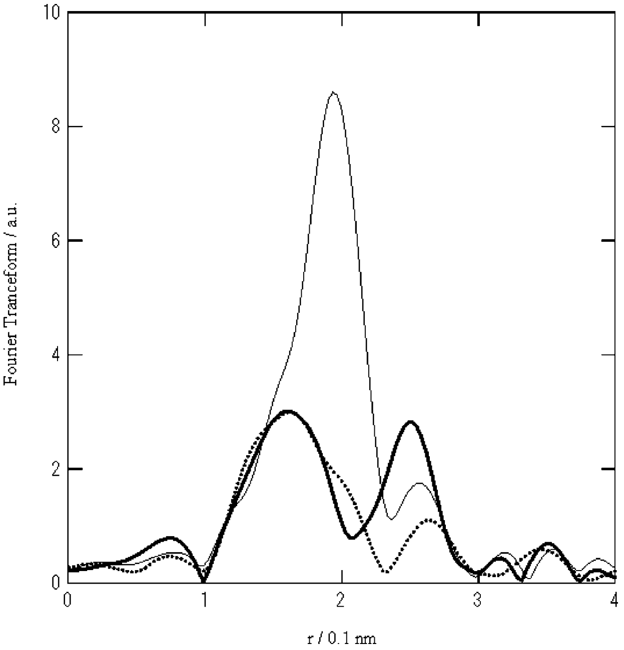

Fig. 7. FTs of k^3-weighted EXAFS oscillations of the Mo K-edge for MoN_x/NaY nitrided at 673 K for 24 h. Before (thick line) and after (dotted line) thiophene HDS at 623 K for 24 h and MoS_x/NaY (thin line).

Therefore, it is concluded that Mo nitride clusters are only partially sulfided during the HDS reaction to form Mo nitride–sulfide clusters. Surface sulfidation of Mo nitride catalysts was reported by several groups [33–36]. It is considered that these nitride–sulfide clusters are stable in the composition during the reaction, since the HDS activity and the H_2S/C_4 mole ratio are different from that for MoS_x/NaY and are not changed in the second and third runs.

4. Conclusions

In summary, it was found that Mo nitride clusters, possibly Mo_2N dimers, encaged in micropores of NaY zeolite were prepared by NH_3 treatments of $Mo(CO)_6$ at 673 K. The Mo nitride clusters were highly dispersed due to a low temperature nitridation reaction. MoN_x/NaY (673–24) was only partially sulfided during the HDS reaction at 623 K. MoN_x/NaY (673–24) was more resistant against the deactivation during the thiophene HDS than MoS_x/NaY, which was prepared by sulfiding $Mo(CO)_6$/NaY.

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