Modification of Potassium-Containing Zeolites Loaded with Mo₃S₄⁴⁺ Clusters by Solid-State Reaction between Zeolites and KCl

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By aqueous ion exchange, cationic molybdenum sulfide $Mo_3S_4^{4+}$ clusters have been successfully introduced into KY and KL without destruction of the zeolite structures as verified by the measurements of X-ray diffraction and low-temperature nitrogen adsorption. Infrared and mass spectra indicate that a large quantity of acid sites is produced in the zeolites during the preparation and activation of the samples. However, through solid-state ion exchange of the zeolites with KCl, the produced acid sites are largely removed upon activation of the samples in vacuo or in helium flow at high temperatures. During sulfidation of the KCl-added samples, the solid-state reaction occurs to a greater extent without loss of zeolite crystallinity, eliminating nearly all the acidic protons and partly suppressing the production of Lewis acid sites in the zeolites. The KCl-added catalysts produce a significant amount of alcohols in CO hydrogenation. This product distribution is considered to reflect the decrease in the acid sites in the zeolites by the solid-state ion exchange.

1. Introduction

Molybdenum-based catalysts have been widely studied because of their excellent properties in a variety of reactions, e.g., hydrodesulfurization, hydrodenitrogenation, methanation syntheses of light hydrocarbons and mixed alcohols from CO hydrogenation, and dehydroaromatization of methane. As a result of the well-known specific properties of zeolites, numerous methods have been attempted to introduce molybdenum species into zeolites.¹⁻⁵ Impregnation of ammonia heptamolybdate on zeolites has been applied to the preparation of molybdenum-loaded zeolites but often gives rise to a poor dispersion of molybdenum species on zeolites.¹ Aqueous ion exchange is an effective method for introducing transition metal cations into zeolites. Molybdenum-loaded Y zeolites have been prepared with Mo₂(ethylenediamine)₄Cl₄ and MoO₂Cl₂ solutions.^{2,3} So far however, only a few studies have succeeded in incorporating molybdenum into zeolites by means of aqueous ion exchange since cationic molybdenum species usually exist in high oxidation states in strongly acidic solutions in which the structures of many zeolites undergo destruction. Alternatively, Dai and Lunsford succeeded in introducing molybdenum species into zeolites by solid-state reactions of HY and ultrastable HY with MoCl₅.⁴ Thermal decomposition of molybdenum hexacarbonyl adsorbed into zeolites has also been frequently used for preparation of molybdenum-loaded zeolites.5

Molybdenum sulfide compound, $[Mo_3S_4(H_2O)_9]Cl_4$, is stable in air and soluble in aqueous solution.^{6–8} The cationic $Mo_3S_4^{4+}$ clusters with incomplete cubane-type structures can be introduced as sulfide species into zeolites (e.g., NaY, HUSY, KL, NaMOR, NaH β) by conventional aqueous ion exchange.^{9,10} The performance of the zeolites loaded with Mo₃S₄⁴⁺ clusters has been tested for CO hydrogenation. The products deviate from the typical Schulz–Flory distribution with the selectivity of C₂ hydrocarbons as high as about 50% based upon the calculation of carbon efficiency. Besides the hydrocarbons, however, no oxygenate products, e.g., alcohols, have been detected.¹⁰

Alkali-promoted, especially potassium-promoted molybdenum catalysts, have been extensively investigated for synthesis of mixed alcohols from CO hydrogenation.¹¹ It has been recognized that properties of catalysts for yielding alcohols are influenced by the basicity of promoters and/or catalysts themselves.¹² The acidity/basicity of zeolites can be adjusted, to some extent, by varying the cations in zeolites. It has been shown that K⁺, Rb⁺ and Cs⁺ cation-exchanged zeolites exhibit higher basicity than NaY.^{13,14} In aqueous solution, however, due to strong hydration of the cations, Rb⁺ and Cs⁺ are too large to penetrate into the small cages of zeolites (e.g., β cages in Y zeolites). It is therefore difficult to obtain Rb⁺ and Cs⁺ zeolites with high exchange degrees by aqueous ion exchange, although they are more basic than K⁺-containing zeolites.^{15,16} In this work, KY and KL were used as supports for loading the cationic $Mo_3S_4^{4+}$ clusters. However, the test reaction of CO hydrogenation over the samples indicates that no oxygenate products can be obtained (see, e.g., ref 10). The restriction of zeolite pore structures where active phases of molybdenum sulfide clusters stay seems not crucial for producing oxygenates with low carbon numbers (e.g., methanol and ethanol). Thus, it is implied that the basicity of potassium-cation-containing zeolites is not high enough for promoting the formation of oxygenates, on one hand,

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and that the acid sites may be produced in the zeolites during activation of the incorporated $Mo_3S_4^{4+}$ species, on the other hand. During ion exchange of the zeolites with $Mo_3S_4^{4+}$, the solution is rather acidic with a pH value of 3–4.5, which may also bring about the production of acid sites in the zeolites. These findings prompt us to investigate in detail the acid properties of the zeolites loaded with $Mo_3S_4^{4+}$ clusters. To suppress the production of the acid sites in the zeolites, KCl was added to the samples and allowed to react with the zeolite protons by solid-state ion exchange at high temperatures. The production and elimination of the acid sites in the zeolites after loading $Mo_3S_4^{4+}$ species were verified by means of techniques of infrared and mass spectroscopies, X-ray diffraction, and lowtemperature nitrogen adsorption.

2. Experimental Section

Zeolite KY was prepared by 5-fold aqueous ion exchange of NaY (FAU, SK-40, Nikka Seiko; Si/Al = 2.3) in 0.1 mol dm⁻³ KCl solution. The exchange degree was 98% based upon chemical analysis of the zeolite. KL (LTL, Tosoh, TSZ-500KOA; Si/Al = 3.1) was used as supplied. The molybdenum sulfide compound, $[Mo_3S_4(H_2O)_9]Cl_4$, was synthesized according to the procedures described by Shibahara et al.⁸ The zeolites loaded with $Mo_3S_4^{4+}$ clusters, denoted as Mo_3S_4 –KY and Mo_3S_4 –KL, were prepared by aqueous ion exchange as described before.^{9,10} The molybdenum contents in the two samples were 5.0 and 2.5 wt %, respectively.

The mixtures of Mo_3S_4 -KY and Mo_3S_4 -KL with KCl with an atomic K/Mo ratio of 1.2 were prepared by a suspension method in order to avoid possible destruction of the zeolite structure and oxidation of $Mo_3S_4^{4+}$ clusters caused by usual grinding in an agate mortar in the air. KCl was ground in a mortar and mixed with Mo_3S_4 -KY and Mo_3S_4 -KL in hexane solvent. The resulting suspension was stirred magnetically for 3 h and then allowed to stand for about 0.5 h. The solvent was decanted, and the residual hexane in the mixtures was evaporated to dryness at room temperature. The resulting samples were denoted as Mo_3S_4 -KY-KCl and Mo_3S_4 -KL-KCl.

The activation of the samples was performed in vacuo ($<10^{-3}$ Pa) at 300 °C or in helium flow (50 mL min⁻¹) at 400 °C for 2 h. The sulfidation of the samples was carried out in a flow of 5% H₂S/H₂ mixed gas (50 mL min⁻¹) at 400 °C for 2 h. Prior to sulfidation, the samples were activated in helium flow at 200 °C for 2 h to remove weakly adsorbed water.

Infrared spectra were recorded on a Perkin-Elmer model 1600 FTIR spectrometer. The samples were pressed into self-supporting wafers and loaded into an infrared cell connected to a vacuum line. Prior to measurements, the samples were dehydrated in vacuo at 200 °C for 2 h. Pyridine was then introduced onto the samples for adsorption for 0.5 h. After outgassing of pyridine at 200 °C for 0.5 h, the spectra were subsequently recorded by accumulating 64 scans at a resolution of 4 cm⁻¹.

Temperature-programmed decomposition of $[Mo_3S_4(H_2O)_9]$ -Cl₄ and $Mo_3S_4^{4+}$ clusters loaded into the zeolites, the solidstate reaction between the zeolite protons and KCl, and the desorption of ammonia adsorbed on the samples were performed in helium flow of 50 mL min⁻¹, and the products were monitored by a M-QA100TS mass spectrometer (Anelva, Japan). The temperature increase was 5 °C min⁻¹. Powder samples, 20 mg of $[Mo_3S_4(H_2O)_9]$ Cl₄ and 50 mg of the zeolites loaded with $Mo_3S_4^{4+}$ clusters, were used.

The surface areas and pore volumes of the samples were measured at -196 °C using nitrogen as the adsorption gas on



Figure 1. Species evolved from the temperature-programmed decomposition of $[Mo_3S_4(H_2O)_9]Cl_4$ in helium flow as monitored by mass spectroscopy: (a) $H_2O(m/z = 18)$; (b) HCl (m/z = 36); (c) HS or $H_2S(m/z = 33)$.

an automatic gas adsorption apparatus (Bel Sorp 285A, Japan). The crystallinities of the samples were determined by means of X-ray powder diffraction carried out on a Rigagu Denki X-ray diffractometer using Cu K α radiation.

The test reaction of CO hydrogenation over the samples was performed in a fixed-bed flow reactor equipped with an online gas chromatograph. The reactant gas was composed of 30% CO, 60% H₂, and 10% N₂. Each measurement was carried out using 0.5 mL (ca. 0.36 g) of the sample. Under the present experimental conditions, only trace amount of CO₂ could be detected by the thermal conductivity detector, and thus the activity mentioned below would be referred to as that with CO₂ free.

3. Results and Discussion

Acid Sites of the Zeolites Loaded with $Mo_3S_4^{4+}$ Clusters and Their Elimination. The evolved species resulting from the decomposition of $[Mo_3S_4(H_2O)_9]Cl_4$ as monitored by mass spectroscopy are shown in Figure 1. A strong desorption peak (m/z = 18) arising from weakly adsorbed water in the compound is observed at about 85 °C (Figure 1, spectrum a). With a further increase in temperature, the intensity of the mass signal of water decreases remarkably and levels off at about 500 °C. The water desorption over 160 °C may correspond to the release of the coordinated water in the compound. The decomposition of the compound starts to occur at about 200 °C as indicated by the evolution of HCl (m/z = 36) (Figure 1, spectrum b).

No mass signals corresponding to HS and H_2S are observed (e.g., Figure 1, spectrum c), suggesting that the sulfur-containing molybdenum species do not form hydrogen sulfide species with the trapped water in the compound but directly decompose into molybdenum sulfide species. For Mo_3S_4 -KY and Mo_3S_4 -KL, in contrast, their mass spectra measured under the same conditions exhibit no evolution of HCl with increasing temperature (Figure 2, spectra a and b). This observation proves the previous conclusions obtained from the chemical analyses and



Figure 2. HCl (m/z = 36) evolved from the temperature-programmed decomposition of the molybdenum sulfide clusters loaded into the zeolites in helium flow, as monitored by mass spectroscopy: (a) Mo₃S₄-KY; (b) Mo₃S₄-KL; (c) Mo₃S₄-KY-KCl; (d) Mo₃S₄-KL-KCl.



Figure 3. Infrared spectra of pyridine adsorbed on (a) Mo_3S_4 -KY activated in vacuo, (b) Mo_3S_4 -KY in helium flow, (c) Mo_3S_4 -KY-KCl in vacuo, (d) Mo_3S_4 -KY-KCl in helium flow, (e) sulfided Mo_3S_4 -KY, and (f) sulfided Mo_3S_4 -KY-KCl.

UV-visible spectra of the samples that the tetravalent $Mo_3S_4^{4+}$ cations are indeed ion-exchanged onto the cationic positions of the zeolites instead of $[Mo_3S_4(H_2O)_9]Cl_4$ molecules being occluded in the zeolites.¹⁰ Similar to the mass spectra of $[Mo_3S_4-(H_2O)_9]Cl_4$, no signals corresponding to HS and H₂S species are detected. The profiles of H₂O desorption from both Mo_3S_4-KY and Mo_3S_4-KL were also monitored by mass spectroscopy. They are similar to those from their parent KY and KL zeolites; that is, substantial amount of physisorbed water desorbs at about 120 °C (not shown in the figures).

The infrared spectra of pyridine adsorbed on Mo_3S_4 -KY activated in vacuo and in helium flow are shown in Figure 3. The spectra of the samples prior to pyridine adsorption display the stretching bands of the typical acidic O-H groups at about 3650 and 3560 cm⁻¹ (not shown in the figures). As shown in Figure 3 (spectra a and b), after pyridine adsorption and subsequent outgassing at 200 °C for 0.5 h, a strong band is observed at 1542 cm⁻¹ for the sample activated in vacuo or in helium flow, indicating the production of Brønsted acid sites in the zeolite. A small quantity of Lewis acid sites are also



Figure 4. Infrared spectra of pyridine adsorbed on (a) Mo_3S_4 -KL activated in vacuo, (b) Mo_3S_4 -KL-KCl in vacuo, (c) sulfided Mo_3S_4 -KL, and (d) sulfided Mo_3S_4 -KL-KCl.

detected, as revealed by the weak band appearing at about 1452 cm⁻¹. The band at 1438 cm⁻¹ arises from the interaction of K⁺ cations in the zeolite with the adsorbed pyridine, in comparison with the spectrum of pyridine adsorbed on the parent KY (not shown in the figure). Similar spectra are also observed with Mo_3S_4 -KL. As an example, the spectrum of pyridine adsorbed on Mo_3S_4 -KL activated in vacuo is presented in Figure 4 (spectrum a). The strong band at 1542 cm⁻¹ and the weak one at 1452 cm⁻¹ correspond to Brønsted and Lewis acid sites, respectively. The infrared spectra of the parent KY and KL zeolites activated in vacuo at 400 °C and after subsequent pyridine adsorption have also been measured, no 1542 and 1452 cm⁻¹ bands corresponding to Brønsted and Lewis acid sites being found (not shown in the figures). Therefore, the acid sites do not originate from the parent zeolites themselves.

As described above, during the aqueous ion exchange step in the preparation of the samples, the acidic $[Mo_3S_4(H_2O)_9]Cl_4$ solution may bring about the production of the acid sites in the zeolites. Considering activation of an aqueous ion-exchanged Cu(II)Y (exchange degree $\sim 85\%$) in vacuo at 400 °C, where a part of the Cu(II) cations underwent autoreduction, the acidic O-H groups were also observed by infrared spectroscopy. It is worthy to mention that in the parent NaY zeolite used for the preparation of Cu(II)Y there were no Brønsted and Lewis acid sites being detected by infrared spectroscopy. Therefore, the acid sites produced in Cu(II)Y should result from the autoreduction of Cu(II) cations.¹⁷ It implies that Brønsted acid sites produced in the activated Mo₃S₄-KY and Mo₃S₄-KL samples may also result from the decomposition of the loaded $Mo_3S_4{}^{4+}$ species, which make the protons from the zeolitetrapped water migrate to the cationic positions of the zeolites.

Brønsted acid sites in zeolties can be eliminated by heat treatment of the zeolites mixed with metal chlorides or oxides via a solid-state ion exchange.^{15,18–26} The process of the solid-state reaction of alkali cations (Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺) in chlorides with zeolite protons has been systematically investigated by Karge et al. using infrared and mass spectros-copies.^{15,21–24} It was found that, upon heat treatment of the mixture, the exchanging species, i.e., the molecules of alkali

chloride, would migrate and diffuse from the outer surface into the pores or channels of the zeolites; thus, the chloride would become well dispersed, although it may not be homogeneously mixed with the zeolites at the very beginning.^{25,26} This method is proved efficient for reducing the number of Brønsted acid sites in the zeolites due to the substitution of the cations in alkali chlorides for the zeolite protons.^{15,21-24} From this point of view, a certain amount of KCl was mixed with the molybdenumsulfide-loaded samples in order to suppress the production of the acid sites, especially Brønsted acid sites. Upon thermal activation, the solid-state ion exchange between the zeolite protons and K⁺ cations in KCl occurred. The infrared spectra of pyridine adsorbed on Mo₃S₄-KY-KCl and Mo₃S₄-KL-KCl activated in vacuo and in helium flow are presented in Figure 3 (spectra c and d) and Figure 4 (spectrum b). It can be seen that with the addition of KCl to the samples the intensity of the band at about 1542 cm⁻¹ is significantly decreased, indicating the removal of Brønsted acid sites in the zeolites by the solidstate ion exchange. The solid-state ion exchange has also been monitored by mass spectroscopy. It starts to occur at about 300 °C, as indicated by HCl evolution (Figure 2, spectra c and d).

Considering the possible oxidation of the $Mo_3S_4^{4+}$ clusters loaded into the zeolites in the air, an alternative treatment was performed by sulfiding the samples in a flow of H₂S/H₂ at 400 °C. The infrared spectra of pyridine adsorbed on the sulfided samples are presented in Figures 3 and 4. Compared with those of pyridine adsorbed on Mo₃S₄-KY and Mo₃S₄-KL activated in vacuo or in helium flow, the infrared spectra of the respective sulfided samples exhibit an even stronger band at about 1542 cm^{-1} . Moreover, the intensity of the band at 1452 cm^{-1} is somehow also increased (Figure 3, spectrum e, and Figure 4, spectrum c). These results imply that, due to the reducing atmosphere of H₂S/H₂, more acid sites are produced in the zeolites during sulfidation. However, with the addition of KCl to the samples, the intensities of the two bands become lower than those for the activated samples (compare spectrum f with a or b in Figure 3, and spectrum d with b in Figure 4). They indicate that the solid-state ion exchange between the zeolite protons and K⁺ cations in KCl occurs to a greater extent during sulfidation than by usual thermal activation and that the production of Lewis acid sites in the zeolites is also suppressed somehow.

The acid properties of KY and KL loaded with $Mo_3S_4^{4+}$ clusters and elimination of the acid sites by the solid-state reaction of the zeolites with KCl have been investigated in detail by temperature-programmed desorption of ammonia adsorbed on the samples monitored by mass spectroscopy. The spectra corrected to those of ammonia adsorbed on the parent KY and KL zeolites are presented in Figures 5 and 6. On the basis of the desorption spectrum of ammonia adsorbed on a standard H-ZSM-5 sample, the concentrations of the acid sites in the samples were calculated as listed in Table 1.

As described above, no acid sites were detected by the infrared spectra of pyridine adsorbed on KY and KL. However, in the case of ammonia adsorption on KY, one desorption peak was observed at about 185 °C on its mass spectrum (not shown in the figure). Niwa et al. ascribed it to the weakly held ammonia in zeolites.^{27–29} For Mo₃S₄–KY activated in helium flow or sulfided at the same temperature, one desorption peak at about 180 °C together with a shoulder at about 230 °C are observed (Figure 5, spectra a and b). The low-temperature peak would be tentatively assigned to the weak acid sites (most probably, Lewis acid sites as described below) in the zeolites, although its assignment remains disputable. The high-temperature shoul-



Figure 5. Profiles of the temperature-programmed desorption of ammonia (m/z = 16) adsorbed on (a) Mo₃S₄-KY activated in helium flow, (b) sulfided Mo₃S₄-KY, (c) Mo₃S₄-KY-KCl activated in helium flow, and (d) sulfided Mo₃S₄-KY-KCl.



Figure 6. Profiles of the temperature-programmed desorption of ammonia (m/z = 16) adsorbed on (a) Mo₃S₄-KL activated in helium flow, (b) sulfided Mo₃S₄-KL, (c) Mo₃S₄-KL-KCl activated in helium flow, and (d) sulfided Mo₃S₄-KL-KCl.

 TABLE 1: Concentrations of the Acid Sites in the

 Molybdenum-Sulfide-Loaded Zeolites Determined by

 Temperature-Programmed Desorption of Ammonia

 Monitored by Mass Spectroscopy

sample	acid sites (mmol/g)			
Mo_3S_4 -KY (activated in He)	1.29			
Mo ₃ S ₄ -KY-KCl (activated in He)	0.81			
Mo_3S_4 -KY (sulfided)	1.85			
Mo ₃ S ₄ -KY-KCl (sulfided)	0.59			
Mo_3S_4 -KL (activated in He)	0.62			
Mo ₃ S ₄ -KL-KCl (activated in He)	0.44			
Mo_3S_4 -KL (sulfided)	0.42			
Mo_3S_4 -KL-KCl (sulfided)	0.11			

der can be assigned to the desorption of ammonia adsorbed on Brønsted acid sites in the zeolites.^{27–31} The quantity of the acid sites in the sulfided Mo_3S_4 –KY is much larger than that in the same sample activated in helium flow (see also Table 1). This result is consistent with the infrared spectra of pyridine adsorbed on the respective samples as mentioned above. With the addition of KCl to the samples, the intensity of the low-temperature peak decreases and the shoulder corresponding to the strong acid sites in the zeolites is completely removed for both sulfided and activated samples (Figure 5, spectra c and d), proving the conclusion drawn from the infrared measurements that the solidstate ion exchange between the zeolites and KCl suppresses not



Figure 7. X-ray diffraction patterns of (a) KY, (b) Mo_3S_4 -KY-KCl activated in vacuo, (c) sulfided Mo_3S_4 -KY-KCl, (d) KL, and (e) sulfided Mo_3S_4 -KL-KCl.

 TABLE 2: Measurements of N2 Adsorption on the

 Molybdenum-Sulfide-Loaded Zeolites

sample	treatment in vacuo	$A_{ m Lang.} \ (m^2/g)$	pore volume (mm ³ /g)
KY	300 °C, 2 h	820.4	291.4
Mo ₃ S ₄ -KY	200 °C, 2 h	758.1	263.0
Mo ₃ S ₄ -KY	300 °C, 2 h	773.8	270.9
Mo ₃ S ₄ -KY	400 °C, 2 h	790.2	278.5
Mo ₃ S ₄ -KY-KCl	400 °C, 2 h	672.5	236.8
sulfided Mo ₃ S ₄ -KY-KCl	200 °C, 2 h	800.3	277.6

only the production of Brønsted acid sites but also, to some extent, that of Lewis acid sites in the zeolite. It is important to mention that for the sulfided Mo_3S_4 -KY-KCl sample the intensity of the low-temperature peak is reduced more remarkably than that for the activated sample; namely, the acid sites of the zeolites are more efficiently eliminated by sulfidation. Compared with that of Mo_3S_4 -KY activated in helium flow, the overall concentrations of the acid sites decrease by about 37% and 55% for the activated and sulfided Mo_3S_4 -KY-KCl samples, respectively (Table 1), with only the weak acid sites remaining (Figure 5, spectra c and d).

In the spectrum of temperature-programmed desorption of ammonia adsorbed on Mo_3S_4 -KL activated in helium flow, two well-resolved desorption peaks are observed (Figure 6, spectra a). The assignment of the low-temperature peak at about 170 °C is the same as that for Mo_3S_4 -KY. The other desorption peak appears at a much higher temperature (~320 °C) compared with that observed for Mo_3S_4 -KY (~230 °C), indicating that stronger acid sites are produced in KL zeolite. Unlike the case with Mo_3S_4 -KY, the low-temperature peak can be mostly removed upon sulfidation of the sample. Instead, an intense peak appears at an even higher temperature (~370 °C) (Figure 6, spectrum b). It reveals that stronger acid sites are formed during sulfidation of the sample in the reducing atmosphere. The concentration of the acid sites in Mo_3S_4 -KL is declined due to

the sulfidation by about 30% in comparison with that given by activation in helium flow, but with 95% of the remaining acid sites being strong ones (Table 1 and Figure 6, spectrum b). In a manner similar to the case of Mo_3S_4 -KY, with the addition of KCl to the sample, the intensities of the low- and high-temperature desorption peaks for Mo_3S_4 -KL-KCl decrease upon activation in helium flow due to the removal of the acid sites by the above-mentioned solid-state ion exchange (Figure 6, spectrum c). After sulfidation, both peaks become very weak (Figure 6, spectrum d). Compared with Mo_3S_4 -KL activated in helium flow, about 83% of the acid sites are removed (Table 1). This verifies the conclusion obtained from infrared measurements that the sulfidation of Mo_3S_4 -KL-KCl not only facilitates the solid-state ion exchange between the zeolites and KCl but also suppresses the production of Lewis acid sites in the zeolites.

Crystallinity and Pore Volume of the Zeolites Loaded with $Mo_3S_4^{4+}$ Clusters. The crystallinity of the zeolites loaded with Mo₃S₄⁴⁺ clusters was evaluated by X-ray diffraction measurements. Some representative patterns of the samples treated under different conditions are presented in Figure 7. The introduction of molybdenum species into zeolites often gives rise to a loss of the zeolite crystallinity because of their acidity. As mentioned above, the $[Mo_3S_4(H_2O)_9]Cl_4$ solutions used for ion-exchanging the cationic $Mo_3S_4^{4+}$ clusters into the zeolites are rather acidic with a pH value of 3-4.5. Nevertheless, the incorporation of $Mo_3S_4^{4+}$ cations into KY and KL does not result in the destruction of the zeolite structures (see, e.g., ref 10). After activation of the samples in vacuo or in helium flow at different temperatures up to 500 °C, no detectable loss of the zeolite crystallinity in Mo₃S₄-KY and Mo₃S₄-KL is observed by their X-ray diffraction patterns (not shown in the figure), in comparison with those of the parent zeolite KY and KL. However, with the addition of KCl to the samples, the activation of the samples at high temperatures results in, to some extent, the loss of the zeolite crystallinity. As an example, the X-ray diffraction patterns of KY and Mo₃S₄-KY-KCl activated in helium flow are presented in Figure 7 (patterns a and b). Compared with the pattern of KY, the relative ratio of the two strongest peaks appearing at 2θ of 6.2° and 23.5° for Mo₃S₄-KY-KCl activated in helium flow is rather small. It indicates the loss of zeolite crystallinity because of the solid-state ion exchange between the zeolite and KCl at high temperature. However, no detectable loss of the zeolite crystallinity is observed for the sulfided Mo₃S₄-KY-KCl and Mo₃S₄-KL-KCl samples (Figure 7, compare pattern c with a and e with d), although, as described above, the solid-state ion exchange during sulfidation occurs to a greater extent.

This conclusion can be further confirmed by the measurements of nitrogen adsorption on the samples at a low temperature (ca. -196 °C). The Langmiur instead of BET adsorption model was used for the calculation of zeolite surface area. The collected data are listed in Table 2. Compared with those of KY, the pore volume and surface area of Mo₃S₄–KY can be gradually recovered upon activation of the sample at elevated temperatures up to 400 °C. With the addition of KCl to Mo₃S₄–

TABLE 3: Performance of CO Hydrogenation over the Molybdenum-Sulfide-Loaded Zeolites^a

sulfided sample		activity (C-mmol/g-Mo min)	hydrocarbons (%CO)				alcohols (%CO)			
	time (h)		C1	C ₂	$(C_{2}=^{b})$	C ₃	C_{4+}	C ₁ OH	C ₂ OH	C ₃₊ OH
Mo ₃ S ₄ -KY	12	0.95	53.3	24.5	(14.5)	16.0	6.2			
Mo ₃ S ₄ -KL	6	3.73	40.7	33.3	(19.8)	7.2	18.8			
	12	2.63	53.1	28.7	(19.6)	5.5	12.7			
Mo ₃ S ₄ -KY-KCl	24	0.85	33.6	16.4	(9.9)	10.8	0.4	22.5	5.7	10.6
Mo ₃ S ₄ -KL-KCl	6	3.90	33.6	28.9	(17.0)	7.3	14.4	11.7	3.8	0.3
	24	3.29	28.3	30.7	(18.2)	7.3	13.2	14.5	5.4	0.6

KY, the activation of the sample in vacuo at 400 °C brings about a loss of about 20% of the zeolite pore volume because of the solid-state ion exchange. For the sulfided Mo_3S_4 -KY-KCl sample, however, the zeolite pore volume is very much similar to that of the parent zeolite KY. This result is in accordance with that obtained from the corresponding X-ray diffraction measurements.

CO Hydrogenation over the Zeolites Loaded with Mo₃S₄⁴⁺ Clusters. It has been reported that over Mo_3S_4 –NaY and Mo_3S_4 –KL pretreated in helium flow at 300 °C only hydrocarbon products, mainly methane and ethane (about 45% and 50%, respectively) were obtained.¹⁰ As mentioned above, the sulfidation of the samples produces a large quantity of acid sites in the zeolites, while, with the addition of KCl to the samples, the produced acid sites can be efficiently eliminated. Therefore, Mo_3S_4 –KY, Mo_3S_4 –KL, and the respective samples added with KCl were sulfided and tested for CO hydrogenation to investigate the effect of the acid sites in the zeolites upon the product distribution. The collected data are listed in Table 3.

Over the sulfided Mo₃S₄-KY and Mo₃S₄-KL samples, only hydrocarbon products are obtained. The selectivities on the two samples are similar, the main products being methane and ethane/ethylene (about 50% and 30%, respectively). The activities decrease with increasing time of stream on the samples (e.g., compare the data in Table 3 obtained from the reaction over the sulfided Mo₃S₄-KL for 6 and 12 h). These results indicate that the acidity of the zeolites may play an important role in CO hydrogenation, which gives rise to mere hydrocarbon products and results in deactivation of the samples, probably due to the coke formation on the acid sites. Similar to the results reported before, the activities obtained with L-type zeolite are much higher than those with Y zeolite.¹⁰ With the addition of KCl to the samples, a substantial amount of alcohol products can be obtained without obvious loss of the activities. It is clear that the formation of the alcohol products is due to the elimination of the acid sites in the zeolites by the abovementioned solid-state ion exchange during sulfidation of the samples. From Table 3, the activity for alcohol formation obtained at the reaction time of 24 h over the sulfided Mo₃S₄-KL-KCl is twice as much as that over the sulfided Mo₃S₄-KY-KCl (0.67 and 0.33 C-mmol (g Mo)⁻¹ min⁻¹, respectively).

As shown in Figure 6 (spectrum b), the solid-state reaction between the zeolite and KCl that occurred during sulfidation of Mo_3S_4 -KL-KCl removes nearly all the weak and strong acid sites in the zeolite. In the case of Mo_3S_4 -KY-KCl (Figure 5, spectrum b), however, large numbers of the weak acid sites remain in KY, although the strong ones are totally removed after sulfidation. The different acid properties of the sulfided Mo_3S_4 -KL-KCl and Mo_3S_4 -KY-KCl may be responsible for the large difference in the activities of alcohol formation between the two samples. Over the sulfided Mo_3S_4 -KY-KCl, about 30% of the alcohol products are C₃₊OH, while in the case of the sulfided Mo_3S_4 -KL-KCl, nearly only methanol and ethanol are obtained. Moreover, the selectivities for alcohols over the latter is also lower. The different product distributions may be due to the different zeolite pore structures.

4. Conclusions

The cationic molybdenum sulfide Mo₃S₄⁴⁺ clusters can be introduced into KY and KL zeolites by aqueous ion exchange.

The activation in vacuo (or in helium flow) or sulfidation of the samples results in the production of acid sites in the zeolites. With the addition of KCl to the samples, however, the production of the acid sites can be suppressed upon activation or sulfidation of the samples because of the solid-state ion exchange between the zeolites and KCl. It has been found that the solid-state reaction occurs to a greater extent during sulfidation of the samples, which removes almost all the acid sites in Mo₃S₄-KL-KCl and almost all the strong ones in Mo₃S₄-KY-KCl. The test reaction of CO hydrogenation over the two samples also indicates the removal of the acid sites in the zeolites.

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