

## Preparation of Zeolites incorporating Molybdenum Sulfide Clusters with High C<sub>2</sub> Hydrocarbon Selectivity in CO–H<sub>2</sub> Reactions

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The incomplete cubane-type cluster, [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup>, and the complete cubane-type cluster, [Mo<sub>3</sub>NiS<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>Cl]<sup>3+</sup>, are incorporated into 12-membered ring zeolites by ion exchange, leading to catalysts which are highly selective for C<sub>2</sub> formation from CO–H<sub>2</sub>.

Few cationic forms are available as simple salts of molybdenum of high oxidation state and most of them exist only in strongly acidic solutions where many zeolites are unstable and where exchangeable cations must compete with protons. Therefore, few studies have succeeded in introducing cationic molybdenum compounds into zeolites by ion exchange.<sup>1,2</sup> During the past decade the incomplete cubane-type molybdenum(IV) cluster [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> **1**,<sup>3</sup> which is stable in water and air, has been studied extensively.<sup>3–5</sup> It has been revealed that **1** is easily converted to mixed-metal clusters with cuboidal Mo<sub>3</sub>MS<sub>4</sub> cores (M = Fe, Co, Ni, etc.<sup>6</sup>). Recently, mixed-metal clusters with an Mo<sub>3</sub>PdS<sub>4</sub> core have been derived from **1** and found to show intriguing reactivities at the Pd site towards alkenes, CO, isonitriles and alkynes.<sup>7,8</sup> The molybdenum–nickel cluster [Mo<sub>3</sub>NiS<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>Cl]<sup>3+</sup> **2** has also been found to uptake CO stoichiometrically to give a new cluster where one CO molecule combines with the Ni atom.<sup>9</sup> Thus, these molybdenum and mixed-metal clusters are of considerable interest in connection with potential application to a variety of catalytic reactions. It occurred to us that the molybdenum and mixed-metal clusters could be incorporated into zeolites by ion exchange and promote unique catalytic reactions. Here we report the prepara-

tion of the incomplete cubane-type sulfur-bridged molybdenum(IV) cluster and cubane-type mixed-metal clusters with Mo<sub>3</sub>MS<sub>4</sub> (M = Ni, Pd) encaged in zeolites by ion-exchanging zeolites with 12-membered rings and their application to CO hydrogenation reactions.

The chloride salt of cluster **1** was synthesized by the reported method.<sup>5</sup> To a suspension of NaY (Si/Al = 2.3) in water was added dropwise a 0.01 mol dm<sup>-3</sup> aqueous solution of the chloride salt of **1** with vigorous stirring at 313 K. The metal cluster-containing zeolite was separated by filtration and washed with distilled water, followed by drying at 313 K under reduced pressure. The resulting material is referred to as Mo/NaY. The chloride salts of cluster [Mo<sub>3</sub>NiS<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>Cl]<sup>3+</sup> **2**<sup>10</sup> and [Mo<sub>3</sub>PdS<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>Cl]<sup>3+</sup> **3**<sup>9</sup> were synthesized according to the respective reported methods and similarly treated with NaY to afford MoNi/NaY and MoPd/NaY. Other zeolites [HUSY (ultrastable Y, Si/Al = 3.1), KL (Si/Al = 3.1)] incorporating the incomplete cubane-type molybdenum cluster, Mo/HUSY and Mo/KL, were similarly prepared.

After ion exchange of NaY (5.0 g) with the solution (100 cm<sup>3</sup>) of **1**, >99% of molybdenum was found to be transferred from the solution to NaY; the resulting Mo/NaY contained 5.0 mass% of molybdenum, which corresponds to the presence of 0.36 Mo<sub>3</sub>S<sub>4</sub> cluster molecules (1.1 Mo atoms) per supercage. The Mo loadings of Mo/HUSY and Mo/KL were 2.3 and 2.1 mass%, respectively. The size of the cluster **1** is estimated to be 0.62 nm, smaller than the diameter of the aperture (0.74 nm) of supercages of the faujasite type structure and the openings (0.70 nm) of the main channel of the type L structure. Chlorine present in Mo/NaY was negligible, suggesting that the cluster **1** acted as a tetravalent cation in ion exchange. The released sodium ion ratio per loaded Mo cluster in the filtrate was 4.6 times (ideally 4 times) as much as the loaded cluster **1**. This slight (15%) excess of exchanged sodium over the supported cluster may be due to the acidity of the cluster salt.

UV–VIS spectra of Mo/NaY [Fig. 1(a)] showed bands at 300, 390 and ca. 650 nm, characteristic of the sulfide cluster [Fig. 1(b)], indicating the cluster structure remained virtually intact after ion exchange. This was substantiated by preliminary

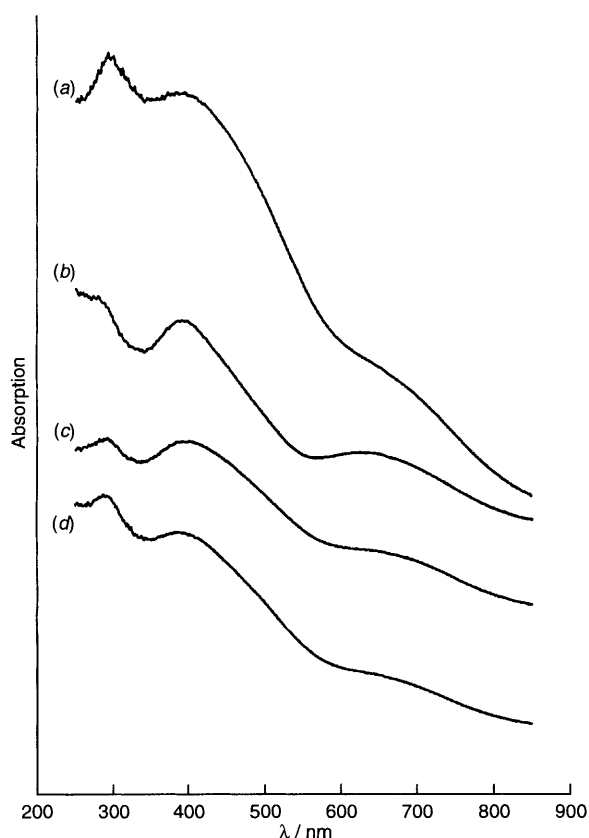


Fig. 1 UV–VIS spectra of (a) Mo/NaY; (b) physical mixture of NaY and the chloride salt of **1**; (c) Mo/HUSY; (d) Mo/KL

Table 1 CO hydrogenation activities and selectivities of molybdenum, molybdenum–nickel and molybdenum–palladium sulfide clusters incorporated into zeolite<sup>a</sup>

Catalyst	Mo loading (mass%)	Activity [C-μmol (g Mo) <sup>-1</sup> min <sup>-1</sup> ]	Selectivity (C-mol%)			
			C <sub>1</sub>	C <sub>2</sub> (C <sub>2</sub> = <sup>b</sup> )	C <sub>3</sub>	C <sub>4</sub> +
Mo/NaY	5.0	14.2	44.7	49.9 (1.7)	4.5	0.9
Mo/SiO <sub>2</sub>	5.0	14.3	67.5	29.5 (0.0)	3.0	0.0
MoNi/NaY	5.0	10.6	21.4	58.2 (3.1)	20.4	0.0
Ni + Mo/NaY	5.0	11.3	29.2	43.7 (2.7)	22.2	5.0
MoPd/NaY	4.5	12.1	31.3	41.1 (2.7)	16.3	11.4
Mo/HUSY	2.3	29.2	23.8	57.6 (2.4)	7.1	11.6
Mo/KL	2.1	237	43.1	49.4 (0.4)	6.7	0.9

<sup>a</sup> Reaction conditions: temperature = 573 K, total pressure = 1.6 MPa, H<sub>2</sub>/CO = 1.0 and W/F = 10 (g cat) h mol<sup>-1</sup>. <sup>b</sup> Ethylene.

EXAFS data.<sup>11</sup> The persistence of the cluster structure in other zeolites was similarly confirmed by UV–VIS spectra [Fig. 1(c),(d)]. UV–VIS spectra of MoNi/NaY also exhibited the existence of the cluster **2**. Since the chloride salts of **1–3** are acidic, zeolite crystals might be decomposed during ion exchange. However, the X-ray powder diffraction patterns were hardly attenuated, indicating retention of crystallinity during ion exchange.

The catalysts were applied to CO hydrogenation reaction in a flow-type fixed-bed reactor after being treated in flowing He at 573 K for 0.5 h and then in flowing H<sub>2</sub> for 1 h. The reaction conditions were as follows: temperature = 573 K, total pressure = 1.6 MPa, H<sub>2</sub>/CO = 1.0 and W/F = 10 g cat h mol<sup>-1</sup>. The stabilized activity and selectivity obtained after 25 hour on stream are shown in Table 1. Mo/NaY produced hydrocarbons, especially ethane and ethylene at a selectivity of 50%. Application of the Schulz–Flory equation leads to the prediction that the maximum selectivity for C<sub>2</sub> compounds is 30%.<sup>12</sup> Mo/SiO<sub>2</sub>, prepared by impregnation of SiO<sub>2</sub> (Fuji Davison ID) with the solution of **1**, mainly produced methane, suggesting that the zeolite pore structure is responsible for the stabilization of active species for the selective C<sub>2</sub> hydrocarbon synthesis. Furthermore, MoNi/NaY gave rise to C<sub>2</sub> selectivity of about 60%. As a control catalyst, Ni + Mo/NaY was prepared by ion-exchanging Mo/NaY with an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Ni/Mo = 0.33). Ni + Mo/NaY exhibited only moderate selectivity for C<sub>2</sub> compounds and high C<sub>2</sub> hydrocarbon selectivity was not obtained with MoPd/NaY. These findings indicate that the cuboidal Mo<sub>3</sub>NiS<sub>4</sub> cluster structure as incorporated into the zeolite is essential to the selective formation of C<sub>2</sub> hydrocarbons. Although the cluster structure may not be retained in the reaction conditions, it is clear that the use of the sulfide clusters as a precursor results in the formation of active species for the particular carbon number distribution in CO hydrogenation. Mo/HUSY and Mo/KL also showed high selectivity for C<sub>2</sub> in the range of 49–58%. The former catalyst

gave a sizeable selectivity for C<sub>4</sub> and C<sub>5</sub> hydrocarbons. The latter showed a high specific activity compared to the other catalyst.

In conclusion, the molybdenum, molybdenum–nickel and molybdenum–palladium sulfide clusters have been successfully incorporated into the 12-membered ring pores of zeolites by ion exchange with retention of zeolite crystallinity. The use of the clusters, together with the pore structure of the zeolites, resulted in unique catalytic performances when applied to CO hydrogenation.

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