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An Infrared Study of Molybdenum Carbonyl-Butadiene Complexes Encaged in a Zeolite. Implication of the Active Molybdenum Carbonyl Species in the Hydrogenation of Butadiene

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Molybdenum carbonyls encaged in a NaY zeolite were found to form stable butadiene complexes; $Mo(CO)_4(C_4H_6)$ and $Mo(CO)_2(C_4H_6)_n$ (n = 1 or 2). These complexes are implied to deactivate the hydrogenation of C_4H_6 over molybdenum carbonyls/zeolite catalysts. The active species is proposed to be $Mo(CO)_3$ ads.

Molybdenum carbonyl species anchored on inorganic matrices show catalytic activities for metathesis of olefins,1,2) hydrogenation of propylene2) and isomerization of butenes.3) We have recently reported that molybdenum hexacarbonyl encaged in a zeolite shows a selective hydrogenation of butadiene to cis-2-butene and that no butane is produced.4-6) On the other hand, molybdenum metal prepared by the decomposition of $Mo(CO)_6$ produces various butenes together with a considerable amount of butane. Molybdenum subcarbonyl species are, accordingly, considered to be catalytically active for the hydrogenation.

As regards the active species for the hydrogenation of butadiene over molybdenum carbonyls/zeolite catalysts, no study has been conducted so far. We have found that molybdenum tricarbonyl species, $Mo(CO)_3$, are stabilized in zeolites exchanged with alkali metal cations5-7) and that $Mo(CO)_3$/zeolite systems show a highly selective hydrogenation of butadiene (cis-2-butene; > 98% at 273 K and 88% at 423 K4-6) for a LiY zeolite). In the present study, we investigated the interactions between butadiene and molybdenum carbonyl species encaged in a NaY zeolite using an infrared spectroscopy with the intention of revealing the molybdenum subcarbonyl species catalytically active for the hydrogenation of butadiene.

A NaY zeolite (JRC-ZY 4.8; Si/Al = 2.38) was supplied by Catalysis Society of Japan as a reference catalyst.5) The zeolite powder was pressed into self-supporting wafers for IR studies.7) The sample was pretreated in a vacuum at 673 K for 1-2 h in an in situ IR cell. After having recorded a background spectrum, the zeolite wafer was exposed to $Mo(CO)_6$ vapor at room temperature (ca. 300 K) for a selected period (15-30 s). The IR spectra were recorded at room temperature in a transmittance mode on a Hitachi double beam spectrophotometer (EPI-G).

The hydrogenation of 1,3-butadiene was carried out over molybdenum carbonyl-/zeolite catalysts at 323-423 K using a closed circulation system.4-6) The initial pressure of an H_2/butadiene (2/1) mixture was ca.20 kPa. The powdered NaY zeolite (50 mg) was exposed to $Mo(CO)_6$ for 1 h at room temperature after an evacuation at

673 K. The reaction gas was analyzed by GLC.

Shown in Fig. 1 is the conversion of butadiene over $Mo(CO)_3$ ads species encaged in the NaY zeolite as a function of the reaction time and temperature. The molybdenum tricarbonyl species was prepared by evacuating $Mo(CO)_6$ at 373 K for 30 min.[7] The selectivity to cis-2-butene was ca. 96%. It is noted in Fig. 1 that the hydrogenation of butadiene smoothly proceeds at > 403 K, while the reaction is strongly suppressed at the lower temperatures than 373 K soon after the reaction begins. The catalyst which had been deactivated at the lower reaction temperature showed a normal catalytic activity at 423 K. These findings suggest the formation of catalytically inactive molybdenum complexes at the low reaction temperature during the hydrogenation of butadiene over the $Mo(CO)_3$/NaY zeolite.

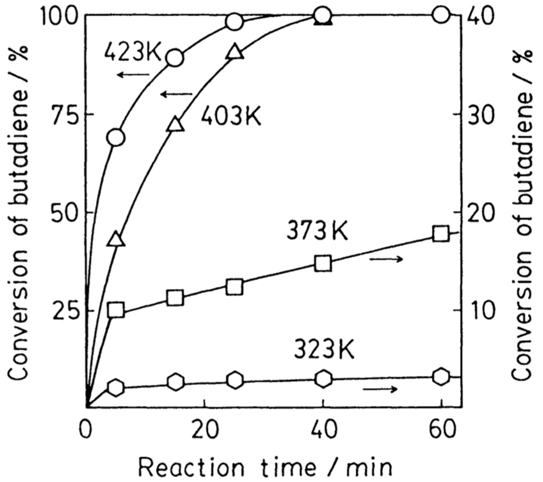

Fig.1. Conversion of C_4H_6 over a $Mo(CO)_3$/NaY catalyst vs. reaction time and temperature.

Figure 2-a shows the IR spectrum of $Mo(CO)_3$ ads species (1912, 1790, and 1758 cm^{-1}) stabilized in the NaY zeolite.[5,7] On an introduction of the reaction gas (butadiene/H_2) at room temperature, two sets of bands rapidly appeared at the expense of the bands due to $Mo(CO)_3$ as shown in Fig. 2-b. Species A is characterized by the bands at 1940 and 1881 cm^{-1} and Species B by the signals at 2047 cm^{-1}. When the catalyst was successively heated at 373 K for 15 min in the presence of the reaction gas, Species A became predominant, while Species B and $Mo(CO)_3$ were reduced in the amounts (Fig. 2-c). A small amount of $Mo(CO)_6$ (2123

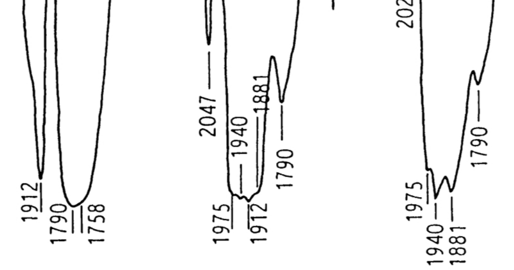

Fig.2. IR spectra of a $Mo(CO)_3$/NaY catalyst. a) $Mo(CO)_3$, b) after an introduction of C_4H_6/H_2 (12 kPa) at ca. 300 K and c) subsequently heat-treated at 373 K for 15 min.

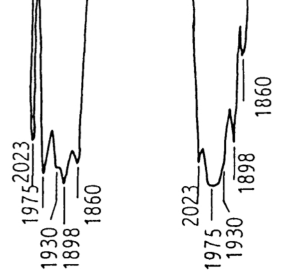

Fig.3. IR spectra of a $Mo(CO)_6$/NaY catalyst. a) after a contact with C_4H_6/H_2 (16 kPa) at 403 K for 10 min and b) then treated with CO (4.7 kPa) at 373 K for 30 min after an evacuation at ca. 300 K for 30 min.

Table 1. IR wavenumbers of the carbonyl species observed in the butadiene-molybdenum carbonyl/zeolite systems

Mo-carbonyl species	Wavenumbers	References
Species A	1940,^{s} 1881^{s}	
Species B	2047	
Species C	2023,^{m} 1930,^{s} 1898,^{s} 1860^{s}	
$Mo(CO)_3$ ads	1912,^{s} 1790,^{s} 1758^{sh}	7
$Mo(CO)_6$	2123,^{w} 1975^{s}	7
$Mo(CO)_5$[a]	2093,^{w} 1972,^{w} 1967,^{s} 1929,^{w} 1926^{s}	8
$Mo(CO)_4$[a]	2057,^{w} 1949,^{m} 1945,^{s} 1927,^{m} 1887^{s}	8
cis-$Mo(CO)_2(C_4H_6)_2$[b]	1980, 1938	9
cis-$Mo(CO)_4(C_8H_{12})$[c]	2036, 1950, 1930, 1883	10

a) At 20 K in a CH_4 matrix. b) C_4H_6; 1,3-butadiene. c) C_8H_{12}; cyclooctadiene.

and 1975 cm^{-1}) was recovered and a new species (C; 2023 cm^{-1}) was found to be formed. After the heat-treatment at 373 K, a selective production of cis-2-butene was confirmed by GLC. Similar spectral changes were observed when the $Mo(CO)_3$/NaY catalyst was contacted with butadiene alone.

Species C was found to be predominantly produced when $Mo(CO)_6$/NaY was exposed to butadiene/H_2 at 403 K as depicted in Fig. 3-a. Species C is characterized by a set of bands at 2023, 1930, 1898, and 1860 cm^{-1}. No change was observed in the $\nu(CO)$ bands after an evacuation at room temperature for 30 min. When the catalyst was subsequently treated at 373 K for 30 min after having introduced CO (4.7 kPa), the amount of Species C was reduced and a significant amount of $Mo(CO)_6$ was restored (Fig. 3-b).

Both Species A and C were found to be produced only in the presence of butadiene. Accordingly, these molybdenum carbonyl complexes are concluded to involve butadiene ligands. Species B was, on the other hand, formed during the decomposition of $Mo(CO)_6$ to $Mo(CO)_3$. Species A was found to be thermally stable at 350 K in vacuum. However, it was almost completely removed by an prolonged evacuation (40 min) or an H_2-treatment (3.9 kPa, 30 min) at 373 K, partially recovering $Mo(CO)_3$ species. Species C behaved similarly to Species A in both thermal stability in vacuum and chemical reactivity toward H_2.

The IR wavenumbers for Species A, B, and C are summarized in Table 1 together with those for reference compounds.[8-10] Comparing the wavenumbers in Table 1, Species B is assigned to $Mo(CO)_4$ ads encaged in the NaY zeolite.[11] The other bands of Species B were unresolved because of the coexistence of the other carbonyl species. Species C is unambiguously attributed to $Mo(CO)_4(C_4H_6)$ (C_4H_6; butadiene) encapsulated in the zeolite on the basis of the four $\nu(CO)$ bands (A_1, A_1, B_1, and B_2 bands in the order of wavenumber) and their wavenumbers.[8,10,12] The doublet bands of Species A is assigned to $Mo(CO)_2(C_4H_6)_2$ or $Mo(CO)_2(C_4H_6)$ ads. This assignment is rationalized by analogous chemical reactions of $Mo(CO)_3$ moieties,[13] for instance, tricarbonyl-η^6-mesitylenemolybdenum reacts with butadiene to produce dicarbonylbis (η^4-C_4H_6) molybdenum complex.[10] The following reactions are proposed to occur during the hydrogenation of butadiene over

$Mo(CO)_6$ or $Mo(CO)_3$/zeolite catalysts.

$$Mo(CO)_n \rightleftharpoons Mo(CO)_{n-1} + CO \quad (n = 6, 5, 4) \qquad (1)$$

$$Mo(CO)_4 + C_4H_6 \rightleftharpoons Mo(CO)_4(C_4H_6) \qquad (2)$$

$$Mo(CO)_3 + nC_4H_6 \rightleftharpoons Mo(CO)_2(C_4H_6)_n + CO \quad (n = 1 \text{ or } 2) \qquad (3)$$

$$Mo(CO)_3 + C_4H_6 \rightleftharpoons Mo(CO)_3(C_4H_6) \qquad (4)$$

$$Mo(CO)_3(C_4H_6) + H_2 \rightleftharpoons Mo(CO)_3(C_4H_6)(H_2) \longrightarrow Mo(CO)_3 + \text{cis-2-butene} \qquad (5)$$

The productions of $Mo(CO)_6$, $Mo(CO)_4$ and $Mo(CO)_4(C_4H_6)$ in Figs. 2-b and -c are initiated by the reaction of $Mo(CO)_3$ ads and CO which is evolved in the reaction (3), followed by the reactions (1) and (2). The IR observations in Fig. 2 are in good conformity with the assignments of Species A and C. The partial recovery of $Mo(CO)_3$ ads on the decomposition of the C_4H_6-complexes is also explained in terms of the reactions (1)-(3).

As shown in Fig. 1, the hydrogenation of butadiene proceeds at > 403 K over the $Mo(CO)_3$/NaY catalyst without the deactivation. The molybdenum carbonyl-butadiene complexes are expected to be considerably decomposed at > 403 K, taking into account the thermal stabilities. Even at the lower reaction temperatures, the initial activities of the catalyst are high in spite of the subsequent deactivations. Accordingly, it is implied that the active species is $Mo(CO)_3$ ads for the hydrogenation (Eqs. 4 and 5). The catalyst is deactivated by the formation of stable molybdenum subcarbonyl-butadiene complexes (Eq. 3). The $Mo(CO)_3(C_4H_6)$ complex is supposed to be relatively unstable because of its coordinative unsaturation (16 electrons) and to adsorb molecular H_2 for the hydrogenation to occur. Recently, coordinatively unsaturated $Mo(CO)_3(PR_3)_2$ complexes (R = C_6H_{11}, i-C_3H_7) in a liquid phase are shown to adsorb H_2, forming $Mo(CO)_3(PR_3)_2(H_2)$ complexes.[14)]

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