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SELECTIVE HYDROGENATION AND ISOMERIZATION OF PENTADIENE OVER MOLYBDENUM HEXACARBONYL ENCAGED IN A NaY ZEOLITE

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Highly stereo-selective hydrogenation of trans-1,3-pentadiene to cis-2-pentene and isomerization of 1,4-pentadiene to cis-1,3-pentadiene were found to take place thermally at 423 K over $Mo(CO)_6/NaY$. Relative hydrogenation rates of pentadiene isomers indicated that s-cis conformation of diene was crucial for the selective hydrogenation to occur. This was substantiated by an IR study.

1. Introduction

Molybdenum carbonyls attached on inorganic oxides have been demonstrated to show catalytic activities for the metathesis of olefins [1–4], hydrogenation of propylene [3], and hydrogenation and isomerization of butenes [5,6]. In our previous study, we have shown that molybdenum hexacarbonyl encaged in an alkalimetal cation exchanged zeolite undergoes selective hydrogenation of butadiene to cis-2-butene [7,8]. No formation of butane was observed. The selective production of cis-2-butene was specific to molybdenum carbonyls encapsulated in the zeolite, since molybdenum carbonyls anchored on Al_2O_3 or TiO_2 provided equilibrated distribution of butenes together with butane [7,8].

An evolution of CO was noted during the thermal hydrogenation of butadiene over $Mo(CO)_6$ supported on zeolite or Al_2O_3 [7,8]. These findings indicate that subcarbonyl species are catalytically active for the reaction. This was substantiated by an IR study on the thermal decomposition of $Mo(CO)_6$ encaged in zeolite [8,9]. On the basis of an IR study of molybdenum carbonyl-butadiene complexes, which were formed on a contact of $Mo(CO)_6$ or $Mo(CO)_{3\,ads}$ with butadiene, $Mo(CO)_{3\,ads}$ were suggested to be catalytically active for the hydrogenation of butadiene [10].

In the present study, the hydrogenation and isomerization of trans- and cis-1,3-pentadiene and 1,4-pentadiene were carried out over $Mo(CO)_6$ encaged in a NaY zeolite in order to obtain information about the reaction mechanism of the selective hydrogenation of 1,3-dienes. $Mo(CO)_6$ supported on Al_2O_3 was also employed for comparison. IR evidence was presented for the formation of molybdenum carbonyl-pentadiene complexes.

2. Experimental

A NaY zeolite (JRC-Z-Y 4.8) and γ-Al_2O_3 (JRC-ALO-4, 163 m^2 g^{-1}) were supplied by Catalysis Society of Japan as reference catalysts [8]. After an evacuation at 673 K for 1.5 h, NaY or Al_2O_3 (50 mg) was exposed to $Mo(CO)_6$ vapor at room temperature for 1 h. The molybdenum loadings were 8.6 and 1.8 wt% Mo for the NaY and Al_2O_3 systems, respectively. The hydrogenation and isomerization of pentadiene were conducted over the $Mo(CO)_6$/NaY or Al_2O_3 catalyst at 20 kPa (H_2/diene = 2/1) and 423 K by utilizing a closed circulation system (ca. 220 cm^3). The pentadienes employed here were trans- and cis-1,3-pentadienes and 1,4-pentadiene. After the reaction, the catalyst was subsequently evacuated at 523 K for 30 min for the preparation of Mo-metal/NaY catalyst [7–9].

The zeolite powder was pressed into a self supporting wafer for an IR study. 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 for 15–30 s. The IR spectra were measured at room temperature in a transmittance mode on a Hitachi double beam spectrophotometer (EPI-G).

3. Results and discussion

Figure 1 shows the compositional change of the reaction gas for the hydrogenation of trans-1,3-pentadiene (trans-PD) over a freshly prepared $Mo(CO)_6$/NaY catalyst at 423 K as a function of the reaction time. It is evident in fig. 1 that trans-PD is stereo-selectively hydrogenated to cis-2-pentene (96%), accompanying very small amounts of 1-pentene and trans-2-pentene. No production of pentane was detected. The initial product distribution is summarized in table 1. A significantly high selectivity to cis-2-olefin was also observed for the hydrogenation of butadiene [7,8].

The results of the cis-1,3-pentadiene (cis-PD) hydrogenation over $Mo(CO)_6$/NaY are depicted in fig. 1. The primary product was cis-2-pentene as presented in table 1. It is noteworthy in table 1 that the hydrogenation rate of trans-PD is several times higher than that of cis-PD over $Mo(CO)_6$ encaged in NaY, while both reaction rates are almost identical for Mo-metal/NaY catalyst. As shown in table 1, the isomerization of cis-PD to trans-PD was found to proceed at a

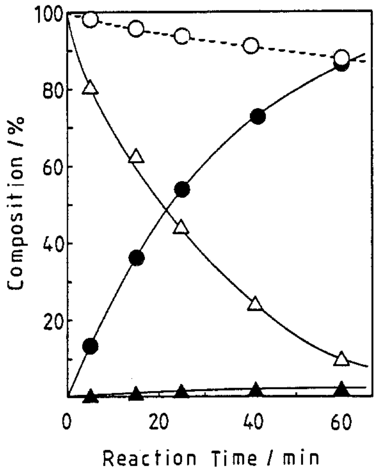


Fig. 1. Hydrogenation of trans-1,3-pentadiene over $Mo(CO)_6$/NaY at 423 K as a function of the reaction time. △: trans-1,3-pentadiene, ●: cis-2-pentene, and ▲: trans-2-pentene. The hydrogenation of cis-1,3-pentadiene is also shown for comparison, but only the consumption of cis-1,3-pentadiene (○) is illustrated for simplicity (see table 1 for the product selectivity).

Table 1

Product distributions in the hydrogenation and isomerization of pentadiene over $Mo(CO)_6$/NaY and $Mo(CO)_6/Al_2O_3$ catalysts at 423 K [a]

Catalyst	Reactant [b]	Hydrogenation [c]					Iso. [c]
		Conversion /%	Product distribution				Conversion /%
			n-p	1-p	t-p	c-p	
$Mo(CO)_6$ /NaY	trans-PD	13.1	0.0	2.2	1.9	95.9	0.0
	cis-PD	2.0	0.0	6.1	0.6	93.3	0.0
	1,4-PD	3.1	0.0	8.5	1.9	89.6	95.1 (140) [d]
	trans-PD [e]	0.0	–	–	–	–	0.0
	cis-PD [e]	0.0	–	–	–	–	0.5
	1,4-PD [e]	0.0	–	–	–	–	93.9 (110) [d]
Mo-metal /NaY	trans-PD	0.7	12.8	13.2	32.3	41.7	0.4
	cis-PD	0.6	3.3	31.1	22.5	43.1	0.9
$Mo(CO)_6$ /Al_2O_3	trans-PD	1.4	4.5	23.6	43.1	28.8	4.1
	cis-PD	0.3	0.0	35.4	29.6	35.0	20.1
	1,4-PD	0.0	–	–	–	–	19.1 (0.27) [d]
Al_2O_3	trans-PD	0.0	–	–	–	–	6.9
	cis-PD	0.0	–	–	–	–	33.1

[a] H_2/PD = 2/1 and total pressure: 20 kPa.

[b] trans-PD: trans-1,3-pentadiene, cis-PD: cis-1,3-pentadiene, 1,4-PD: 1,4-pentadiene.

[c] Conversions at 5 min of the reaction time. n-p: pentane, 1-p: 1-pentene, t-p: trans-2-pentene, c-p: cis-2-pentene. No production of 1,4-PD was observed from the cis- or trans-PD isomerization.

[d] cis-PD/trans-PD ratio.

[e] He was used instead of H_2.

comparable rate to the hydrogenation, indicating a significantly slow direct hydrogenation of cis-PD over Mo(CO)$_6$/NaY.

Wrighton and Schroeder [11] have demonstrated that Cr(CO)$_6$ undergoes photoassisted and selective hydrogenation of 1,3-dienes to produce cis-2-olefins in homogeneous solution systems (benzene or isooctane) at 283 K and that

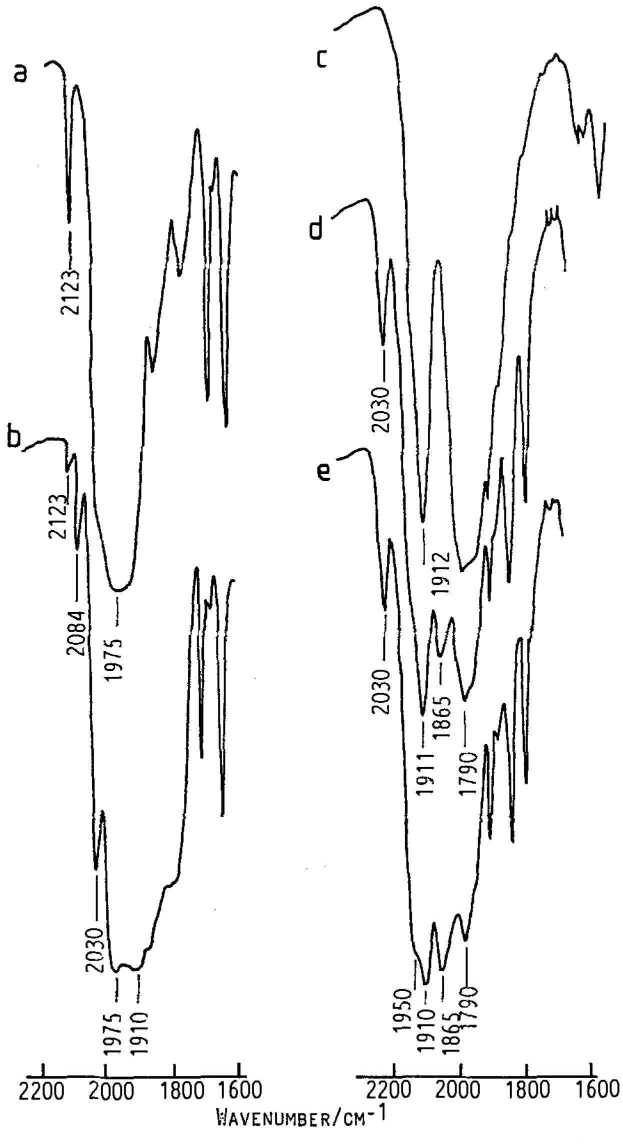


Fig. 2. IR spectra of trans-1,3-pentadiene-molybdenum carbonyl encaged in a NaY. a) Pentadiene (1.6 kPa) was introduced to Mo(CO)$_6$/NaY at room temperature, b) after heating at 373 K for 10 min, c) after evacuating at 373 K for 30 min, d) after a subsequent exposure to pentadiene (1.6 kPa) for 16 h at room temperature, and e) after heating at 373 K for 10 min. All the spectra were recorded at room temperature.

cis-PD is hydrogenated at an initial rate of less than one-tenth that of trans-PD. Besides, $Cr(CO)_6$ system was shown to be thermally active after the photolysis. The present thermally activated $Mo(CO)_6/NaY$ heterogeneous catalyst exhibited similar selectivity and activity sequence, demonstrating that analogous reaction mechanisms are operating in both heterogeneous and homogeneous systems. This suggests that s-cis conformation is required for the hydrogenation of 1,3-dienes over the heterogenized $Mo(CO)_6$ as for the $Cr(CO)_6$ photoassisted hydrogenation [11].

According to Wrighton and coworkers [12,13], however, $Mo(CO)_6$ showed only a rather non-selective hydrogenation of dienes in homogeneous photoassisted systems as a consequence of considerable isomerizations of resulting olefins and dienes. The isomerizations are proposed to be resulted from the photolysis of the diene-metal pentacarbonyl complex [12,13]. Our results may support their proposition. With $Mo(CO)_6$ catalysts for diene hydrogenation, the present thermally activated $Mo(CO)_6/NaY$ is much superior to the photoassisted homogeneous catalyst system in both reaction rate and selectivity.

The non-selective hydrogenation of pentadienes over $Mo(CO)_6/Al_2O_3$ presented in table 1 is partly ascribed to a strong isomerization activity of the bare Al_2O_3 surface. The production of paraffin is characteristic of the Al_2O_3-supported $Mo(CO)_6$ catalyst [7,8]. As suggested by Laniecki and Burwell [14], molybdenum carbonyl-support interaction modes determine the catalytic nature of molybdenum carbonyl species.

We tried to obtain IR spectroscopic evidence for the difference in the interaction mode of cis- and trans-PD with $Mo(CO)_6$ encaged in NaY. Figure 2 shows the IR spectra of the CO stretching region for $Mo(CO)_6/NaY$. The spectrum 2-a

Table 2
IR wavenumbers of molybdenum carbonyl species

Carbonyl species	Wavenumbers	Reference
$Mo(CO)_5$ [a]	2093^{w}, 1972^{w}, 1967^{s}, 1929^{w}, 1926^{s}	15
$Mo(CO)_4$ [a]	2057^{w}, 1949^{m}, 1945^{s}, 1927^{m}, 1887^{s}	15
$Mo(CO)_3$ [a]	1981^{m}, 1866^{m}, 1862^{s}	15
$Mo(CO)_2$ [a]	1915^{m}, 1911^{s}	15
$Mo(CO)_6/Z$ [b]	2123^{w}, 1975^{s}	9
$Mo(CO)_4/Z$ [b]	2047	10
$Mo(CO)_3/Z$ [b]	1911^{s}, 1790^{vs}	9
cis-$Mo(CO)_4(C_8H_{12})$ [c]	2036, 1950, 1930, 1883	16
cis-$Mo(CO)_2(C_4H_6)_2$ [d]	1980, 1938	17
$Mo(CO)_4(C_4H_6)/Z$ [b,d]	2023^{m}, 1930^{s}, 1898^{s}, 1860^{s}	10
$Mo(CO)_2(C_4H_6)_{1 or 2}/Z$ [b,d]	1940^{s}, 1881^{s}	10

[a] At 20 K in a CH_4 matrix.
[b] Encaged in a NaY zeolite.
[c] C_8H_{12}: cyclooctadiene.
[d] C_4H_6: 1,3-butadiene.

was recorded after $Mo(CO)_6/NaY$ was exposed to trans-PD at room temperature. The bands at 2123 and 1975 cm^{-1} are characteristic of $Mo(CO)_6$ anchored on zeolites [9,10]. After a heat treatment at 373 K, new bands appeared at 2084, 2030, and 1910 cm^{-1} (2-b). On the basis of the wavenumber in table 2, the band at 2084 cm^{-1} is assigned to a $Mo(CO)_5(\eta^2\text{-PD})$ complex, since the band was not observed in the absence of pentadiene under similar conditions. On an evacuation at room temperature for 30 min, the band at 2084 cm^{-1} was eliminated, indicating that $Mo(CO)_5(\eta^2\text{-PD})$ is thermolabile.

Thermally stable subcarbonyl species $Mo(CO)_3$ anchored in NaY, which is characterized by the bands at 1912 and 1790 cm^{-1} (2-c) [8,9], was found to react with trans-PD to form a pentadiene complex exhibiting a set of four bands at 2030, 1950, 1910, and 1865 cm^{-1} (2-d). The proportion of the complex increased on heating at 373 K at the expense of $Mo(CO)_3$ species as depicted in fig. 2-e. The molybdenum carbonyl-pentadiene complex is assigned to $Mo(CO)_4(\eta^4\text{-PD})$ on the basis of the number of the bands and their wavenumbers in table 2. The formation of the $Mo(CO)_4$ complex from $Mo(CO)_3$ must induce a partial degradation of $Mo(CO)_3$ species to Mo-metal. The decomposition of molybdenum

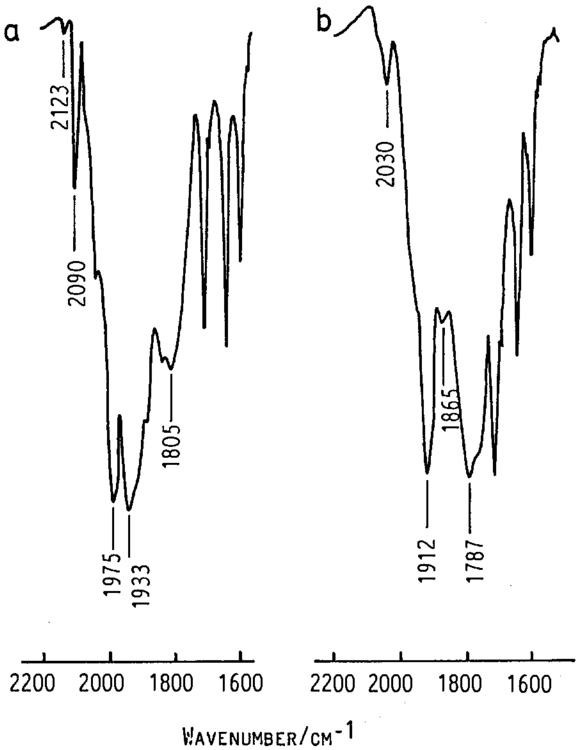


Fig. 3. IR spectra of cis-1,3-pentadiene-molybdenum carbonyl encaged in a NaY. a) After a contact of $Mo(CO)_6/NaY$ with pentadiene (2.1 kPa) at 373 K for 10 min and b) after a contact of $Mo(CO)_3/NaY$ with pentadiene (1.3 kPa) at 373 K for 10 min. Both spectra were measured at room temperature.

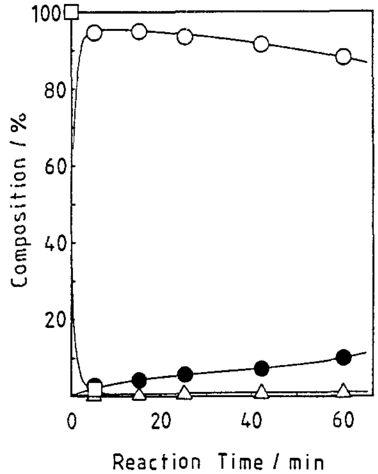


Fig. 4. Hydrogenation of 1,4-pentadiene over $Mo(CO)_6/NaY$ at 423 K as a function of the reaction time. □: 1,4-pentadiene, ○: cis-1,3-pentadiene, △: trans-1,3-pentadiene, and ●: cis-2-pentene.

carbonyls to Mo-metal is considered to be strongly suppressed in the presence of gaseous CO (ca. 1.3 kPa under the present reaction conditions because of a partial decomposition of $Mo(CO)_6$ to subcarbonyl species).

In contrast to trans-PD, cis-PD was found to yield exclusively a $Mo(CO)_5(\eta^2$-PD) complex (2090, 1933, and 1805 cm^{-1}) on a contact with $Mo(CO)_6/NaY$ at 373 K as shown in fig. 3-a. The complex was readily eliminated by an evacuation at room temperature. Besides, it was found that cis-PD did not interact with $Mo(CO)_{3ads}$ species under reaction conditions similar to trans-PD (fig. 3-b). Significantly weak structures observed in fig. 3 are considered to be a consequence of the isomerization of cis-PD to trans-PD, followed by a complex formation. Accordingly, it is concluded that the low activity of $Mo(CO)_6/NaY$ for the cis-PD hydrogenation is resulted from low ability of cis-PD to form a η^4-complex with molybdenum subcarbonyl species and a subsequent cis-π-allyl intermediate because of a steric hindrance for the s-cis conformation.

Figure 4 presents the results of the hydrogenation of 1,4-PD over $Mo(CO)_6/NaY$ at 423 K. It was found that 1,4-PD was rapidly consumed to yield almost exclusively cis-PD (94.4% at the conversion of 98.2%) together with a small amount of the hydrogenation product cis-2-pentene and a trace amount of trans-PD (cis-PD/trans-PD = 140). The highly selective isomerization of 1,4-PD to thermodynamically unfavorable cis-PD was confirmed to occur in the absence of H_2 as depicted in fig. 5 (cis-PD/trans-PD = 110 at the conversion of 94%). Accordingly, it is concluded that no direct hydrogenation of 1,4-PD takes place and that the double bond migration reaction is resulted from an intramolecular 1,3-hydrogen shift. The interaction mode of 1,4-PD and isomerization mechanism

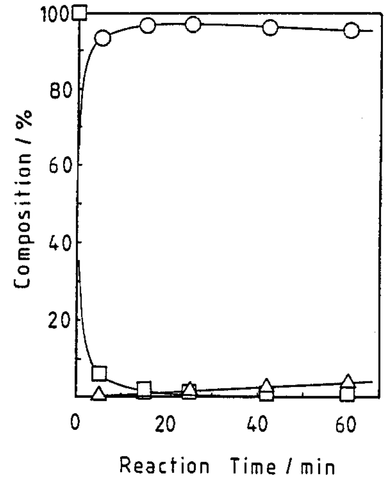
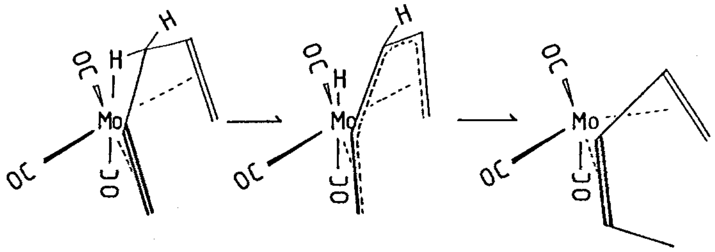


Fig. 5. Isomerization of 1,4-pentadiene over $Mo(CO)_6/NaY$ at 423 K as a function of the reaction time (He was used instead of H_2). □: 1,4-pentadiene, ○: cis-1,3-pentadiene, and △: trans-1,3-pentadiene.



Scheme 1. A proposed reaction mechanism for the selective isomerization of 1,4-pentadiene to cis-1,3-pentadiene.

are proposed in scheme 1, where 1,4-PD is assumed to coordinate to catalytically active $Mo(CO)_3$ forming a Mo-H-C three center-two electron (electron deficient) bond as well as an η^4-interaction. These $\eta^{4:\mathrm{CH}}$ interaction modes are well known for conjugated diene-chromium carbonyl complexes [18].

A non-selective isomerization of 1,4-PD was observed to occur on $Mo(CO)_6/Al_2O_3$. As shown in table 1, thermodynamically favorable trans-PD was obtained as a major product, probably, because of rapid equilibration over the Al_2O_3 surface.

4. Conclusion

It was found that trans-PD was stereo-selectively hydrogenated to cis-2-pentene over $Mo(CO)_6$ anchored in a NaY zeolite. On the basis of the relative rates of cis- and trans-PD and 1,4-PD, it is concluded that s-cis conformation of diene is required for the hydrogenation of dienes. This was substantiated by IR results, showing that trans-PD formed a $Mo(CO)_4(\eta^4\text{-PD})$ complex, while cis-PD yielded only $Mo(CO)_5(\eta^2\text{-PD})$. It was found that 1,4-PD was selectively isomerized to cis-PD on a $Mo(CO)_6$ catalyst encaged in a NaY zeolite. It was demonstrated that $Mo(CO)_6$/NaY was superior to photoassisted $Mo(CO)_6$ catalysts in homogeneous phases for the hydrogenation of pentadienes. In contrast to $Mo(CO)_6$/NaY, $Mo(CO)_6$ anchored on Al_2O_3 showed nonselective hydrogenation and isomerization as a consequence of strong acid base properties of the Al_2O_3 surface and molybdenum carbonyl-support interactions.

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