Highly Selective Hydrogenation of Buta-1,3-diene to *cis*-But-2-ene over Molybdenum Subcarbonyl Species encapsulated in Alkali Metal Cation Exchanged Y-Zeolites

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Molybdenum subcarbonyl species encaged in a zeolite, particularly in LiY, showed a high activity for the selective hydrogenation of buta-1,3-diene to *cis*-but-2-ene (>96%), providing the first example of hydrogenation activity of molybdenum subcarbonyl species immobilized on inorganic matrices.

Hexacarbonylmolybdenum supported on inorganic matrices is a potential precursor of well-dispersed low valent molybdenum catalysts.[1] The catalytically active species consist of Mo subcarbonyls, Mo metal, and partially oxidized species. There have so far been only a few reports of the catalytic properties of molybdenum subcarbonyls stabilized on oxide surfaces. With $Mo(CO)_6/Al_2O_3$ catalysts, Brenner and Burwell[2] demonstrated that a subcarbonyl species, $Mo(CO)_3$, formed at 373 K showed activity for the metathesis of propene at 326 K which was 20—30 times lower than that of the partially oxidized Mo species produced by higher temperature activation. O'Neill and Rooney[3] and Brenner *et al.*[4] made similar observations. There have so far been no further studies of the catalytic properties of molybdenum subcarbonyls immobilized on inorganic materials.

An NaY zeolite (Si/Al 2.78) and its alkali-metal cation exchanged forms (M^+–Y; M^+ = Li, K, and Cs) were employed for the encapsulation of $Mo(CO)_6$. A decationized zeolite (HY), TiO_2 (Degussa, P-25), and γ-Al_2O_3 were also examined. The zeolite was exposed to $Mo(CO)_6$ vapour at room temperature for 12 h after evacuation at 673 K for 1—2 h. The amount of $Mo(CO)_6$ encaged in the zeolite was about two molecules/supercage irrespective of the cation involved. The hydrogenation of buta-1,3-diene was conducted over the molybdenum species at 19.3 ± 0.7 kPa (H_2/butadiene = 2) and 423 K using a closed circulation system (200 cm^3), with 50 mg of the zeolite. Reaction gases were analysed by g.l.c.

The compositional change of the reaction gas is depicted in Figure 1 for the hydrogenation of butadiene over a freshly prepared $Mo(CO)_6$/LiY catalyst as a function of the reaction time. Butadiene is preferentially hydrogenated to *cis*-but-2-ene (>96%) at a significant rate, while the hydrogenation of *cis*-but-2-ene is not promoted at all and a slow isomerization is observed only after the complete consumption of butadiene. Carbon monoxide was evolved by partial decomposition of $Mo(CO)_6$ and its pressure was *ca.* 1.3 kPa during the reaction. This was also observed with the other freshly prepared $Mo(CO)_6$ catalyst systems. It was found that the catalyst could be reused in spite of a gradual activity loss, so long as CO was present during the reaction. When completely decarbonylated at 473 K, the molybdenum catalyst exhibited a significantly reduced activity and a different product distribution. The selectivity was not altered by the presence of CO.

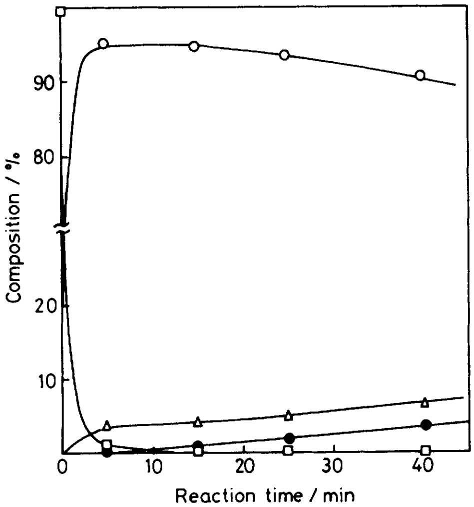

Figure 1. Composition of the reaction gas as a function of time for the hydrogenation of buta-1,3-diene over a $Mo(CO)_6$/LiY zeolite catalyst at 423 K. □, butadiene; ○, *cis*-but-2-ene; △, but-1-ene; ●, *trans*-but-2-ene.

Table 1. Hydrogenation of buta-1,3-diene over $Mo(CO)_6$ encaged in zeolites at 423 K.

		% Conversion	Selectivity/%[c]			
Zeolite[a]	Activation[b]	at 5 min/%	n-b	1-b	*t*-2-b	*c*-2-b
LiY (45)	F	97.2	0.0	3.7	0.3	96.0
	473 K	6.6	5.3	42.2	11.2	41.3
	373 K[d]	6.0[d]	0.0	1.6	0.0	98.4
NaY	F	79.2	0.1	3.2	0.2	96.5
	373 K[d]	2.7[d]	0.0	0.3	0.0	99.7
KY (51)	F	12.9	0.0	3.2	0.3	96.5
CsY (58)	F	7.6	0.0	3.2	0.0	96.8
HY (76)	F	1.7	4.9	13.6	51.8	29.7
	473 K	14.2	10.4	34.1	14.9	40.6
TiO_2 (3.1)[e]	F	4.5	3.2	55.4	12.5	28.9
Al_2O_3 (2.0)[e]	F	3.1	2.1	53.3	12.2	32.4

[a] Number in parentheses: degree of ion exchange. [b] F: non-treatment; $Mo(CO)_6$ was used as prepared. After the reaction, the catalyst was evacuated at 473 K. [c] n-b; n-butane, 1-b; but-1-ene, *t*-2-b and *c*-2-b; *trans*- and *cis*-but-2-ene, respectively. [d] Reaction temperature 273 K and % conversion at 1 h. [e] Loading level of Mo (wt. %).

These catalytic results for the $Mo(CO)_6$/LiY catalyst are summarized in Table 1, together with those for the other $Mo(CO)_6$ catalysts. M^+–Y zeolites show excellent selectivity for formation of *cis*-but-2-ene in the hydrogenation of butadiene. However, the activity decreases in the order LiY > NaY ≫ KY > CsY. On the other hand, the HY zeolite and other non-zeolitic materials showed non-selective hydrogenation properties under the present activation and reaction conditions.

It is well established that Mo subcarbonyl species thermally stable at *ca.* 420 K are reversibly formed in the supercages of M^+–Y[5,6] and HY[7] zeolites during the decomposition of $Mo(CO)_6$. The subcarbonyl species was shown to be $Mo(CO)_3$ on the basis of i.r.,[6] temperature programmed decomposition,[6] and ^{13}CO-isotopic labelling techniques.[8] Mo carbonyls, $Mo(CO)_x$ (x = 6—4), were found to be unstable at the reaction temperature in the zeolite cages.[5—7] On evacuation at 473 K, $Mo(CO)_3$ was irreversibly decomposed to Mo metal for M^+–Y zeolites[5,6] or to partially oxidized Mo species for HY,[7] Al_2O_3,[9] and, probably, TiO_2. Accordingly, it is concluded that molybdenum subcarbonyl species encaged in M^+–Y zeolites are responsible for the highly selective hydrogenation of buta-1,3-diene to *cis*-but-2-ene, whereas Mo metal and partially oxidized Mo species are responsible for the non-selective hydrogenation. The catalytically active subcarbonyl species is considered to be $Mo(CO)_3$, considering the much lower thermal stability of the other carbonyls at the reaction temperature. As shown in Table 1, $Mo(CO)_3$ produced in LiY or NaY by evacuation at 373 K shows highly selective hydrogenation activity at 273 K and further decarbonylation did not occur during the reaction. The hydrogenation is considered to proceed *via* a $Mo(CO)_3$(butadiene) complex, on the basis of i.r. evidence.

Extremely high activities for the hydrogenation of propene reported by Brenner[10] over $Mo(CO)_6/Al_2O_3$ catalysts at 423—473 K in a flow reaction system should be ascribed to highly dispersed Mo metal and/or partially oxidized Mo species, since the subcarbonyls show no alkene hydrogenation actvities as deduced from Table 1. This was confirmed by separate experiments.

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