CHEMISTRY LETTERS, pp. 241-244, 1988.

Thermal Stabilities and Catalytic Activities of Molybdenum Carbonyls Encapsulated in Zeolites

Akinori MAEZAWA, Hiroshige KANE, Yasuaki OKAMOTO,* and Toshinobu IMANAKA

Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

The thermal stabilities of $Mo(CO)_6$ and subcarbonyl species encaged in a zeolite were found to depend markedly on the Si/Al ratio and cation involved. A highly selective formation of cis-2-butene was observed for the hydrogenation of butadiene over the subcarbonyl species. These thermal and catalytic properties of the carbonyls are correlated to the basicity of the zeolite.

Transition-metal complexes supported on inorganic matrices have been used for the preparation of well-defined catalysts.[1)] In particular, zeolites are expected to provide potential media for producing well-defined catalytically active species because of their well-characterized structures. Low-valent molybdenum species prepared from $Mo(CO)_6$ encapsulated in zeolites[2,3)] are included in such systems. Some catalytic properties of the molybdenum species in decationized zeolites (HY) have recently been reported by Yashima et al.[4)] In their systems, $Mo(CO)_6$ was completely decarbonylated.

The preparation of molybdenum catalysts involves thermal decomposition of $Mo(CO)_6$ to subcarbonyl species and subsequent degradation to Mo metal aggregates[2,5)] or to oxidized Mo species.[4,5)] However, no detailed behaviors of the thermal decomposition of $Mo(CO)_6$ and subcarbonyl species encaged in zeolites have been reported yet in spite of the importance in tailoring catalysts. In addition, the catalytic properties of the molybdenum subcarbonyl species immobilized on inorganic matrices rarely have been explored up to now.[6)] In the present study, the thermal stabilities of $Mo(CO)_6$ and subcarbonyl species in a variety of zeolites were systematically investigated using temperature programmed decomposition (TPDE) and XPS techniques. The hydrogenation of butadiene was carried out to show remarkable catalytic features of a thermally stable subcarbonyl species.

NaY zeolite (Si/Al = 2.78) was supplied by Catalysis Society of Japan as a reference catalyst. Commercial zeolites, SK-40 (NaY, Si/Al = 2.43) and NaX (Si/Al = 1.23), were also employed here. The NaY and NaX zeolites were ion-exchanged with a series of alkali-metal cations to produce MY (X) zeolites (M; Li, Na, K, or Cs). The degree of ion-exchange is summarized in Table 1. The XP spectra of the zeolites were measured on a Hitachi 507 photoelectron spectrometer (an Al anode).

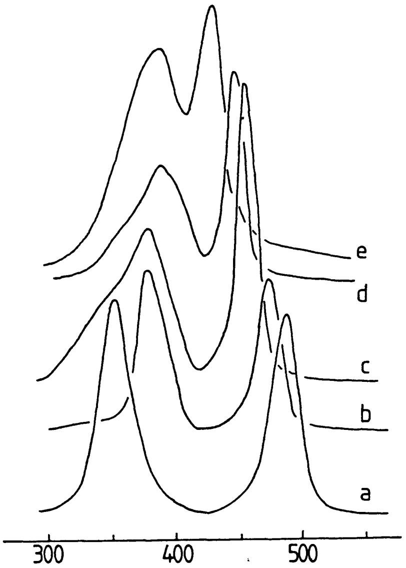

Fig.1. TPDE profiles of CO (m/e=28) for $Mo(CO)_6$ encaged in the Y-zeolites. a) CsY, b) KY, c) NaY, d) LiY, and e) HY.

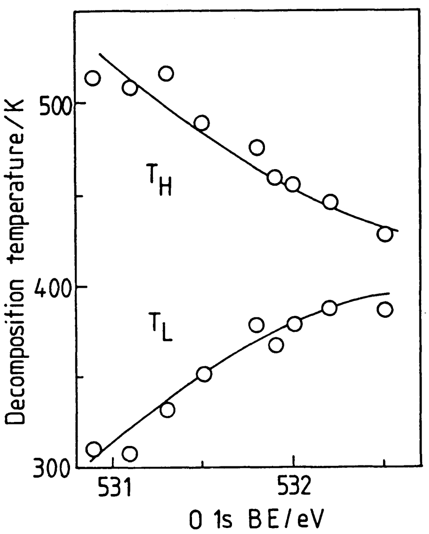

Fig.2. Dependencies of the decomposition temperatures T_L and T_H upon the O 1s binding energy.

The binding energies (BE) were referenced to the C 1s band at 285.0 eV due to adventitious carbon. The O 1s BEs for the zeolites are shown in Table 1.

After an evacuation at 673 K for 1-2 h, the powdered zeolites (0.1 g) were exposed to $Mo(CO)_6$ vapor (ca.20 Pa) at room temperature for 12 h. The TPDE study of $Mo(CO)_6$ encaged in the zeolite was conducted in a dynamic vacuum and evolving gases were analyzed by a mass filter. The temperature was raised at a rate of 1.85 K min^{-1} from room temperature to ca. 600 K. In the present zeolite systems,

Table 1. TPDE and XPS Results on $Mo(CO)_6$ Encaged in a Zeolite

Zeolite	Degree of ion exchange$^{a)}$/%	O1s BE /eV	$Mo(CO)_6$/ Supercage	Decomp.temp/K		Peak intensity ratio; T_L/T_H
				T_L	T_H	
HY	76	532.5	1.9	386	427	1.23
LiY	45	532.2	2.1	387	445	1.48
NaY		532.0	2.0	378	454	1.37
SK-40		531.9	1.3	366	459	1.27
KY	51	531.8	1.8	378	475	1.29
CsY	58	531.5	1.5	351	489	1.25
NaX		531.1	0.4	308	508	1.00
KX	68	531.3	0.4	331	516	1.39
CsX	50	530.9	0.4	310	513	0.86

a) Obtained from the XPS intensity of the Na KLL Auger band.

CO (m/e =28 or 12) was a predominating species, accompanied by a small amount of H_2 (m/e = 2). The amount of $Mo(CO)_6$ adsorbed on the zeolite was chemically analyzed after the TPDE experiments. The hydrogenation of 1,3-butadiene was carried out over molybdenum species at 19.3 ± 0.7 kPa (H_2/butadiene = 2) and 273 K using a closed circulation system. The reaction gas was analyzed by GLC.

Figure 1 shows the TPDE profiles of CO for $Mo(CO)_6$ encaged in the Y-zeolites. It is apparent that the CO profile consists of two distinct peaks, indicating the formation of definite intermediate subcarbonyl species at > ca. 370 K in vacuo during the decomposition of $Mo(CO)_6$ to Mo metal or to oxidized species (HY). The existence of the thermally stable subcarbonyl species has been reported for HY[3)] and NaY[2)] zeolites by IR studies. The intensity ratio of the peaks at lower (T_L) and higher (T_H) decomposition temperatures is summarized in Table 1. It seems that the ratio is not varied very much with the zeolite. Assuming that all the amount of CO detected here corresponds to the composition of $Mo(CO)_6$, the average ratio in Table 1 suggests the composition of the subcarbonyl species to be $Mo(CO)_{2.6-2.7}$, which is close to $Mo(CO)_3$. Accordingly, it seems that the subcarbonyl species thermally stable at ca. 420 K in vacuo is $Mo(CO)_3$ rather than $Mo(CO)_4$ which has been claimed by Gallezot et al.[3)] and Yon-Sing et al.[2)] for HY and NaY zeolites, respectively.

The decomposition temperatures T_L and T_H are shown in Table 1. It is revealed that T_L and T_H depend both on the cation involved in the zeolite and on the Si/Al ratio. T_L decreases and, on the contrary, T_H increases with decreasing the Si/Al ratio and the electronegativity of the cation. Figure 2 depicts T_L and T_H as a function of the O 1s BE of the zeolite. It is clearly demonstrated that the effects of the cation and composition of the zeolite on T_L and T_H are delineated by the O 1s BE of zeolite. At a higher BE, T_L and T_H seem to merge into the thermal decomposition temperature (420 K)[7)] of $Mo(CO)_6$ in a gas phase. It is considered that the O 1s BE is correlated to the basic strength of the framework oxygen (O^{2-}); a decrease in the BE indicates an increase in the basic strength.

Table 2. Hydrogenation of Butadiene at 273 K over Molybdenum Species Encaged in a Zeolite

Zeolite	Subcarbonyl[a)]					Metal[b)]				
	TOF[c)]	Selectivity[d)]/%				TOF[c)]	Selectivity[d)]/%			
	h^{-1}	b	1-b	t-2-b	c-2-b	h^{-1}	b	1-b	t-2-b	c-2-b
LiY	0.55	0	1.6	0	98.4	2.12	10.5	72.1	9.9	7.5
NaY	0.25	0	0.3	0	99.7	1.88	5.3	74.2	14.7	5.8
CsY	0.09	0	0	0	100	<0.01				
HY	0.06	2.4	23.9	10.4	63.3	0.58	10.6	53.6	9.8	26.0

a) Prepared by an evacuation at 373 K for 30 min.
b) Prepared by an evacuation at 473 K for 30 min.
c) Turnover frequency measured at the reaction time of 1 h.
d) b;butane, 1-b;1-butene, t-2-b;trans-2-butene, and c-2-b;cis-2-butene.

Therefore, it is concluded that the partial decomposition of $Mo(CO)_6$ to the subcarbonyl species is accelerated by the basic nature of the framework oxygen, whereas the thermal stability of the subcarbonyl species is enhanced also by the basic sites. It is speculated that $OC{-}{-}O^{2-}$ interactions cause the decompositions of $Mo(CO)_x$ species ($x = 6$, 5, and probably 4). On the contrary, the subcarbonyl species, perhaps $Mo(CO)_3$, is stabilized by the framework oxygen through $Mo \leftarrow O^{2-}$ coordinative bondings.

The activity and selectivity of the molybdenum subcarbonyl species encaged in the zeolite are summarized in Table 2 for the hydrogenation of butadiene at 273 K as well as those of Mo metal (partially oxidized for the HY zeolite as evidenced by XPS). The subcarbonyl species and Mo metal species were prepared by the evacuation at 373 and 473 K, respectively, for 30 min. The formations of the subcarbonyl species were confirmed by IR techniques in separate experiments. No further evolution of CO was detected during the hydrogenation. A selective formation (>98%) of cis-2-butene was found over the subcarbonyl species in the Li, Na, and CsY zeolites. No productions of trans-2-butene and butane were detected. The product distributions were not altered with the reaction time. The diversified products for the subcarbonyl species in the HY zeolite are probably due to a sequential isomerization of the primary product. The formation of butane suggests the presence of Mo metal or partially oxidized species. The products of the butadiene hydrogenation over Mo metal are completely different from those over the subcarbonyl species, substantiating that cis-2-butene is selectively formed over the subcarbonyl species.

The catalytic activity of the subcarbonyl species decreases in a order of LiY > NaY >CsY. This is inversely correlated to the order of the thermal stability of the subcarbonyl species or the strength of the interactions between the subcarbonyl species and zeolite framework oxygens. However, it is not ruled out that the size effects of cation control the apparent rate of the catalytic reaction. The low activity of the HY zeolite may be ascribed to the acidic sites in the zeolite.

Therefore, it is concluded that the thermal stability and catalytic properties of the molybdenum subcarbonyl species are regulated by the cation and composion of the zeolite. This provides a promising clue to the preparation of well-defined molybdenum catalysts.

References

1) E.g. D.C.Bailey and S.H.Langer, Chem. Rev., 81, 109 (1981).
2) Y.Yon-Sing and R.F.Howe, J. Chem. Soc., Faraday Trans. 1, 82, 2887 (1986).
3) P.Gallezot, G.Coudurier, M.Primet, and B.Imelik, "Molecular Sieves II," ed by J.R.Katzer, ACS Symp. Ser. (1977), Vol.40, p.144.
4) T.Yashima, T.Komatsu, and S.Namba, Chem. Express, 1, 701 (1986) and references therein.
5) T.Komatsu, S.Namba, T.Yashima, K.Domen, and T.Onishi, J. Mol. Catal., 33, 345 (1985).
6) A.Brenner and K.L.Burwell, J. Catal., 52, 364 (1978).
7) E.M.Fednova and J.V.Krykova, Russ. J. Inorg. Chem., 11, 141 (1966).

(Received October 28, 1987)