Thermal Stabilities of Hexacarbonyl and Subcarbonyls of Molybdenum encapsulated in NaY and NaX Zeolites

Yasuaki Okamoto,* Akinori Maezawa, Hiroshige Kane, Isao Mitsushima and Toshinobu Imanaka

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

Decompositions of $Mo(CO)_6$ and the resulting subcarbonyl species adsorbed on NaY and NaX zeolites have been investigated utilizing i.r., temperature-programmed decomposition and X.p.s. techniques. It was found that $Mo(CO)_6$ encapsulated in the NaX zeolite was considerably less stable than that contained in the NaY zeolite, while intermediate subcarbonyl species, $Mo(CO)_{3ads}$, showed a completely reversed thermal stability. The drastic difference in the stabilizing properties between X and Y zeolites is thought to result from the difference in the basic strength of the zeolite framework oxygen. The structure of $Mo(CO)_{3ads}$ is proposed on the basis of i.r. spectra. The X.p.s. results suggest that the adsorbed $Mo(CO)_a$ species is decomposed to Mo-metal aggregates at 473 K.

Transition-metal carbonyls supported on organic or inorganic matrices show prominent catalytic properties. Various types of interaction modes between metal carbonyls and (surface) functional groups have been proposed and recently reviewed.^{1,2} Among inorganic materials having high specific surface areas, zeolites provide potential media for producing well defined catalytically active metal species, because of their well characterized structures.³ Low-valent molybdenum catalysts prepared from Mo(CO)₆ encapsulated in zeolites are examples of such systems. Interesting catalytic features of Mo(CO)₆ supported on decationized Y zeolites (HY) have been reported by Yashima *et al.*⁴ for polymerization and hydrogenation of ethylene and metathesis of propylene. Their results suggest great potential for a precise control of catalytic reactions by employing zeolites as supporting matrices.

Infrared studies of adsorption and decomposition of $Mo(CO)_6$ on NaY and HY zeolites have been conducted by Gallezot *et al.*⁵ and Howe *et al.*^{6,7} to elucidate interaction modes between the carbonyls and the zeolites and to reveal intermediate subcarbonyl species. With NaY zeolite, it is suggested that $Mo(CO)_6$ is thermally decomposed to molybdenum metal^{6,7} in contrast to $Mo(CO)_6$ encaged in HY zeolite, ⁴⁻⁶ where Mo is shown to be oxidized by the reaction with surface hydroxyl groups in the zeolite. The subcarbonyl species $Mo(CO)_{4ads}$ has been suggested to be thermally stable in HY⁵ and NaY⁷ zeolites. On the other hand, $Mo(CO)_{3ads}$ has been proposed as a stable intermediate subcarbonyl species on $A1_2O_3^{8-10}$ and $ZnO.^{11}$ The difference in the stable subcarbonyl species between these matrices seems to be important to the understanding of the chemistry of anchoring metal carbonyls. Thermal properties of metal carbonyls adsorbed on supporting materials provide fundamental knowledge about the interaction modes between the carbonyls and the surface functional groups and about the optimization of catalyst preparation.

In the present study, decompositions of $Mo(CO)_6$ and the resulting subcarbonyls encapsulated in sodium-type zeolites were investigated by utilizing i.r., temperature-

Thermal Stabilities of Molybdenum Carbonyl Compounds in Zeolites

programmed decomposition, and X.p.s. as a function of zeolite compositional Si/Al ratio (NaY and NaX). It was found that decomposition temperatures of the carbonyl species depended strongly on the zeolite composition.

Experimental

Two kinds of NaY zeolites of different composition (Si/A1 = 2.43: SK-40, Nikka Seiko Co. and Si/A1 = 2.78: JRC-Z-Y5.6, Catalysis Society of Japan¹²) and an NaX zeolite (Si/A1 = 1.23: 13X, Gasukuro Kogyo Co.) were utilized in the present study. Hexacarbonylmolybdenum was supplied by Strem Chemicals and was used as received.

Powdered zeolites were pressed into self-supporting wafers (thickness, ca. 10 mg cm⁻²) for i.r. studies. The samples were pretreated in a vacuum ($< 1 \times 10^{-3}$ Pa) at 673 K for 1-2 h in an in situ i.r. cell. After having recorded a background spectrum, the zeolite wafers were exposed to $Mo(CO)_6$ vapour (ca. 8 Pa¹³) at room temperature (ca. 295 K) for a selected period. The i.r. spectra were recorded at room temperature in the transmittance mode on a Hitachi double beam spectrophotometer (EPI-G). The resolution was 2.5 cm^{-1} at 3000 cm^{-1} .

In t.p.d. (temperature-programmed decomposition) studies of $Mo(CO)_6$ encaged in zeolites, zeolite samples were used in powder form. After having been evacuated at 673 K for 1-2 h, the zeolites were exposed to Mo(CO)₆ vapour at room temperature for 12 h. The decomposition of Mo(CO)₆ adsorbed on the zeolites was conducted in a dynamic vacuum and the evolved gases were continuously and repeatedly analysed by a mass filter (ULVAC, MSQ-150A) over a mass range of m/z = 1-51 (1 cycle; 130 s). The decomposition temperature was increased at a rate of 1.8 K min⁻¹ from room temperature to ca. 600 K. In the present zeolite systems CO (m/z = 12 and 28) was the only major desorption product, accompanying a negligible amount of H_2 (m/z = 2). No formation of CH_4 (m/z = 15) and CO_2 (m/z = 44) was detected during the decomposition of Mo(CO)₆-NaY or -NaX under vacuum.

The X.p. (X-ray photoelectron) spectra of the zeolites were measured at room temperature on a Hitachi 507 photoelectron spectrometer using an A1- K_{r} radiation (1486.6 eV; 9 kV, 50 mA). The zeolite samples were mounted on double-sided adhesive tape and were evacuated at room temperature in a pretreatment chamber ($< 1 \times 10^{-3}$ Pa) prior to the X.p.s. measurements. The binding energies were referenced to the C 1s band at 285.0 eV due to adventitious carbon. Mo(CO)₆-NaY samples that were prepared and activated at elevated temperatures in a conventional vacuum line were transferred to the pretreatment chamber by using a nitrogen-filled glove box. In these samples, the binding energy of the Si 2p level from the NaY zeolite predetermined above was utilized for establishing the charging correction.

Results and Discussion

The i.r. spectra of Mo(CO)₆ adsorbed on NaY₁ (JRC-Z-Y5.6) are depicted in fig. 1. It is evident that on room-temperature adsorption, the structure of $Mo(CO)_6$ is retained almost intact with some distortions in the symmetry of the molecule. The lowering of the molecular symmetry is evidenced by the appearance of the normally infrared-inactive v_1 bands around 2120 cm⁻¹ [fig. 1 (b)]. The wavenumbers of the fundamental vibrations of Mo(CO)₆ encapsulated in the NaY and NaX zeolites were calculated from the various combination bands at 2500-1900 cm⁻¹. They are summarized in table 1 and compared with the literature values¹⁴⁻¹⁶ for Mo(CO)₆ in various phases. Our results are in excellent agreement with those calculated from the data reported by Yon-Sing and Howe⁷ except for the additional v, band at 2117 ± 2 cm⁻¹ in the present study. The fundamental frequencies of Mo(CO)₆ encaged in the NaY seem to be rather close to those for vapour

View Article Online

Y. Okamato et al.



Fig. 1. Infrared spectra of adsorption and decomposition of $Mo(CO)_6$ on NaY (JRC-Z-Y5.6) zeolite: (a) background (evacuated at 673 K for 1 h); (b) exposed to $Mo(CO)_6$ vapour for 1 min, followed by evacuation for 10 min at room temperature; (c) evacuated at 373 K for 20 min; (d) evacuated at 423 K for 20 min.

or for solutions, implying weak adsorptive interaction of $Mo(CO)_6$ in the zeolite supercage.

Concerning the doubled v_1 band in fig. 1(b), equivalent pair peaks were also observed for NaY₂ (SK-40). The spectral intensities of these two v_1 bands were found to grow simultaneously with increasing adsorption of the carbonyl up to saturation. However, the 2117 cm⁻¹ band seemed to be removed more easily on evacuation of the sample at room temperature than the band at 2123 ± 2 cm⁻¹, resulting in the formation of subcarbonyl species (*e.g.* 1808 cm⁻¹). Accordingly, the double peak may suggest the existence of two kinds of Mo(CO)₆ with slightly different configurations as a result of different interaction modes with the zeolite framework. A similar double v_1 peak has also been noted for Mo(CO)₆ dissolved in CHCl₃¹⁵ as quoted in table 2. This was reconfirmed in the present study.

On evacuation of the sample at room temperature, three new bands appeared at 1835, 1808 and 1790 cm⁻¹ as shown in fig. 1(*b*) and gradually grew with increasing evacuation time, accompanied by a colour change from white to light yellow. The yellow colour may indicate the formation of $Mo(CO)_5$ species. These observations show a gradual decomposition of $Mo(CO)_6$ to produce subcarbonyls.

The i.r. spectrum changed drastically on evacuation of the sample at 373 K, showing the formation of a new fairly stable subcarbonyl species [fig. 1(c)]. Some of this species remained anchored even at 423 K [fig. 1(d)] and disappeared completely on further evacuation at 473 K. This subcarbonyl species is characterized by major absorption bands at 1915, 1796 and 1768 cm⁻¹. These spectral features for the NaY zeolite are quite consistent with the results reported by Howe and coworkers.^{6, 7}

854 Thermal Stabilities of Molybdenum Carbonyl Compounds in Zeolites

Table 1.	Fundamental	frequencies	of	Mo(CO)	encaged in	NaY	and NaX	zeolites
----------	-------------	-------------	----	--------	------------	-----	---------	----------

				NaY					
annroximate	normal ^a	spectrala	this				solu	tions	
mode	normai	activity	work	Howeb	NaX	vapour	$\mathrm{CHCl}_{3}{}^{d}$	$\mathrm{CH}_{2}\mathrm{Cl}_{2}{}^{a}$	solid ^a
v ₁	v(CO)	R ^e	2123	2127 - 2123	2123	2124	2115	2117	2112
	<u> </u>		2117				2110		
v_2	v(MC)	R	415	418	_	392			401
v_3	v(CO)	R	2016	2014		2027	2021	2019	2003
v_4	v(MC)	R			_	344		394	389
v_5	δ (MCO)	IA			_	481		<u> </u>	555
v ₆	v(CO)	i.r.	1973	1975	1955	2004	1983		1990
v_7	δ (MCO)	i.r.				593			593
v_8	v(MC)	i.r.	357	357		368			370
v	$\delta(CMC)$	i.r.	81	84		81			
v_{10}	$\delta(MCO)$	R				506		448	468
v ₁₁	$\delta(CMC)$	R	110	109		81		91	100
v_{12}	δ (MCO)	IA				512			478
v ₁₃	δ(CMC)	IA				62			

^a Ref. (14). ^b Calculated from the data of ref. (7). ^c Ref. (16). ^d Ref. (15). ^e R: Raman; i.r.: infrared; IA: inactive.

	-		
zeolite	carbonyl species	i.r. bands ^{<i>a</i>} observed/cm ⁻¹	assignments
NaY	Mo(CO) ₆	2123 _w , 2117 _w , 2048 _{sh} 1970	Mo(CO) ₆
	I	1810	$Mo_{o}(CO)_{10}$
	II	2046, 1953, 1835	Mo(CO) _{5ads}
	III	2020, 1918, 1789	Mo(CO) _{4ads}
	IV	1955 _{sh} , 1925 _{sh} , 1913 _s	Mo(CO) _{3ads}
		$1810_{w,sh}^{sh}$, 1793 _s , 1765 _{sh}	
NaX	Mo(CO),	2123, 1955,	Mo(CO) ₆
	ÌI′ ́°	2047, 1828	Mo(CO)
	$\mathbf{III'}$	1910, 1782	Mo(CO) _{Ands}
	IV′	1916 _s , 1896 _s 1763 _{vs}	Mo(CO) _{3ads}

 Table 2. CO stretching frequencies of molybdenum carbonyls encaged in NaY and NaX zeolites

^a Only resolved bands are shown here: vs: very strong; s: strong; w: weak; and sh: shoulder peak.

In the present study, more detailed decomposition steps were investigated by increasing stepwise the evacuation temperature up to 370 K. Fig. 2 depicts such i.r. spectra for NaY₂ zeolite. NaY₁ showed essentially the identical characteristics. However, it was recognized that NaY₂ decomposed Mo(CO)₆ more readily at room temperature than NaY₁, resulting in stronger bands at 1835, 1810 and 1788 cm⁻¹ in a similar treatment sequence [fig. 1(b) vs. 2(a)]. After a prolonged evacuation at room temperature, the 1789 cm⁻¹ band became the most intensified [fig. 2(b)]. At slightly elevated temperatures (313–318 K), several new bands appeared as shown in fig. 2(c) together

Y. Okamato et al.

with the intensified band around 1790 cm⁻¹. On further evacuation at 317–331 K [fig. 2(*d*) and (*e*)], the 2123 cm⁻¹ band due to $Mo(CO)_6$ was completely removed and the 2045 and 1953 cm⁻¹ signals were reduced in intensity. However, the absorption bands at 2020 and 1918 cm⁻¹ showed maximum intensity at 317–320 K [fig. 2(*d*)]. At temperatures higher than 333 K [fig. 2(*f*)] the stable carbonyl species was observed as in the case of NaY₁ zeolite [fig. 1(*c*)], which remained intact even after a prolonged evacuation at 383 K [fig. 1(*g*)]. These decomposition steps were completely reversible with regard to evacuation and CO introduction. Treatment at 423 K *in vacuo* reduced appreciably the whole spectral intensity [fig. 2(*h*)], whereas thermal treatment at 450 K almost eliminated the carbonyl bands. The intensities of the bands at 1913 and 1925 cm⁻¹ were reversed at 423 K. A similar observation was made with NaY₁ [fig. 1(*c*) *vs.* 1(*d*)]. These findings imply that a few stabilized subcarbonyl species with slightly different configurations exist as a consequence of different adsorption sites in the supercage (*e.g.* S_{II} and S_{III}).

It is apparent from the i.r. studies that $Mo(CO)_6$ encaged in the NaY zeolite is decomposed to the stable subcarbonyl species through several intermediate subcarbonyls. On the basis of the spectral changes, subcarbonyl species I–IV are tentatively proposed and summarized in table 2. It seems that $Mo(CO)_6$ is thermally decomposed stepwise from I and/or II through IV. Comparing NaY₁ and NaY₂ zeolites, it is revealed that the thermal stabilities of $Mo(CO)_6$ and intermediate subcarbonyl species (I–III) are greater in NaY₁ (Si/Al = 2.78) than in NaY₂ (Si/Al = 2.43), while the stability of species IV is entirely reversed in these NaY zeolites.

The oxidation state of molybdenum species in the NaY zeolite was examined utilizing X.p.s. Fig. 3 shows the X.p. spectra of the Mo 3*d* level for the Mo(CO)₆-NaY₁ evacuated at elevated temperatures (A) and subsequently exposed to air at room temperature for controlled periods (B). The binding energies of the Mo 3*d* levels are summarized in table 3 and compared with those for several molybdenum compounds relevant to this system.^{17, 18} The Mo $3d_{5/2}$ energies for the Mo(CO)₆-NaY₁ activated at various conditions are very close to those for molybdenum metal and molybdenum carbonyl complexes within the accuracy of the X.p.s. measurements (±0.2 eV). Slightly broadened Mo 3*d* spectra observed at high evacuation temperatures (> 470 K) are ascribable to the molybdenum species oxidized to some extent during heat treatment perhaps by adsorbed (residual) water. Accordingly, it is concluded that molybdenum is retained essentially in a zero-valent state during the thermal treatments of Mo(CO)₆ encaged in the NaY zeolites with formation of zero-valent subcarbonyl species at 370 K and final decomposition to molydenum metal (> 470 K).

With the molybdenum/NaY zeolites, the reactivity of molybdenum species to air was examined by X.p.s. As depicted in fig. 3(e), the molybdenum species (subcarbonyl IV in table 2) produced by evacuation at 373 K was completely oxidized to an Mo⁶⁺ species, when exposed to air at room temperature for 50 s. This was also inferred by the instantaneous colour change from brown to white observed. On the other hand, the X.p. spectra for the Mo species activated at > 473 K were slightly broadened by relatively short oxidation treatments (50 or 130 s) at room temperature, suggesting that only a small part of metallic species is oxidized to higher-valent species. A prolonged exposure to air produced high oxidation states of molybdenum; Mo⁴⁺ and Mo⁶⁺ as deduced from the X.p.s. binding energies. These findings indicate that molybdenum metal aggregates are formed rather than atomically dispersed metal particles, even at 470 K. The aggregation of Mo metal is suggested to occur at 673 K from the pore volume measurements of Mo(CO)₆-NaY.⁷

Fig. 4 depicts the i.r. spectra of $Mo(CO)_6$ encapsulated in the NaX zeolite following progressive evacuation at ambient and elevated temperatures. In sharp contrast to the NaY zeolites, the NaX zeolite is shown to decompose $Mo(CO)_6$ drastically even at room temperature, producing stepwise several subcarbonyl species. Upon mere contact of



Fig. 2. Infrared spectra of the decomposition of Mo(CO)₆ adsorbed on NaY (SK-40) zeolite preevacuated at 673 K for 1 h: (a) exposed to Mo(CO)₆ vapour for 30 s, followed by a 10-min evacuation at 293 K; (b) additional evacuation for 60 min at 295 K; (c) evacuated at 313–318 K for 10 min; (d) at 317–320 K for 10 min; (e) at 322–331 K for 10 min; (f) at 333–341 K for 20 min; (g) at 383 K for 6.5 h; (h) at 415–423 K for 10 min, successively.



Fig. 3. X-Ray photoelectron spectra of $Mo(CO)_6$ -NaY (JRC-Z-Y5.6) zeolite: (A) (a) $Mo(CO)_6$ adsorbed on NaY at room temperature: (b) evacuated at 373 K for 20 min: (c) evacuated at

adsorbed on NaY at room temperature; (b) evacuated at 373 K for 20 min; (c) evacuated at 473 K for 20 min, and (d) evacuated up to 633 K in a temperature-programmed decomposition experiment at a rate of 1.8 K min⁻¹: (B) (e) exposure of sample (b) to air for 50 s at room temperature; (f) exposure of sample (c) to air for 50 s; (g) subsequent exposure of sample (f) to air for 24 h; (h) exposure of sample (d) to air for 130 s.

 $Mo(CO)_6$ with the NaX, the i.r. spectrum appeared to be quite different from that for $Mo(CO)_6$ adsorbed on the NaY [fig. 4(b)]. The sample turned orange in colour. The bands due to subcarbonyls prevailed over the signals attributable to $Mo(CO)_6$ (v_1 2123 and v_6 1955 cm⁻¹ in table 1). With increasing evacuation time [fig. 4(c)], the bands at 1782 cm⁻¹ increased in intensity, while the signal intensities at 1828, 1910 and 2047 cm⁻¹ decreased simultaneously, perhaps after a slight initial enhancement. The appearance of a shoulder peak at 1763 cm⁻¹ on prolonged evacuation [100 min; fig. 4(e)] may explain the somewhat complicated behaviour of the bands around 1910 cm⁻¹, since the 1763 cm⁻¹ band accompanies two strong bands at 1916 and 1896 cm⁻¹, as shown in fig. 4(f). No band due to subcarbonyl I (1810 cm⁻¹) in the NaY zeolites was detected with the NaX zeolite.

On evacuation of the sample at elevated temperatures, stable subcarbonyl species, characterized by three bands, was formed [fig. 4(f)] and retained even at 473 K in spite of a slight decrease in the relative intensity of 1896 cm⁻¹ band [fig. 4(g)], as observed with the corresponding absorption bands for the NaY zeolites [(fig. 1(d) and 2(h)]. The carbonyl bands vanished at 573 K. Introduction of CO (3.3×10^3 Pa) at room temperature into the subcarbonyl-NaX system activated at 473 K readily restored the original spectrum. However, after the sample had been treated at 573 K under vacuum, no carbonyl absorption bands were restored on exposure of the sample to CO

<u> </u>	binding ene		
temperature/K	Mo 3 <i>d</i> _{5/2} Mo 3 <i>d</i> ₅		ref.
<i>ca.</i> 290	228.5	231.8	this work
373	228.6	231.6	
	233.0%	235.6 ^b	
473	228.2	231.2	
	228.4	231.1°	
	229.9, 232.6°		
633	228.4	231.0	
	228.4^{d}	231.0 ^d	
MoO ₃	233.1		17"
Mo ^v	231.9		
MoO ₂	229.9		
Mo metal	228.4		18 ^f
$[(\eta^{5}-C_{5}H_{5})Mo(CO)_{3}]_{2}$	227.8		
$Mo(\eta^{5}-C_{5}H_{5})(CO)_{3}Cl$	229.2		
$(CH_3)_3SnMo(CO)_3(\eta^5-C_5H_5)$	228.9		
$Cl(CH_3)_2SnMo(CO)_3(\eta^5-C_5H_5)$	228.4		

858 Thermal Stabilities of Molybdenum Carbonyl Compounds in Zeolites

Table 3. X-Ray	photoelectron	spectroscopy	data for	Mo(CO) ₆ –NaY	zeolite	treated	at elevated
	temperat	ures in vacuo a	and for 1	reference compo	unds		

^a Referenced to the Si 2p level at 102.5 eV. ^b Exposed to air at room temperature for 50 s. ^c For 24 h. ^d For 135 s. ^e Referenced to C 1s = 285.0 eV. ^f The binding energies are shifted by + 1.4 eV to adjust the Mo 3d binding energy for MoO₃ to that of ref. (17).

 $(3.5 \times 10^3 \text{ Pa})$ at room temperature. These findings indicate that the decomposition of $Mo(CO)_6$ to the subcarbonyl species is reversible in the NaX zeolite, while the subcarbonyl species are irreversibly decomposed to molybdenum metal. Similar observations were made for the NaY zeolites.

The i.r. bands observed during the decomposition of $Mo(CO)_6$ in NaX are tentatively attributed to the species II'-IV' in table 2 on the basis of the spectral features on the thermal activations in fig. 4. $Mo(CO)_6$ decomposes stepwise to the subcarbonyls II', III', IV', and finally to Mo metal. The subcarbonyl species (IV') encaged in the NaX zeolite is considerably more stable than the corresponding species IV in the NaY zeolites, whereas $Mo(CO)_6$ and the intermediate subcarbonyls show completely reversed thermal stabilities in these matrices.

T.p.d. experiments were conducted in a dynamic vacuum to confirm the aforementioned i.r. results. Fig. 5 depicts the t.p.d. spectra for $Mo(CO)_6$ encapsulated in the NaY and NaX zeolites. It is clearly demonstrated that $Mo(CO)_6$ decomposes in two main steps in these zeolites. This decomposition feature substantiates the existence of thermally stable subcarbonyl species on the zeolites. In the vapour phase, $Mo(CO)_6$ is known to decompose thermally to Mo metal at 423 K.¹⁹ Accordingly, it is evident that in the zeolite matrices the decomposition of $Mo(CO)_6$ is initiated at considerably lower temperature, whereas the final decomposition of the subcarbonyl species is markedly suppressed.

The carbonyl decomposition temperatures, $T_{\rm L}$ (lower) and $T_{\rm H}$ (higher), for the zeolites employed herein are summarized in table 3. $T_{\rm L}$ decreases in the order of NaY₁ > NaY₂ > NaX, whereas $T_{\rm H}$ increases as NaY₁ < NaY₂ < NaX. Comparing these thermal stabilities of hexa- and sub-carbonyl species with those observed in the aforementioned i.r. results, it is concluded that the $T_{\rm L}$ peak corresponds to the formation of the subcarbonyl species IV and IV' by the successive decomposition of Mo(CO)₆ and intermediate subcarbonyls, whereas the $T_{\rm H}$ peaks arise from the thermal decomposition of species IV and IV' to Mo metal.





Fig. 4. Infrared spectra of adsorption and decomposition of $Mo(CO)_6$ on NaX zeolite: (a) background (evacuated at 673 K for 1 h); (b) exposed to $Mo(CO)_6$ vapour for 1 min, followed by an evacuation for 10 min at room temperature; (c) evacuated for 40 min; (d) for 70 min; (e) for 100 min at room temperature; (f) for 20 min at 373 K; (g) for 20 min at 473 K.



Fig. 5. Temperature-programmed decomposition spectra of $Mo(CO)_6$ adsorbed on (a) NaY (JRC-Z-Y5.6); (b) NaY (SK-40); (c) NaX zeolites. Solid line, CO (m/z = 28); broken line, H₂ (m/z = 2).

The stoichiometries, CO/Mo ratio, of subcarbonyl species IV and IV' can be estimated from the t.p.d. spectra. The amount of evolved CO is considered to be proportional to the spectral area. The peak area ratios of the $T_{\rm L}$ and $T_{\rm H}$ peaks were 1.4, 1.3 and 1.0 for NaY₁, NaY₂ and NaX, respectively. These are close to unity. Furthermore, it is considered that the total peak area corresponds to the stoichiometry of CO/Mo = 6, since no formation of CH₄ and CO₂ were detected in the present systems. Therefore, it is concluded that the major subcarbonyl species stable at *ca*. 370 K are Mo(CO)_{3ads} rather than Mo(CO)_{4ads} or Mo(CO)_{2ads}. The existence of stable Mo(CO)_{3ads} species has also been proposed for some oxide supports, Al₂O₃⁸⁻¹⁰ and ZnO,¹¹ while Howe *et al.*⁷ have claimed the formation of stable Mo(CO)_{4ads} on NaY zeolite. The cause of the difference in the stoichiometry between the present and Howe's studies is not clear at present. However, the i.r. spectra for species IV and IV', which have been regarded as evidence of Mo(CO)_{4ads},⁷ do not seem to be in conflict with the Mo(CO)_{3ads} species as discussed below.

As shown in the i.r. studies, $Mo(CO)_6$ is decomposed stepwise to species IV or IV'. Taking into account the stoichiometries of the stable subcarbonyls, the subcarbonyl species differentiated by the i.r. bands are tentatively assigned in table 3. The proposed decomposition steps are given in scheme 1.



Scheme 1

Y. Okamato et al.

In the NaX zeolite, the i.r. peak assigned here to $Mo_2 (CO)_{10}$ was not observed. This may be due to a higher reactivity of the NaX than the NaY zeolites toward the rather unstable species. The existence of stable intermediate species, such as $Mo(CO)_2$, was not suggested by the i.r. studies during the decomposition of $Mo(CO)_{3ads}$ to Mo metal. This may also be evidenced by sharpened t.p.d. peaks at T_H relative to the peaks at T_L . Further studies are required for a decisive conclusion.

The i.r. spectrum due to species IV in fig. 1(c) or 2(f)-(h) consists mainly of three bands. Mo(CO)₃ compounds with C_{3v} symmetries should show only two bands, as observed in many organometallic compounds. However, when the structure of Mo(CO)₃ is distorted to a lower symmetry, more than two bands are anticipated. Very recently, Kirlin *et al.*²⁰ have reported the i.r. spectra of the surface species prepared from the reaction of H₃Re₃(CO)₁₂ with Al₂O₃ or MgO. Their spectral features are very close to those for species IV. They have assigned the surface species to Re(CO)₃(OM)-(HOM)₂ (M = Mg or Al) on the basis of i.r., electron tunnelling, and u.v. spectra. Therefore, it seems reasonable to assign the i.r. spectra of species IV to an Mo(CO)₃ moiety adsorbed on an oxygen triad with a significantly distorted octahedral symmetry. The structure is proposed in fig. 6.

The Mo(CO)₃ moiety is considered to be greatly stabilized by forming three dative bonds with zeolite oxygens. From considerations analogous to those of Kirlin *et al.*,²⁰ it is proposed that two Mo \leftarrow —O bonds are weaker than the remaining one in NaY and the reversed structure in NaX. The coordinations of oxygen lone-pair electrons to the Mo(CO)₃ moiety are readily broken to restore Mo—CO bonds upon an exposure to CO. Stabilization of surface M(CO)_x species by dative bonds from surface hydroxy groups and/or lattice oxygens are also proposed for Mo(CO)_x on Al₂O₃⁹ and Re(CO)₃ on MgO and Al₂O₃.²⁰ The other small shoulder peaks may suggest the presence of more than one Mo(CO)_{3ads} species with slightly different structures (*e.g.* on site II or site III) and/or possible small perturbations of v(CO) by Na⁺ cations (Lewis acid–carbonyl interactions).

Finally, the electronic structure of the zeolites was evaluated on the basis of the X.p. spectra to understand the dominant factors in elucidating the drastic differences between the zeolites in the thermal stabilities of $Mo(CO)_6$ and the subcarbonyls. The binding energies of the A1 2p, Si 2p and O1s levels for the zeolites examined here are summarized in table 4. The electronic structure of a zeolite system will be discussed in more detail elsewhere.²¹ The binding energy or charge density of aluminium atoms seems to be invariant over the present range of zeolite composition. However, the Si 2pand O 1s binding energies decrease with increasing the Al content, suggesting a decrease in the positive charge on the silicon atoms and an increase in the negative charge on the oxygen atoms. It is unlikely that silicon and aluminium atoms act as Lewis acid sites accessible to adsorbed molecules, since they are well shielded by four oxygen anions. Accordingly, it is natural to propose that the lattice oxygens in the zeolite framework act as interaction sites with the Mo-carbonyls. The X.p.s. results in table 3 clearly demonstrate that the base strength of lattice oxygen increases with increasing Al content. As mentioned above, $T_{\rm L}$ decreases as the Al content increases, while $T_{\rm H}$ increases. These results lead us to conclude that the decompositions of $Mo(CO)_x$ (x = 6-4) are promoted by the basic sites in the zeolite, whereas Mo(CO)_{3ads} is stabilized by the identical nature of the sites; stronger basic sites induce a greater stabilization of Mo(CO)_{3ads}.

The contribution of basic sites to the carbonyl-zeolite interactions is reflected on the observed band positions in table 2. The bands of the carbonyls in the zeolites are considerably red-shifted, compared with those of corresponding organometallic compounds as noted by Howe *et al.*^{6,7} This is interpretable in terms of the dative interactions with zeolite framework oxygen, resulting in the increased electron density on the molybdenum atom and subsequent red-shifts of the v(CO) bands. In addition, the carbonyl species in the NaX zeolite always exhibit lower wavenumbers than the corresponding species in the NaY zeolites, as shown in table 2. This is apparently due



Fig. 6. Proposed model for Mo(CO)_{3ads}. on NaY zeolites.

Table 4. X-Ray photoelectron spectroscopy results on the zeolites and decomposition temperature
obtained by t.p.d. of $Mo(CO)_s$ adsorbed on the zeolites

		composition .	decomposition ^a T/K		b.e./eV ^b		
zeolite		Si/Al	T _L	T _H	Si 2p	Al 2p	O 1s
NaY ₁	JRC-Z-Y 5.6	2.78	378	454	102.5	74.2	532.0
NaY ₂	SK-40	2.43	366	459	102.5	74.2	531.8
NaX	13X	1.23	333	498	101.9	74.1	531.1

^a Rate of temperature increase: 1.8 K min⁻¹. $T_{\rm L}$ lower decomposition temperature; $T_{\rm H}$ higher one. ^b Referenced to C 1s = 285.0 eV.

to a stronger electron donation of the NaX zeolite compared with the NaY zeolites. The stronger electron donation induces stronger Mo—C bonds, resulting in the higher thermal stability of $Mo(CO)_{aads}$.

Conclusions

The decompositions of $Mo(CO)_6$ encapsulated in NaY and NaX zeolites were investigated to examine the effect of zeolite composition using i.r., temperatureprogrammed decomposition, and X.p.s. techniques. The salient findings and conclusions in this study are as follows: (*i*) $Mo(CO)_6$ decomposes stepwise in a vacuum through intermediate carbonyl species to a thermally stable subcarbonyl species, $Mo(CO)_{3ads}$ and finally to molybdenum metal aggregates; (*ii*) the thermal stabilities of $Mo(CO)_6$ and of the intermediate subcarbonyl species are considerably lower in the NaX zeolite than in the NaY zeolites, while the stability of $Mo(CO)_{3ads}$ is completely reversed in these zeolites; (*iii*) the marked differences in the thermal stabilities of the molybdenum carbonyl species between the NaX and NaY zeolites are explained in terms of the difference in the basic strength of framework oxygen in the zeolite; (*iv*) the structure of $Mo(CO)_{3ads}$ is proposed on the basis of the i.r. and X.p. spectra.

References

- 1 D. C. Bailey and S. H. Langer, Chem. Rev., 1981, 81, 109.
- 2 J. Phillips and J. A. Dumesic, Appl. Catal., 1984, 9, 1.
- 3 J. M. Thomas, in *Chemistry and Physics of Solid Surfaces VI*, ed. R. Vanselow and R. F. Howe (Springer-Verlag, Berlin, 1986), p. 107.
- 4 (a) T. Yashima, T. Komatsu and S. Namba, Chem. Express, 1986, 1, 701 and references therein; (b) T. Yashima, T. Komatsu and S. Namba, in Proc. Climax Fourth Int. Conf. Chemistry and Uses of

Y. Okamato et al.

Molybdenum, ed. H. F. Barry and P. C. H. Mitchell (Climax Molybdenum Comp. Ann. Arbor, Michigan, 1982), p. 274.

- 5 P. Gallezot, G. Coudurier, M. Primet and B. Imelik, in *Molecular Sieves II*, ed. J. R. Katzer (ACS Symp. Ser., 1977), vol. 40, p. 144.
- 6 S. Abdo and R. F. Howe, J. Phys. Chem., 1983, 87, 1713.
- 7 Y. Yon-Sing and R. F. Howe, J. Chem. Soc., Faraday Trans. 1, 1986, 82, 2887.
- 8 A. Brenner and R. L. Burwell, J. Am. Chem. Soc., 1975, 97, 2565.
- 9 A. Brenner and R. L. Burwell, J. Catal., 1978, 52, 353.
- 10 A. Kazusaka and R. F. Howe, J. Mol. Catal., 1980, 9, 183.
- 11 K. Tanaka, Y. Zhai and K. Aomura, in *Proc. Climax Int. Conf. Chemistry and Uses of Molybdenum*, ed. H. F. Barry and P. C. H. Mitchell (Climax Molybdenum Comp. Ann Arbor, Michigan, 1982), p. 278.
- 12 T. Hattori, H. Matsumoto and Y. Murakami, 4th Int. Symp. Preparation of Heterogeneous Catalysts (Louvain-la-neuve, 1986).
- 13 R. R. Monchamp and F. A. Cotton, J. Chem. Soc., 1960, 1438.
- 14 R. L. Amster, R. B. Hannan and M. C. Tobin, Spectrochim. Acta, 1963, 19, 1489.
- 15 L. H. Jones, J. Chem. Phys., 1962, 36, 2375.
- 16 L. H. Jones, Spectrochim. Acta, 1963, 19, 329.
- 17 Y. Okamoto, K. Oh-Hiraki, T. Imanaka and S. Teranishi, J. Catal., 1981, 71, 99.
- 18 S. O. Grim and L. J. Matienzo, Inorg. Chem., 1975, 14, 1014.
- 19 E. M. Fednova and J. V. K. Krykova, Russ. J. Inorg. Chem., 1966, 11, 141.
- 20 P. S. Kirlin, F. A. DeThomas, J. W. Bailey, H. S. Gold, C. Dybowski and B. C. Gates, J. Phys. Chem., 1986, 90, 4882.
- 21 Y. Okamoto, A. Maezawa, M. Ogawa and T. Imanaka, unpublished work.

Paper 7/532; Received 24th March, 1987

863