Reversible photodissociation of $Mo(CO)_6$ in a zeolite cage

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Photodissociation of $Mo(CO)_6$ in a NaY zeolite was studied under vacuum and CO atmosphere by FTIR. The stepwise CO-dissociation under vacuum proceeded to form $Mo(CO)_3$ via $Mo(CO)_5$ and $Mo(CO)_4$. The $Mo(CO)_6$ was regenerated by introduction of CO to $Mo(CO)_3$. Irradiation under gaseous CO favored the formation of $Mo(CO)_4$.

Keywords: $Mo(CO)_6$; photodecomposition; NaY; FTIR; UV–Vis

1. Introduction

Photochemistry of transition metal carbonyl compounds is a field of vigorous research [1]. A series of simple metal carbonyls $M(CO)_6$ ($M = Cr$, Mo, W) is studied by many researchers [2–8]. The structures of the photoreaction products of these compounds in solution and in matrices have already been investigated [2,3]. Detailed IR and ultraviolet–visible (UV–vis) spectroscopic studies of the $M(CO)_6$ ($M = Cr$, Mo, W) in low temperature matrices [2,3], in solutions [4], in gas phase [5], on glass [6] and on semiconductor surfaces [7] have been reported. In these studies various unsaturated metal carbonyls $M(CO)_x$ ($x = 3$–5) were detected as photodissociation products and vacant sites of these unsaturated carbonyls were found to be occupied by atoms or molecules in the surrounding systems [2,3]. Recently, pump–probe measurements using picosecond or femtosecond laser pulses were applied to reveal the dynamical behavior of these metal carbonyls in photochemical processes [8]. UV photodissociation of $Mo(CO)_6$ in matrices of CH_4, Ar and so on, has been investigated by Turner et al. by means of IR and UV–vis spectroscopies at 20 K [2,3]. $Mo(CO)_5$ was found to be the primary photodissociation product, and two secondary products assigned to $Mo(CO)_4$ and $Mo(CO)_3$ were also found to grow sequentially during the photoreaction. ^{13}CO substitution and theoretical studies showed that $Mo(CO)_5$, $Mo(CO)_4$, and $Mo(CO)_3$ have C_{4v}, C_{2v}, and C_{3v} symmetries, respectively, whose vacant sites of CO interacted with matrix molecules, e.g., $Mo(CO)_x \cdots CH_4$ in the case of a CH_4 matrix.

On the other hand, zeolites were employed as matrices of metal carbonyls for providing high dispersion and high stereoselective catalytic reactions of metal carbonyls. Structures and thermal properties of metal carbonyls trapped in zeolite cages were studied [9–15]. These metal carbonyls and their decomposition products trapped in zeolite cages are isolated from the others by zeolite walls. Adsorption and decomposition of $Mo(CO)_6$ in zeolite HY were first reported by Gallezot et al. [9] Since then studies of adsorption and thermal decomposition of $Mo(CO)_6$ in zeolite cages have been investigated by other workers [10–15]. The structures of thermally stable subcarbonyl species of $Mo(CO)_6$ in NaY and NaX zeolites were investigated by Okamoto et al. [12–14] using infrared (IR) and X-ray photoelectron (XP) spectroscopies, temperature programmed desorption (TPD) [12], and extended X-ray absorption fine structure (EXAFS) [14]. They proposed that thermal treatment of $Mo(CO)_6$ in the cages of NaY, HY, and NaX zeolites below 420 K under vacuum produced a subcarbonyl species, $Mo(CO)_3$, which was supported by a stoichiometric study using a ^{13}CO substituted sample [12]. It was also found that the $Mo(CO)_3$ species interacted with oxygen of the zeolite framework with C_3 symmetry [13,14].

The present study was motivated by the question whether and how the photochemistry of metal carbonyls is affected by the interaction with oxygen atoms on the zeolite surface. Another subject, stemmed from consideration of the catalytic property of zeolite, was to compare the feature derived under vacuum condition with that attained in the presence of atmospheric CO. Described in this report are the results of the investigation by FT-IR and UV–vis spectroscopies of photoin-

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duced dissociation of $Mo(CO)_6$ in a NaY type zeolite under vacuum and atmospheric CO. The stability of the photodissociation product in the presence of gaseous CO was also examined.

2. Experimental

The used zeolite was a sodium type Y-zeolite (NaY), JRC-Z-Y-5.6 (SiO_2/Al_2O_3 ratio, 5.6), distributed by the Catalysis Society of Japan as a reference catalyst. A commercial molybdenum hexacarbonyl (Kanto Chemicals inc.) was used after outgassing without further purification. Zeolite samples were pressed into a self-supporting wafer of 7–15 mg/cm^2 for IR measurements. A sample wafer was placed in a quartz IR cell attached to a closed gas circulation system. The IR cell was equipped with NaCl windows (transparency > 210 nm) for use of UV–vis photoirradiation and IR measurement. The zeolite was dehydrated by evacuation at 823 K for over 60 min. The pretreated zeolite was exposed to $Mo(CO)_6$ vapor at ca. 0.06 Torr at 298 K by controlling the time (5–15 s). Carbon monoxide (99.95%) and nitrogen (99.9%) gases were purified by slowly passing through a liquid-nitrogen cooled trap. A Xe arc lamp (500 W) with a water filter to remove thermal emission was employed as the light source of irradiation on IR experiments, and a quartz lens (> 150 nm) was used to collimate the light. IR spectra were recorded on a Jasco FT/IR-7000 spectrometer at 2 cm^{-1} resolution with an averaging of 32 or 16 scans for rapid measurement after irradiation. About 90 s were required for 32 scans. UV pulses (15–30 ns) of 266 nm of wavelength and repetition rate of 10 Hz were produced by fourth harmonic generation from a MY-30 Nd:YAG laser (Molectron Corporation) and were used as irradiation source (800 μJ) in diffuse reflectance (DR) UV–vis measurements. UV–vis spectra were measured by a UV-240 (Shimadzu) spectrometer.

3. Results and discussion

The FT-IR spectrum measured after exposure of the zeolite wafer to 0.85 Torr of $Mo(CO)_6$ for 15 s at 298 K is shown in fig. 1 (a). Two ν(CO) bands due to $Mo(CO)_6$ were observed at 1974 and 2125 cm^{-1}. The exposure at 0.85 Torr for more than 15 s resulted in complicated spectra due to physisorption and partial decomposition, as reported in previous publications [10,11]. Although the absolute amount of adsorbed $Mo(CO)_6$ was not determined in this study, it was estimated to be much less than that of one $Mo(CO)_6$ molecule per zeolite cage by comparison of the relation between the spectral line shape and the amount of encaged $Mo(CO)_6$ per unit cell of NaY zeolite [10]. The vibrational frequencies and their assignments to the bands of $Mo(CO)_6$ as well as other molybdenum carbonyl species are summarized in table 1 together with those observed in CH_4 matrix [3] and in NaY zeolite (thermal decomposition) [13].

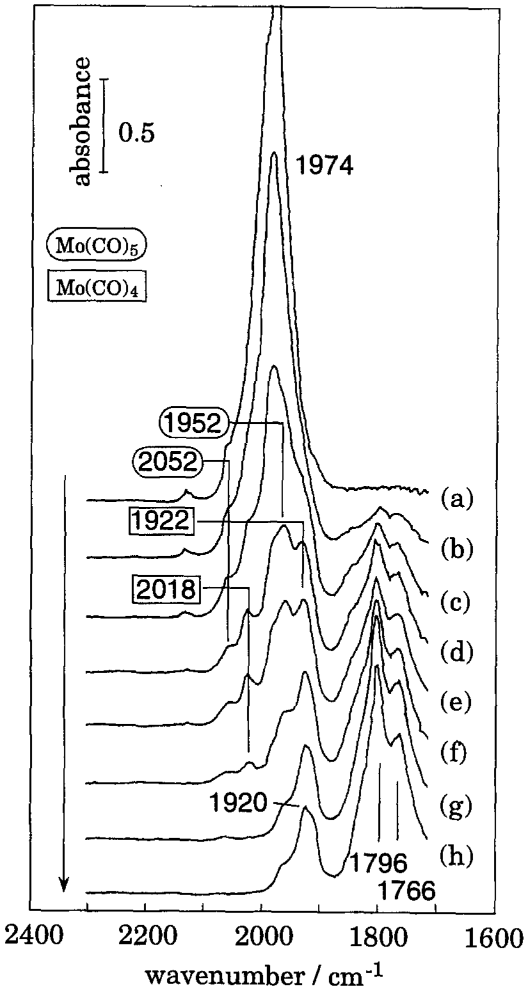


Fig. 1. FT-IR spectra during photo irradiation of $Mo(CO)_6$/NaY-5.6 zeolite under vacuum: (a) without irradiation under vacuum for 1 min, (b) without irradiation under vacuum for 60 min, (c) irradiation for 1 min, (d) 2 min, (e) 3 min, (f) 5 min, (g) 15 min, and (h) 30 min.

When the adsorbed $Mo(CO)_6$ was subjected to evacuation (~ 10^{-3} Torr) at 298 K for 60 min without light irradiation, new bands below 1800 cm^{-1} (fig. 1 (b)) appeared. These bands are assigned to a decomposition product of $Mo(CO)_6$ as described below: slow thermal decomposition of $Mo(CO)_6$ in the zeolite cage occurred at 298 K. A remarkable change took place right after the irradiation by the Xe lamp under vacuum at 298 K (fig. 1 (c)–(h)). The main peak of $Mo(CO)_6$ at 1974 cm^{-1} became weaker and several bands at lower frequencies appeared simultaneously. After the irradiation for 15 min three main peaks at 1920, 1796 and 1766 cm^{-1} became distinct and the change was accompanied by a change of the sample color from white to orange. Any further change was not observed during the additional

Table 1
Assignments and frequencies of IR bands of molybdenum carbonyl species

System (symmetry)	IR assignment	IR bands (cm^{-1})		
		in CH_4 at 20 K ref. [3]	in NaY ref. [13]	in NaY this work
$Mo(CO)_6$ (O_h)	Raman active		2124	2127
	T_{1u}	1993	1970	1974
		1987		
$Mo(CO)_5$ (C_{4v})	A_1	2093	2046	2052
	E	1972	1953	1952
		1967		
	A_1	1929	1835	1840
		1926		
$Mo(CO)_4$ (C_{2v})	A_1	2057	2020	2018
	B_2	1949	1915	1922
		1945		
	E	1927	1796	1808
	B_1	1887		
$Mo(CO)_3$ (C_{3v})	A_1	1981	1913	1920
	E	1866	1796	1796
		1862	1761	1766

15 min of irradiation as shown in fig. 1 (h). The produced bands are attributed to tricarbonyl species (table 1), which was also observed in the thermal decomposition of $Mo(CO)_6$ in NaY zeolite cage at 348–373 K [13].

During the photodissociation process from hexa-to tricarbonyl species, appearance and disappearance of several peaks were observed indicating the existence of other unsaturated carbonyl species in addition to hexa- and tri-carbonyls. The change of IR spectra under irradiation at 298 K was similar to that observed during thermal decomposition of $Mo(CO)_6$ at 373 K reported by Okamoto et al. [13]. They assigned the subcarbonyl species utilizing IR, TPD, and XPS, and found that $Mo(CO)_6$ in NaY zeolite decomposed to $Mo(CO)_3$ through $Mo(CO)_5$ and $Mo(CO)_4$. The assignments of IR frequencies of observed unsaturated carbonyl species are also listed in table 1 together with those observed in CH_4 matrix [3]. The bands due to $Mo(CO)_5$ and $Mo(CO)_4$ are marked by rounded and rectangular enclosures, respectively, in fig. 1 and subsequent figures. It was found that the $Mo(CO)_6$ decomposed by the UV irradiation to $Mo(CO)_3$ through $Mo(CO)_5$ and $Mo(CO)_4$. The peak positions observed for $Mo(CO)_6$ in NaY zeolite are red shifted from those observed in matrices [2,3], presumably as a result of the stronger interaction with the zeolite framework.

Regeneration of $Mo(CO)_6$ by exposing CO to the thermal decomposition product was found on γ-Al_2O_3 [16] and NaY zeolite [10]. On NaY zeolite $Mo(CO)_6$ was also recovered by the introduction of 25 Torr of CO at 298 K after thermal decomposition at 373 K, although the reaction scheme was not mentioned in detail. Here, we examined the photodissociation and regeneration of $Mo(CO)_6$ in the presence of CO in gas phase. On exposing 0.5 Torr of CO to $Mo(CO)_3$ formed by photodissociation of $Mo(CO)_6$ in NaY zeolite at 298 K, regeneration of $Mo(CO)_6$ was observed as shown in fig. 2. Introduction of CO immediately led to the disappearance of the peaks of $Mo(CO)_3$. As seen in fig. 2 (b) peaks at 1922 and 1809 cm^{-1} as well as a weak band at 2018 cm^{-1}, which are assigned to $Mo(CO)_4$, appeared immediately. It is noted that some $Mo(CO)_6$ was also formed at the initial stage as evidenced by the appearance of the band at 1980 cm^{-1}. A peak appeared at 1952 cm^{-1}, located between the peaks at 1980 cm^{-1} ($Mo(CO)_6$) and 1922 cm^{-1} ($Mo(CO)_4$), after 6–12 min exposure and was assigned to $Mo(CO)_5$. The steps of the photodissociation and the reproduction of $Mo(CO)_6$ in the presence of CO in gas phase were confirmed to be reversible. The reaction of $Mo(CO)_3$ with CO to $Mo(CO)_4$ was found to be rapid as confirmed by immediate disappearance of $Mo(CO)_3$. On the other hand, the rate of the reaction from $Mo(CO)_4$ to $Mo(CO)_5$ was slower than that from $Mo(CO)_5$ to $Mo(CO)_6$ leading to weak intensity of the bands of $Mo(CO)_5$. The regeneration behavior is in contrast to the decomposition one in the sense that no distinct difference was seen in the rate of each reaction step, i.e., the transformation of the species took place gradually.

Next, photodissociation of $Mo(CO)_6$ in gaseous CO atmosphere was studied. When $Mo(CO)_6$ in NaY zeolite was irradiated under 0.2 Torr of CO, subcarbonyl species were produced on increasing the irradiation time (fig. 3). The IR spectrum measured after 60 min of irradiation was the same as that after 30 min, and the reaction was regarded to reach an equilibrium under

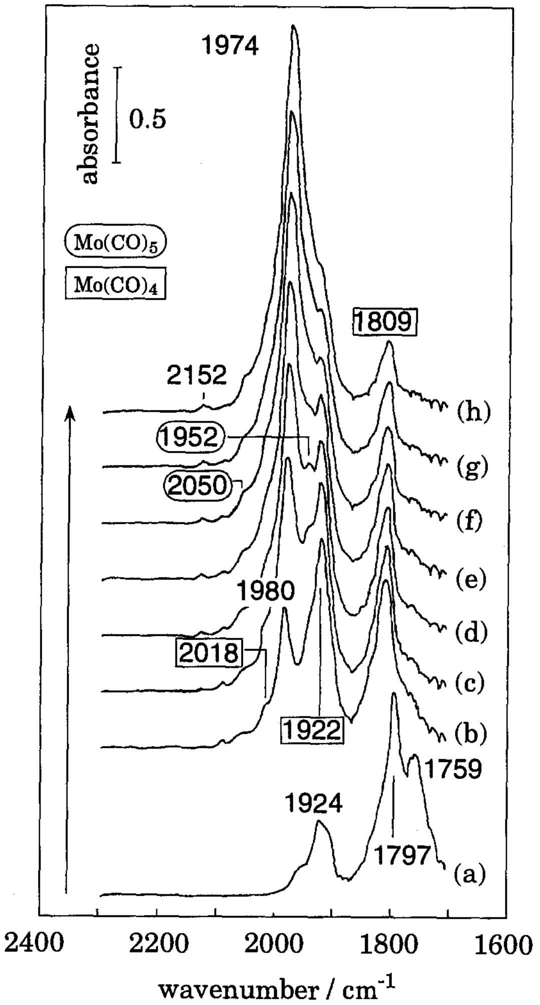


Fig. 2. FT-IR spectra of CO-exposed Mo(CO)$_3$/NaY-5.6 zeolite as photodecomposition product of Mo(CO)$_6$/NaY-5.6: (a) Mo(CO)$_3$/NaY-5.6 under vacuum, (b) immediately after CO introduction, (c) after 3 min, (d) 6 min, (e) 9 min, (f) 10 min, (g) 15 min, and (h) 30 min.

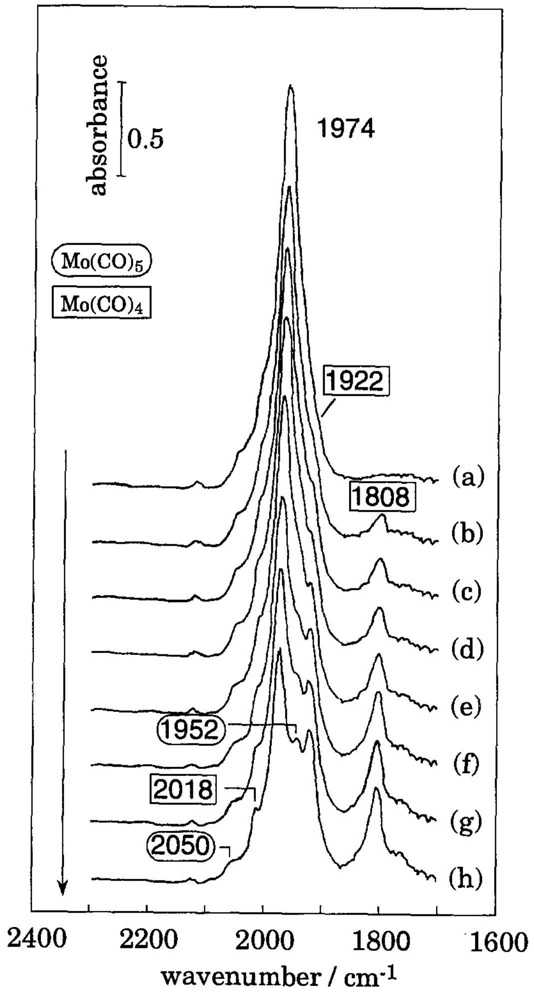


Fig. 3. FT-IR spectra of Mo(CO)$_6$/NaY-5.6 under 0.2 Torr of CO: (a) before irradiation, (b) irradiation for 1 min, (c) 2 min, (d) 3 min, (e) 5 min, (f) 10 min, (g) 15 min, and (h) 30 min.

irradiation in 0.5 Torr of CO after 30 min. It is noted that a considerable amount of Mo(CO)$_6$ remained, and that the main photodissociation product was different from that produced under evacuation; Mo(CO)$_3$ was not produced but Mo(CO)$_4$ was mainly formed (2018, 1922 and 1808 cm^{-1}) with a small amount of Mo(CO)$_5$ (1952 cm^{-1}). For the sake of further confirmation, UV–vis spectra were observed under the same conditions (in the presence of CO in gas phase). A spectrum before irradiation of UV pulses at 266 nm with pulse duration time of 15–30 ns is shown in fig. 4 (a). Three bands at 230, 290 and 330 nm are due to Mo(CO)$_6$ as assigned by referring to the spectra observed in CH$_4$ matrix [3]. The reported absorption bands in UV–vis spectra of molybdenum subcarbonyl species are compared in table 2 with those observed in the present study. After irradiation of 500 pulses, new bands appeared at 390 and 245 nm. These bands increased in intensity by increasing the number of UV pulses and commenced to decrease after 5000 pulses. The decrease of these two bands was accompanied by the appearance and growth of another band at 505 nm. The former two bands and the band at 505 nm are reasonably assigned to Mo(CO)$_5$ and Mo(CO)$_4$, respectively. The UV–vis bands are better resolved than IR bands, and the stepwise transformation of Mo(CO)$_6$ to Mo(CO)$_5$ and to Mo(CO)$_4$ was clearly confirmed. The absence of decarbonylation to Mo(CO)$_3$ under CO atmosphere was also supported.

The absence of Mo(CO)$_3$ formation under gaseous CO of 0.2 Torr is explained by rapid reaction of Mo(CO)$_3$ with CO, as seen in the observation of vibrational and electronic bands of Mo(CO)$_4$ as dominant species in figs. 3 and 4. In order to clarify the transformation between Mo(CO)$_3$ and Mo(CO)$_4$, the equilibrium state giving fig. 4 (h) was maintained under evacuation and without irradiation. Both gaseous CO and irradiation were eliminated from the equilibrium system which had been reached under irradiation and 0.5 Torr of CO at 298 K. The change of the spectra during evacuation is shown in fig. 5, which clearly manifests the quick formation of Mo(CO)$_3$. It is noticed that

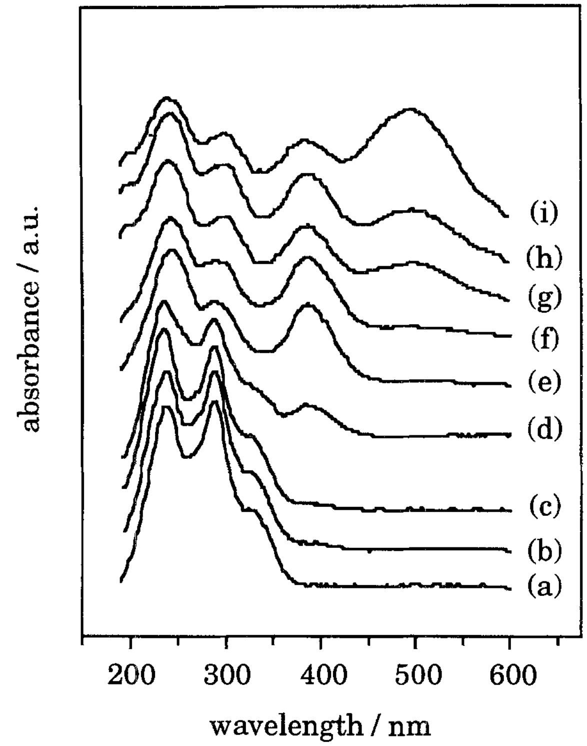


Fig. 4. UV–vis spectra of $Mo(CO)_6$/NaY-5.6 under 0.2 Torr of CO: (a) before irradiation, (b) after irradiation of 100, (c) 200, (d) 500, (e) 1000, (f) 5000, (g) 10000, (h) 20000 and (i) 50000 pulses of a light at 266 um with pulse time width of 15–30 ns and 800 μJ of energy.

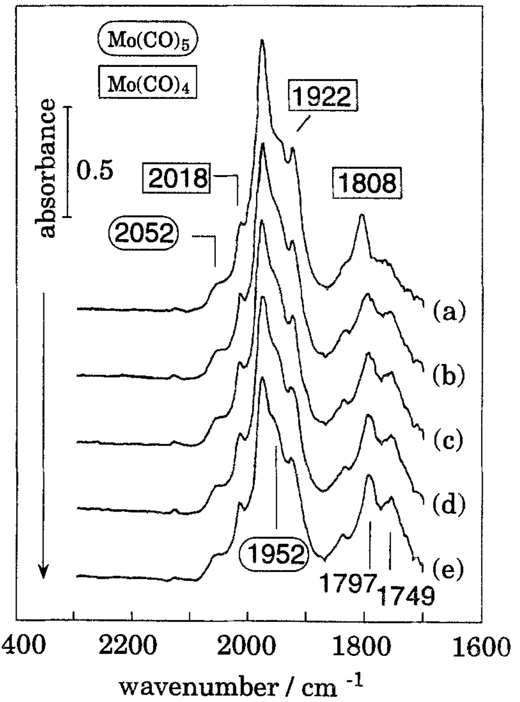


Fig. 5. Change of FT-IR spectra of $Mo(CO)_4$ under evacuation at 298 K without irradiation: (a) $Mo(CO)_4$ under 0.5 Torr of CO after irradiation for 30 min, (b) evacuation for 3 min, (c) 6 min, (d) 9 min, and (e) 15 min.

$Mo(CO)_4$ changed to $Mo(CO)_3$ without irradiation under vacuum condition at 298 K. This suggests that thermal decomposition at 373 K and photodecomposition at room temperature from $Mo(CO)_6$ to $Mo(CO)_3$ do not essentially include the reaction step from $Mo(CO)_4$ to $Mo(CO)_3$.

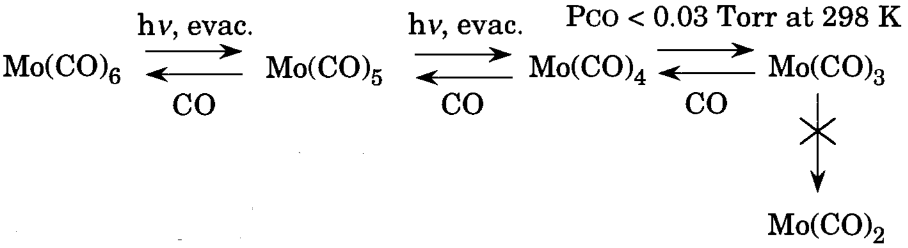
The relative amounts of Mo carbonyl species in the equilibrium state depended on the CO pressure under irradiation at 298 K as seen from fig. 6, which shows the IR spectra observed after 4.2 Torr of CO was introduced to $Mo(CO)_6$ on the zeolite at 298 K (fig. 6 (a)), and irradiation of UV light for 30 min (fig. 6 (b)), and when the CO pressure was decreased to the stated pressure. The system reached the equilibrium state by the irradiation for 30 min (fig. 6 (c)–(h)). The intensity of the peak of $Mo(CO)_6$ became weaker while those of $Mo(CO)_4$ at 2018, 1924 and 1808 cm^{-1} increased as the CO pressure decreased. Above 10 Torr of CO, on the other hand, no clear peaks assigned to Mo subcarbonyl species were observed.

Table 2
UV–vis bands of molybdenum carbonyl species

System	UV–vis bands (um)	
	in CH_4 at 20 K ref. [3]	in NaY this work
$Mo(CO)_6$	223	230
	285.5	290
	324	330
$Mo(CO)_5$	247	245
	411	390
$Mo(CO)_4$	530	505
$Mo(CO)_3$	317	not observed

The observation under N_2 atmosphere instead of CO gave a similar change in spectrum; dissociation of $Mo(CO)_6$ to $Mo(CO)_4$, occurred under irradiation. The spectral feature after 30 min of irradiation under 2.5 Torr of N_2 resembled those observed after irradiation under gaseous CO at 0.17 Torr (fig. 5 (e)). This is interpreted as that the decomposition product, CO, formed from $Mo(CO)_6$ under irradiation gave a partial pressure of about 0.17 Torr to result in the similarity.

The presently observed steps of photodissociation of $Mo(CO)_6$ in NaY zeolite at 298 K are depicted in scheme 1. Photoirradiated $Mo(CO)_6$ in the NaY zeolite cage under vacuum was found to decompose to $Mo(CO)_3$ through intermediate species ($Mo(CO)_5$ and $Mo(CO)_4$), but further dissociation was not observed. The behavior of these species was similar to that observed during the thermal decomposition process. On the other hand, $Mo(CO)_6$ in NaY zeolite cage under gaseous CO (> 0.03 Torr) produced $Mo(CO)_4$ as dominant species under irradiation of UV light. This fea-



Scheme 1. Proposed photolysis steps of Mo(CO)$_6$.

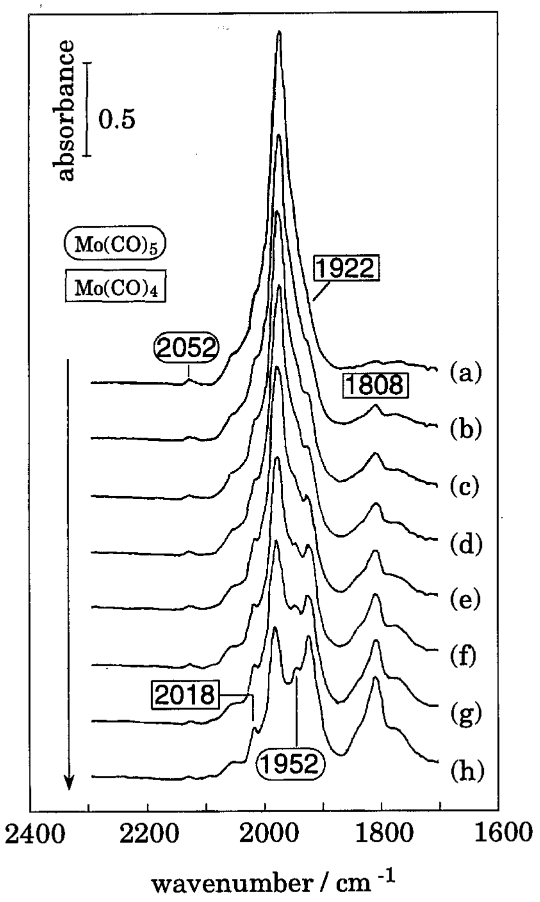


Fig. 6. FT-IR spectra of photoirradiated (for 30 min) Mo(CO)$_6$ under various CO pressures: (a) CO 4.2 Torr before irradiation, (b) CO 4.2 Torr after irradiation, (c) 1.3 Torr, (d) 0.42 Torr, (e) 0.17 Torr, (f) 0.11 Torr, (g) 0.07 Torr, and (h) 0.03 Torr.

ture was found for the first time in this study. It was also confirmed that the decomposition of Mo(CO)$_4$ to Mo(CO)$_3$ proceeded by evacuation at 298 K and without irradiation.

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References

[1] G.L. Geoffroy and M.S. Wrighton, *Organometallic Photochemistry* (Academic Press, New York, 1979), and references therein.
[2] R.N. Perutz and J.J. Turner, Inorg. Chem. 14 (1975) 262.
[3] R.N. Perutz and J.J. Turner, J. Am. Chem. Soc. 97 (1975) 4800.
[4] J.N. Kelly, J. Organomet. Chem. 69 (1974) 259.
[5] W. Wang, Y. Liu, P. Ji, Y. She and K.-J. Fu, J. Phys. Chem. (1992) 1278.
[6] H.D. Gefney, Inorg. Chem. 27 (1988) 2733.
[7] L.J. Rither, S.A. Buntin, P.M. Chu and R.R. Cavanagh, J. Chem. Phys. 100 (1994) 3187.
[8] T.P. Dougherty and E.J. Heilweil, Chem. Phys. Lett. 227 (1994) 19.
[9] G. Coudurier, P. Gallezot, H. Praliaud, M. Primet and B. Imelik, C.R. Hebd. Seances Acad. Sci. C 282 (1976) 311.
[10] Y. Yon-Sing and R.F. Howe, J. Chem. Soc. Faraday Trans. I 82 (1986) 2887.
[11] S. Abdo and R.F. Howe, J. Phys. Chem. 87 (1983) 1713.
[12] Y. Okamoto, A. Maezawa and H. Kane, J. Catal. 112 (1988) 585.
[13] Y. Okamoto, A. Maezawa, I. Mitsushima and H. Kane, J. Chem. Soc. Faraday Trans. I 84 (1988) 851.
[14] Y. Okamoto, T. Imanaka, K. Asakura and Y. Iwasawa, J. Phys. Chem. 95 (1991) 3700.
[15] C.L. Twey and T.M. Apple, Inorg. Chem. 31 (1992) 2885.
[16] A. Brenner and R.L. Burwell Jr., J. Am. Chem. Soc. 97 (1975) 2565.