

Stoichiometry of Molybdenum Subcarbonyl Species Encaged in NaY and HY Zeolites

Transition-metal carbonyls supported on inorganic matrices show prominent catalytic properties (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 catalysts prepared from $\text{Mo}(\text{CO})_6$ encapsulated in zeolites are involved in such systems (2). The structure and chemical reactivity of intermediate carbonyl species produced during the decomposition of $\text{Mo}(\text{CO})_6$ are very intriguing for tailoring and synthesizing catalytically active species from $\text{Mo}(\text{CO})_6$.

Infrared studies of adsorption and decomposition of $\text{Mo}(\text{CO})_6$ on NaY and HY zeolites have been conducted by Gallezot *et al.* (3) and Yon-Sing and Howe (4) to elucidate interaction modes between the carbonyls and the zeolites. The formation of definite subcarbonyl species has been found at 370–420 K (3, 4). A stoichiometry of $\text{Mo}(\text{CO})_4$ has been claimed for the subcarbonyl species in the HY zeolite on the basis of the amount of evolved CO during the decomposition (3). A gravimetric study of the decomposition also suggested formation of $\text{Mo}(\text{CO})_4$ or $\text{Mo}_2(\text{CO})_8$ for a NaY zeolite (4). On the other hand, $\text{Mo}(\text{CO})_3$ and/or its dimeric species have been proposed for a stable intermediate subcarbonyl species under similar conditions on non-zeolitic oxide matrices: Al_2O_3 (5) and ZnO (6). The difference, if any, in the stable subcarbonyl species between matrices would be quite important to understand the chemistry of anchoring metal carbonyls.

In the present study, an exact stoichiometry of the thermally stable molybdenum

subcarbonyl species was examined for NaY and HY zeolites by using temperature-programmed decomposition (TPDE) techniques coupled with a ^{13}C isotopic labeling technique. Contrary to the results of previous workers (3, 4), it has been found here that the stoichiometry of the definite subcarbonyl species on the NaY and HY zeolites is $\text{Mo}(\text{CO})_3$ as observed on non-zeolitic metal oxides (5, 6).

NaY and its decationized HY zeolites ($\text{Si}/\text{Al} = 2.78$) were supplied by the Catalysis Society of Japan as reference catalysts (JRC-Z-Y5.6 and HY5.6) (7). The degree of decationization was nominally 72% but 91% by XPS analysis. After evacuation at 673 K for 1–2 h, the powdered samples were exposed to $\text{Mo}(\text{CO})_6$ vapor (ca. 8 Pa) at room temperature for a selected period (usually for 12 h). The TPDE studies of $\text{Mo}(\text{CO})_6$ encaged in zeolites were conducted in a dynamic vacuum and evolving gases were continuously and repeatedly analyzed by a mass filter over a mass range of $m/e = 1$ –51. The decomposition temperature was raised at a rate of 1.85 K min^{-1} from room temperature to ca. 600 K. In the zeolite system, CO ($m/e = 12$ and 28) and H_2 ($m/e = 2$) were the only desorbed gases. No formation of CO_2 ($m/e = 44$) or CH_4 ($m/e = 15$) was observed within the detection limit. The amount of $\text{Mo}(\text{CO})_6$ adsorbed on the zeolite was chemically analyzed after the TPDE experiments.

IR spectra of the molybdenum carbonyls adsorbed on the NaY or HY zeolite were measured at room temperature by using an *in situ* cell (9). The zeolite wafer was also evacuated at 673 K for 1–2 h, followed by

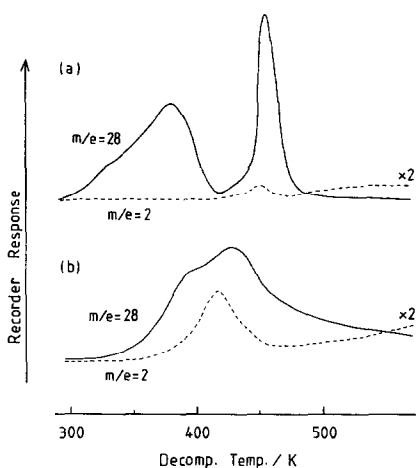


FIG. 1. Temperature-programmed decomposition profiles of CO ($m/e = 28$) and H_2 ($m/e = 2$) for $Mo(CO)_6$ encapsulated in the NaY (a) and HY (b) zeolites. The adsorption amounts of $Mo(CO)_6$ were 2.0 and 1.4 molecules/supercage for the NaY and HY zeolites, respectively. (—) CO; (---) H_2 (the intensity is doubled for clarity).

an exposure to $Mo(CO)_6$ for 10–60 s at room temperature.

Figure 1 shows the TPDE profiles of CO and H_2 for $Mo(CO)_6$ engaged in the NaY and HY zeolites. The CO profile for the NaY zeolite consists of two distinct peaks, indicating the formation of definite intermediate molybdenum subcarbonyl species at 370–420 K *in vacuo* during the decomposition of $Mo(CO)_6$ to Mo–metal aggregates (4, 8, 9). It is considered that the thermally stable subcarbonyl species is formed at the lower decomposition temperature (T_L), whereas the subcarbonyl species is decomposed at the higher decomposition temperature (T_H). In the case of the HY zeolite, two CO peaks were observed but not well resolved; T_L increased, while T_H decreased, compared with those for the NaY zeolite. A characteristic production of H_2 in the HY zeolite at >390 K is consistent with partial oxidation of molybdenum by reactions with surface hydroxyl groups (2, 3, 8) as observed for $Mo(CO)_6/Al_2O_3$ systems (5). These zeolite-dependent decomposition behaviors of $Mo(CO)_6$ reside in the base strength of zeolite framework oxygen (9)

and have been discussed in detail elsewhere (10, 11). In this report, the stoichiometry of the subcarbonyl species is to be examined below.

The CO/Mo stoichiometry of the thermally stable subcarbonyl species was estimated for the NaY zeolite from the area intensity ratio of the peaks at T_L and T_H in the TPDE profile. The ratio of 1.25 ± 0.10 suggests the composition of the subcarbonyl species to be $Mo(CO)_{2.7 \pm 0.1}$, assuming that all of the CO detected here corresponds to the composition of $Mo(CO)_6$. In the other TPDE experiments, the decomposition temperature was raised to 373 K and kept constant (1–2 h) until the evolution of CO essentially ceased. Subsequently, the decomposition temperature was increased again for a complete decomposition of the subcarbonyl species. On a prolonged evacuation at 373 K, selective formations of the thermally stable subcarbonyl species were confirmed in the separate IR studies (9). The area ratios of the TPDE peaks observed at <373 and >373 K indicated the compositions of $Mo(CO)_{2.6}$ for the subcarbonyl species engaged in the NaY zeolites. Similar TPDE experiments suggested the formation of $Mo(CO)_{2.7}$ as a thermally stable subcarbonyl species on the HY zeolite. These stoichiometries are very close to $Mo(CO)_3$ rather than to $Mo(CO)_4$ (3, 4).

However, these TPDE procedures might involve some ambiguities for the determinations of an exact composition of the subcarbonyl species; some part of $Mo(CO)_6$ might be decomposed directly to molybdenum metal (NaY) (4, 8, 9) or to partially oxidized molybdenum species (HY) (2, 3, 8) at T_L or T_H and/or undetected carbon-containing products might be formed at the expense of CO. $Mo(CO)_6$ and subcarbonyl species might sublime from the zeolite cage during the TPDE experiments. In order to remove these ambiguities in the above TPDE experiments, a ^{13}C isotopic labeling technique was applied by utilizing the fact that the subcarbonyl species is reversibly converted to original $Mo(CO)_6$ at room

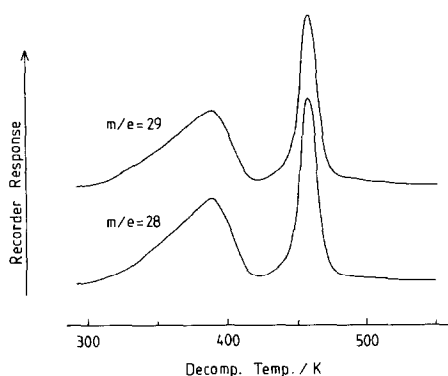


FIG. 2. Temperature-programmed decomposition profiles of ^{12}CO ($m/e = 28$) and ^{13}CO ($m/e = 29$) for $\text{Mo}(\text{CO})_6$ reproduced by a ^{13}CO introduction to the subcarbonyl species engaged in the NaY zeolite (0.6 $\text{Mo}(\text{CO})_6/\text{supercage}$).

temperature (3, 4, 9). After evacuation at 373 K until no evolution of CO was detected, ^{13}CO (MSD, 99.3%) was introduced stepwise to the subcarbonyl species in the zeolites at 300–330 K to reproduce $\text{Mo}(\text{CO})_6$. The formation of $\text{Mo}(\text{CO})_6$ was confirmed by a color change of the sample (from brown to white). After measurement of the amounts of ^{12}CO and ^{13}CO in the gas phase, TPDE profiles were obtained for ^{12}CO ($m/e = 28$ and 12) and ^{13}CO ($m/e = 29$ and 13).

Figure 2 shows the profiles thus obtained for the NaY zeolite. The $^{12}\text{CO}/^{13}\text{CO}$ ratio was invariant all over the decomposition and close to unity (1.1). Taking into consideration the amounts of ^{12}CO and ^{13}CO in the gas phase and the amount of adsorbed molybdenum, the composition of $\text{Mo}(\text{CO})_{3.2}$ was obtained for the subcarbonyl species encapsulated in the NaY zeolite. Duplicated experiments confirmed the results. In the case of the HY zeolite, the stoichiometry of the stable subcarbonyl species was calculated to be $\text{Mo}(\text{CO})_{2.9}$. These results unambiguously substantiate the stoichiometry of $\text{Mo}(\text{CO})_3$ for the subcarbonyl species encapsulated in the NaY and HY zeolites.

It should be noted here that the stoichiometry obtained above is possibly an aver-

aged one over the several subcarbonyl species with different CO/Mo ratios. In the case of the NaY zeolite, the subcarbonyl species is characterized by a set of the IR bands at 1915, 1796, and 1770 cm^{-1} as shown in Fig. 3a. This is in conformity with the results of other workers (4, 12). A more detailed IR study (9), however, has suggested the coexistence of two kinds of subcarbonyl species on the basis of the findings that an additional band appears at 1923 cm^{-1} on an evacuation at 423 K or on a prolonged heat treatment at 383 K *in vacuo*. These subcarbonyl species are considered from the very close IR spectra to have identical compositions and very close configura-

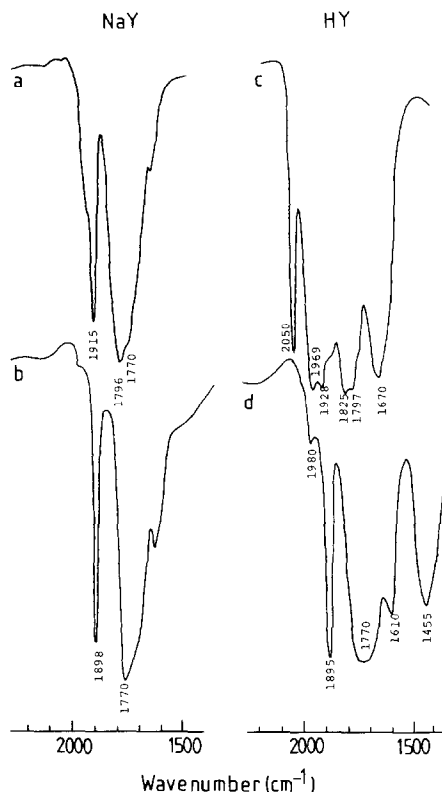


FIG. 3. IR spectra of the molybdenum subcarbonyl species engaged in the NaY and HY zeolites. (a and c) Evacuated at 373 K for 30 min after the adsorption of $\text{Mo}(\text{CO})_6$ at room temperature on the NaY and HY zeolites, respectively; (b and d) the samples (a) and (c) after introduction of NH_3 (ca. 2 kPa) at room temperature, respectively.

rations but slightly different thermal stabilities. Accordingly, it is concluded that the molybdenum subcarbonyl species engaged in the NaY zeolite are predominantly $\text{Mo}(\text{CO})_3$. On the basis of the similarity of the IR spectrum in Fig. 3a to those for $\text{Re}(\text{CO})_3$ supported on MgO and Al_2O_3 (13), $\text{Mo}(\text{CO})_3$ moiety is expected to be stabilized on an oxygen triad in the NaY framework with a significantly distorted octahedral symmetry.

The above conclusion is further supported by the IR spectrum in Fig. 3b. An introduction of NH_3 to the subcarbonyl species provided a new set of the IR bands at 1898 and 1770 cm^{-1} , accompanied by an immediate color change from orange to white or very pale yellow. No evolution of CO was detected by IR. These IR bands are assigned to *cis*- $\text{Mo}(\text{CO})_3(\text{NH}_3)_3$ (1880^{vvs} and 1730^{vvs} cm^{-1}) (14) rather than $\text{Mo}(\text{CO})_4(\text{NH}_3)_2$ (2010^m, 1915^{vvs}, 1837^{vvs}, and 1780^{vvs} cm^{-1}) (14). It is evident that the subcarbonyl species, $\text{Mo}(\text{CO})_3$, stabilized on the NaY zeolite react with NH_3 to produce $\text{Mo}(\text{CO})_3(\text{NH}_3)_3$.

With the HY zeolite, a very small portion of molybdenum is irreversibly oxidized at 373 K as deduced from a small amount of H_2 evolution up to this temperature (Fig. 1b). This is consistent with the results of other workers (2, 8). A majority of $\text{Mo}(\text{CO})_6$ is reversibly decomposed to subcarbonyl species at 373 K (12). The ¹³CO TPDE suggests the composition of $\text{Mo}(\text{CO})_3$ for these stable subcarbonyls.

As depicted in Fig. 3c, a more complicated IR spectrum is observed for the molybdenum subcarbonyls engaged in the HY zeolite than that in the NaY zeolite. From the behavior of relative band intensities, it was found that the spectra consisted of, at least, two sets of bands. Subcarbonyl species A is characterized by the main bands at 2050, 1969, 1825, and 1670 cm^{-1} and species B by the resolved bands at 1928 and 1797 cm^{-1} . Species B showed a slightly higher thermal stability *in vacuo* than species A. Species A was formed in preference to spe-

cies B in a highly decationized HY zeolite. The assignment of these subcarbonyl species is not straightforward here.

An introduction of NH_3 to these subcarbonyl species immediately brought about a dramatic change in the IR spectrum as well as markedly faded color. The resultant spectrum is shown in Fig. 3d and is unambiguously assigned to *cis*- $\text{Mo}(\text{CO})_3(\text{NH}_3)_3$ as in the NaY zeolite. The extra bands at 1610 and 1455 cm^{-1} are attributed to ν_2 and ν_4 deformations of NH_4^+ , respectively (15). A weak band at around 1980 cm^{-1} that is not assigned here was readily eliminated by an evacuation at room temperature. No apparent formation of $\text{Mo}(\text{CO})_4(\text{NH}_3)_2$ was detected. Molybdenum tetra- and tricarbonyl complexes provide preferentially $\text{Mo}(\text{CO})_4(\text{NH}_3)_2$ and $\text{Mo}(\text{CO})_3(\text{NH}_3)_3$, respectively, on contact with dry NH_3 at room temperature (14). Accordingly, it is deduced that species A and B in the HY zeolite are attributed to subcarbonyls with an identical composition of $\text{Mo}(\text{CO})_3$ but in different configurations rather than assigned to $\text{Mo}(\text{CO})_4$ and $\text{Mo}(\text{CO})_2$ species. The higher IR wavenumbers of these subcarbonyl species than those in the NaY zeolite are explicated in terms of lower electron donations from the framework oxygens in the HY zeolite due to their weaker basicity (10, 11).

In conclusion, the stoichiometry of the molybdenum subcarbonyl species thermally stable at 370–420 K *in vacuo* is unambiguously elucidated to be $\text{Mo}(\text{CO})_3$ for NaY and HY zeolites by using IR and temperature-programmed decomposition techniques coupled with a ¹³CO isotopic labeling.

REFERENCES

1. (a) Bailey, D. C., and Langer, S. H., *Chem. Rev.* **81**, 109 (1981); (b) Phillips, J., and Dumesic, J. A., *Appl. Catal.* **9**, 1 (1984).
2. Yashima, T., Komatsu, T., and Namba, S., *Chem. Express.* **1**, 701 (1986), and references therein.
3. Gallezot, P., Coudurier, G., Primet, M., and Imelik, B., "Molecular Sieves II" (J. R. Katzer,

- Ed.), ACS Symp. Ser. Vol. 40, p. 144. Amer. Chem. Soc., Washington, DC, 1977.
4. Yon-Sing, Y., and Howe, R. F., *J. Chem. Soc. Faraday Trans. 1* **82**, 2887 (1986).
 5. (a) Brenner, A., and Burwell, R. L., *J. Amer. Chem. Soc.* **97**, 2567 (1975); (b) *J. Catal.* **52**, 353(1978); (c) Kazusaka, A., and Howe, R. F., *J. Mol. Catal.* **9**, 183 (1980).
 6. Tanaka, K., Zhai, Y., and Aomura, K., "Proc. Climax Intern. Conf. Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 278. Climax Molybdenum Co., Ann Arbor, MI, 1982.
 7. Hattori, H., Matsumoto, H., and Murakami, Y., "Fourth Intern. Symp. Preparation of Heterogeneous Catalysts, Louvain-la-neuve, 1986."
 8. Komatsu, T., Namba, S., Yashima, T., Domen, K., and Onishi, T., *J. Mol. Catal.* **33**, 345 (1985).
 9. Okamoto, Y., Maezawa, A., Kane, H., Mitsushima, I., and Imanaka, T., *J. Chem. Soc. Faraday Trans. 1* **84**, 851 (1988).
 10. Maezawa, A., Kane, H., Okamoto, Y., and Imanaka, T., *Chem. Lett.*, 241 (1988).
 11. Okamoto, Y., Maezawa, A., Kane, H., and Imanaka, T., "Proceedings on the 9th International Congress on Catalysis" (M. J. Phillips and M. Ternan, Eds.), Vol. 1, p. 11. The Chemical Institute of Canada, Ottawa, 1988.
 12. Abdo, S., and Howe, R. F., *J. Phys. Chem.* **87**, 1713 (1983).
 13. Kirilin, P. S., DeThomas, F. A., Bailey, J.W., Gold, H.S., Dybowski, C., and Gates, B.C., *J. Phys. Chem.* **90**, 4882 (1986).
 14. Barlow, C. G., and Holywell, G. C., *J. Organometal. Chem.* **16**, 439 (1969).
 15. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," p. 108. Wiley, New York, 1970.

YASUAKI OKAMOTO¹
AKINORI MAEZAWA
HIROSHIGE KANE
TOSHINOBU IMANAKA

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

Received July 14, 1987; revised February 23, 1988

¹ To whom correspondence should be addressed.