Inorganica Chimica Acta, 76 (1983) L71–L73 L71

Photochemistry of Ruthenium Cluster Carbonyls Supported on Silica Surface. Isolation of Coordinatively Unsaturated Species

YOSHIHARU DOI and KAZUHISA YANO

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Received October 2, 1982

Homogeneous catalysis by transition-metal cluster carbonyls has been extensively investigated both for its mechanistic and synthetic value [1–4]. It has been demonstrated [5–14] that catalytically-active species are formed thermally or photochemically from the original metal cluster carbonyls *via* dissociation of carbon monoxide or metal–metal bond cleavage. In fluid solution such coordinatively unsaturated species react with each other to form inactive large clusters. An approach to this problem seems to be the preparation of surface-stabilized active species by pyrolysis or photolysis of metal cluster carbonyls supported on inorganic oxides. Immobilization of the species on a support may prevent intermolecular reaction resulting in aggregation. Platinum cluster carbonyls adsorbed on a silica surface have been shown to be decarbonylated by pyrolysis under vacuum at 250 °C while keeping the original platinum cluster framework [15]. However, thermal decarbonylation of ruthenium cluster carbonyls on silica at high temperature of 400 °C results in aggregation to yield ruthenium microcrystallites [16]. In this communication we report the photochemical behavior of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ adsorbed on a silica surface, and discuss the nature of surface species formed by photolysis at the low temperature of 25 °C.

Experimental

The ruthenium cluster carbonyls, $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$, were adsorbed from heptane solution onto a non-porous spherical silica (Cabosil) with a specific surface area of 320 m^2 per gram in high dispersion (0.24–0.48 Ru wt.%). The SiO_2 support had been partially dehydroxylated by treatment under vacuum at 300 °C for 4 h. Photolysis of the silica-supported ruthenium cluster carbonyls was carried out at 25 °C under hydrogen or nitrogen in a pyrex infrared cell as follows. A small portion (40 mg) of the supported cluster was pressed into wafer and fitted to a pyrex support, which was placed inside the infrared cell (of 30 mm outside diameter). The infrared cell has two NaCl windows for the measurement of infrared spectra of sample wafers and can work under any controlled atmosphere and temperature. Irradiation of sample wafers was conducted at 25 °C in the infrared cell using a 450-W medium-pressure Hg lamp equipped with pyrex and water filters ($\lambda \geqslant 310$ nm). Infrared spectra of sample wafers were recorded on a Hitachi 295 spectrometer with an optically equivalent silica wafer in the reference beam. Electronic absorption spectra were recorded on a Shimazu MPS-5000 spectrophotometer.

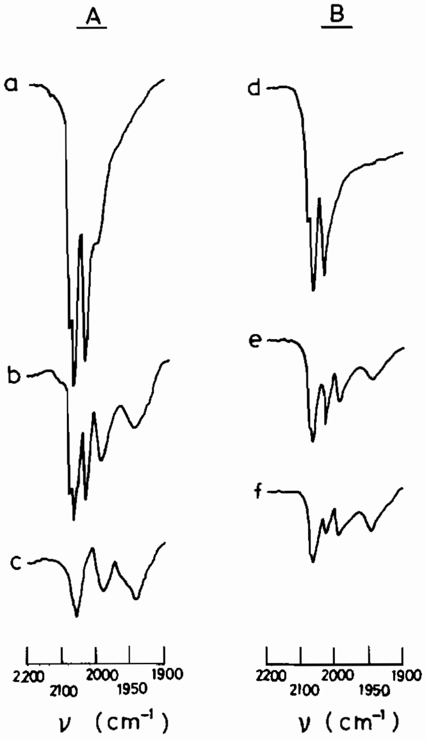


Fig. 1. Infrared spectra of products formed by photolysis of $Ru_3(CO)_{12}/SiO_2$ at 25 °C under hydrogen (A) and nitrogen (B). (a) $Ru_3(CO)_{12}$ supported by adsorption from heptane solution (0.48 wt.% Ru); (b) after irradiation with near-UV light in 200 Torr H_2 for 5 h; (c) after irradiation in H_2 for 20 h; (d) $Ru_3(CO)_{12}$ supported by adsorption from heptane solution (0.24 wt.% Ru); (e) after irradiation with near-UV light in N_2 atmosphere for 5 h; (f) after irradiation in N_2 for 20 h.

Results and Discussion

Figure 1 shows changes of infrared spectra in the carbonyl stretching region of the silica-supported $Ru_3(CO)_{12}$ during irradiation ($\lambda \geqslant 310$ nm) at 25 °C

0020-1693/83/0000-0000/$03.00

TABLE I. Spectroscopic Data for Various Ruthenium Compounds.

Compound	IR ν_{CO}, cm^{-1}	UV-vis λ_{max}, nm	Ref.
$Ru_3(CO)_{12}$ in heptane	2060(vs), 2030(s), 2010(m)	390	this work
$Ru_3(CO)_{12}/SiO_2$	2075(sh), 2063(s), 2031(s), 2000(sh)	330	this work
$Ru(CO)_4/SiO_2$	2060(s), 1990(m), 1945(m)	–	this work
$Ru(CO)_4(PPh_3)$	2061(s), 1986(m), 1954(vs)	n.d.	(21)
$Ru(CO)_4(PPh_2Me)$	2060(s), 1984(m), 1946(vs)	254	(22)
$H_4Ru_4(CO)_{12}$ in heptane	2080(m), 2066(s), 2030(sh), 2025(m), 2005(sh)	366	this work
$H_4Ru_4(CO)_{12}/SiO_2$	2081(m), 2067(s), 2030(sh), 2021(m), 2000(sh)	360	this work

under hydrogen (A) or nitrogen (B). As can be seen in Fig. 1 and Table I, the infrared spectrum (a and d) of $Ru_3(CO)_{12}$ on silica before irradiation is apparently different in peak location from the spectrum of $Ru_3(CO)_{12}$ in heptane solution. A heptane solution of $Ru_3(CO)_{12}$ exhibits an intense maximum at 390 nm (ϵ_m 6500) in the near-UV region attributable to $\sigma \rightarrow \sigma^*$ transition of Ru–Ru bonds in the Ru_3 framework [17]. The lowest energy transition was blue shifted toward 330 nm upon adsorbing $Ru_3(CO)_{12}$ on the surface of silica (see Table I). Such a shift clearly indicates the existence of strong interaction between $Ru_3(CO)_{12}$ and silica surface. However, the position and intensity of the band at 3740 cm^{-1}, associated with hydroxyl groups on the silica surface, was unaffected by the presence of the cluster and remained unchanged during irradiation with UV-visible light. These observations exclude the possibility of the chemical reaction between ruthenium complexes and surface hydroxyl groups.

Photolysis of the silica-supported $Ru_3(CO)_{12}$ under hydrogen caused gradual changes in the infrared spectra, as shown in Fig. 1-A. Spectra b and c were recorded after irradiation for 5 and 20 h respectively, and show a reduction in intensity of the dominant $Ru_3(CO)_{12}$ bands and the appearance of new bands. The original $Ru_3(CO)_{12}$ bands are completely removed after irradiation for 20 h. The final spectrum c shows three bands at 1945, 1990 and 2060 cm^{-1}. The electronic spectrum of the irradiated sample c showed the disappearance of the absorption at 330 nm, suggesting the occurrence of complete Ru–Ru bond scission leading to formation of mononuclear complexes on the surface of silica. As shown in Fig. 1-B, the infrared spectral changes under nitrogen are essentially consistent with those observed under hydrogen, though the rate of spectral changes is slower. It may then be concluded that the same ruthenium species are formed photochemically on the silica surface under hydrogen and nitrogen.

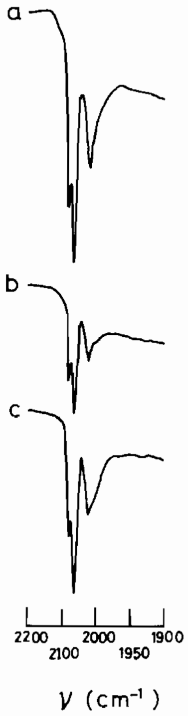
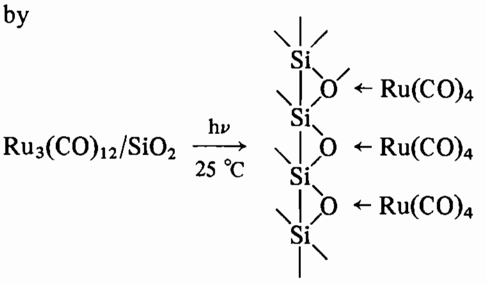


Fig. 2. Infrared spectra of $H_4Ru_4(CO)_{12}/SiO_2$. (a) following adsorption of $H_4Ru_4(CO)_{12}$ from heptane solution (0.24 wt.% Ru); (b) after irradiation with near-UV light in N_2 atmosphere at 25 °C for 20 h; (c) after exposure of 200 Torr CO at 70 °C for 2 hr.

The photochemistry of $Ru_3(CO)_{12}$ in hydrocarbon solvents has been investigated by Johnson *et al.* [18] and Grevels *et al.* [19]. Irradiation of $Ru_3(CO)_{12}$ in solution with near-UV light induces cleavage of Ru–Ru bonds resulting in quantitative formation of monometric $Ru(CO)_4L$ complexes in the presence of appropriate ligand L-like phosphines and olefins. In contrast, prolonged photolysis of Ru_3-

$(CO)_{12}$ in solution under hydrogen or nitrogen atmosphere leads to formation of larger ruthenium cluster carbonyls [20], because of the absence of any appropriate ligands. The surface of silica must stabilize the photogenerated and coordinatively unsaturated species $[Ru(CO)_4]$, which is the principal reactive intermediate in the photochemical and thermal solution substitution reactions, as illustrated by



(1)

The infrared spectrum of the photogenerated Ru species (Fig. 1 and Table I) is nearly identical to those of $Ru(CO)_4L$ ($L = PPh_3$ or PPh_2Me), which again supports the formation of surface-bound $Ru(CO)_4$ species.

Figure 2 shows infrared spectral changes of silica-supported $H_4Ru_4(CO)_{12}$ during irradiation with near-UV light at 25 °C under nitrogen. The infrared and electronic spectra (Fig. 2 a, and Table I) of $H_4Ru_4(CO)_{12}$ on silica are almost identical to those of $H_4Ru_4(CO)_{12}$ in heptane solution, indicating that $H_4Ru_4(CO)_{12}$ adsorbs very weakly on the silica surface. The difference in the adsorption strength of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ on the silica surface may be due to a difference in the molecular structure of both clusters. Photolysis of silica-supported $H_4Ru_4(CO)_{12}$ under nitrogen caused a reduction in intensity of the original $H_4Ru_4(CO)_4$ bands. However, no new bands appeared during the course of irradiation, as can be seen in Fig. 2b. Exposure of the irradiated cluster sample b to carbon monoxide (200 Torr) at 70 °C for 2 h caused an increase in intensity of the original $H_4Ru_4(CO)_{12}$ bands (see Fig. 2c), though the regeneration of carbonyl bands was not completely reversible in the intensity. The observed results suggest that photolysis of $H_4Ru_4(CO)_{12}$ adsorbed on the silica surface induces the dissociation of carbonyl ligands while keeping the Ru_4 cluster framework, leading to the formation of coordinatively unsaturated tetraruthenium cluster as

$$H_4Ru_4(CO)_{12}/SiO_2 \underset{70\ ^\circ C,\ +CO}{\overset{h\nu,\ -CO}{\rightleftarrows}} H_4Ru_4/SiO_2 \qquad (2)$$

We could not detect the intermediate species as $H_4Ru_4(CO)_{12-x}$ present in the photochemical decarbonylation process on the infrared spectra.

In solution photochemistry of larger clusters where one metal is bonded to more than three other metal atoms, it has been demonstrated [10, 23, 24] that cluster photofragmentation is inhibited to reform the metal–metal bond and ligand photosubstitution is a common reaction pathway. For example, $H_4Ru_4(CO)_{12}$ in solution has been shown to yield $H_4Ru_4(CO)_{11}L$ upon photolysis of 366 nm light in the presence of ligand L as $P(OMe)_3$ or PPh_3 [10]. Then, it is reasonable to assume that photodissociation of CO from $H_4Ru_4(CO)_{12}$ takes place on the surface of silica without breaking up the tetraruthenium cluster framework.

The results obtained indicate that silica surface is capable of isolating reduced coordination number species as the intermediate in the photochemical solution reactions.

Acknowledgement

We thank Professors T. Keii and Y. Ono for valuable discussion.

References

1 E. L. Muetterties, *Science, 196,* 839 (1977).
2 A. K. Smith and J. M. Basset, *J. Mol. Catal., 2,* 279 (1977).
3 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker and W. R. Pretzer, *Chem. Rev., 79,* 91 (1979).
4 R. M. Laine, *J. Mol. Catal., 14,* 137 (1982).
5 J. B. Keister and J. R. Shapley, *J. Organomet. Chem., 85,* C29 (1975);
J. Am. Chem. Soc., 98, 1056 (1976).
6 M. Valle, D. Osella, G. A. Vaglio and M. Valle, *Inorg. Chim. Acta, 20,* 213 (1976).
7 R. C. Ryan, C. U. Pittman, Jr., and J. P. O'Conner, *J. Am. Chem. Soc., 99,* 1986 (1977).
8 A.J. Sivak and E. L. Muetterties, *J. Am. Chem. Soc., 101,* 4878 (1979).
9 J. L. Graff, R. D. Sanner and M. S. Wrighton, *J. Am. Chem. Soc., 101,* 273 (1979).
10 J. L. Graff and M. S. Wrighton, *J. Am. Chem. Soc., 102,* 2123 (1980).
11 J. Vidal and W. E. Walker, *Inorg. Chem., 19,* 896 (1980).
12 H-K. Wang, H. W. Choi and E. L. Muetterties, *Inorg. Chem., 20,* 2661 (1981).
13 Y. Doi, K. Koshizuka and T. Keii, *Inorg. Chem., 21,* 2732 (1982).
14 Y. Doi, S. Tamura and K. Koshizuka, *Inorg. Chim. Acta, 65,* L63 (1982).
15 M. Ichikawa, *J. Chem. Soc., Chem. Commun.,* 11 (1976); *Chem. Lett.,* 335 (1976).
16 V. L. Kuznetsov, A. T. Bell and Y. I. Yermakov, *J. Catal., 65,* 374 (1980).
17 D. R. Tyler, R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc., 100,* 7888 (1978).
18 B. F. G. Johnson, J. Lewis and M. V. Twigg, *J. Organomet. Chem., 67,* C75 (1974).
19 F-W. Grevels, J. G. A. Reuvers and J. Takats, *J. Am. Chem. Soc., 103,* 4069 (1981).
20 K. Yano and Y. Doi, unpublished data.
21 R. Hug, A. J. Poë and S. Chawla, *Inorg. Chim. Acta, 38,* 121 (1980).
22 D. K. Liu and M. S. Wrighton, *J. Am. Chem. Soc., 104,* 898 (1982).
23 B. F. G. Johnson, J. W. Kelland, J. Lewis and S. K. Rehani, *J. Organomet. Chem., 113,* C42 (1976).
24 H. C. Foley and G. L. Geoffroy, *J. Am. Chem. Soc., 103,* 7176 (1981).