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EVIDENCE IN THE FORMATION OF HEXACOBALT CARBONYL SPECIES ON OXIDE SUPPORTS

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Interaction between $Co_2(CO)_8$ and TiO_2, NaY zeolite, or dehydroxylated alumina resulted in the formation of a surface cobalt cluster carbonyl whose structure is probably $[Co_6(CO)_{16-n}(L_s)_n]$(L_s : the surface O^{2-} or OH group). On the alumina the cluster was observed only at the limited Co loadings. On the zeolite the formation of $[Co(CO)_4]^-$ and $[Co_6(CO)_{15}]^{2-}$ were also presumed.

Recently, a method of catalyst preparation by means of the reactions between metal carbonyl compounds and oxide supports has greatly attracted many workers, since a wide variety of novel catalysts such as fixed metal carbonyls, anchored metal ions, supported ultra-dispersed metals etc. can be prepared by the method. The resulting catalysts often show remarkable catalytic activities and selectivities in various reactions especially in the hydrogenation of CO, CO_2, olefins, etc. In this field interest has been focused not only on the catalysis but also on the chemistry in the catalyst preparation to answer the questions what kind of surface species can be prepared from a certain starting metal carbonyl by the selection of preparation conditions and support materials.[1-11] In the previous paper we reported the evidence in the formation of the surface di- and tetracobalt carbonyl species **2** and **3** (see later) by the reaction between $Co_2(CO)_8$ and γ-Al_2O_3 or SiO_2 under certain conditions.[12]

This paper describes the chemistry of $Co_2(CO)_8/TiO_2$, NaY, or γ-Al_2O_3 at the limited conditions and reports the evidence in the formation of multinuclear cobalt carbonyl species on the supports which have not been reported in the heterogeneous system and are not common even in homogeneous systems.

$Co_2(CO)_8$(from Alfa-Products) was purified by recrystallization and used as a pentane solution (ca. 10 μmol cm^{-3}). NaY, TiO_2, and γ-Al_2O_3 supports were JRC-Z-1, JRC-TIO-1, and JRC-ALO-4 (the reference catalysts supplied from Catalyst Society of Japan), respectively. BET surface areas of the respective supports were 650, 70, and 175 $m^2 g^{-1}$. The TiO_2 was almost anatase in structure and contained 3.64% SO_4^{2-}. Another TiO_2(surface area = 30 $m^2 g^{-1}$) which was designated as TiO_2 (r) was prepared by the hydration of $TiCl_4$, followed by air calcination at 550 °C for 2 h. It was almost rutile in structure and did not contain sulfur. Before the impregnation of $Co_2(CO)_8$ the supports were heated *in situ* in flowing helium for 1 h at 950 °C for γ-Al_2O_3 or at 500 °C for the other supports. The resulting alumina (160 $m^2 g^{-1}$) was almost fully dehydroxylated γ-Al_2O_3 and was designated as γ-Al_2O_3(DA). Ultra pure helium used as a carrier gas was obtained by the purification method described in our previous paper.[12]

The impregnation of $Co_2(CO)_8$(**1**) onto the preheated supports was done at 25 °C by injection of the pentane solution of 1 with a gas-tight syringe, followed by evaporating the solvent in flowing helium. The resulting solid was decomposed at 25 °C for 1 h and then used in TPDE (temperature programmed decomposition) experiments. The gases evolved during the impregnation and decomposition were analyzed by the method developed by Burwell et al.[1)] The samples used in IR studies were prepared by the same manner described above except that the support was used as a disk (ca. 50 mg). The IR spectra were recorded on a JASCO FT/IR-3 spectrometer at room temperature.

Table 1. Compositions of the Surface Carbonyls in $Co_2(CO)_8$/Oxides[a,b)]

Sample No.	Support	Co loading wt%	Average composition of surface Co carbonyls
I	TiO_2	2.0	$Co(CO)_{2.75\pm0.1}$
II	NaY	1.5	$Co(CO)_{2.8\pm0.1}$
III	γ-Al_2O_3 (DA)	0.4	$Co(CO)_{3.0\pm0.05}$
IV		3.0	$Co(CO)_{2.9\pm0.1}$
V		4.5	$Co(CO)_{2.7\pm0.1}$

a) After the decomposition at 25 °C for 1 h. b) Only CO was evolved during the impregnation and decomposition.

The average compositions of the surface cobalt carbonyls in the 1/oxide samples decomposed at 25 °C for 1 h are listed in Table 1. The TPDE and IR spectra of the samples are shown in Figs 1 and 2, respectively. We can see in Fig. 1 six different TPDE peaks which are designated as P1 - P6, respectively. The results indicated that the structures of the surface carbonyl species are strongly influenced not only by the nature of the supports but also by the loading of cobalt. It is especially interesting that the TPDE spectra of three 1/γ-Al_2O_3(DA) samples with 0.4, 3.0, and 4.5 wt% Co are distinctly different each other and are characterized by the major peaks P5, P3, and P2, respectively, suggesting that the structures of the major surface carbonyls in the respective samples are completely different. What are the structures of the surface cobalt carbonyls which correspond to P1 - P6?

In the previous paper we showed that P5 and P3 corresponded to the decomposition peak of $[Co_2(CO)_6(L_s)_2]$ (2) on γ-Al_2O_3 and that of $[Co_4(CO)_{12-m}(L_s)_m]$(m = 0 - 2) (3) on γ-Al_2O_3 or SiO_2, respectively (L_s denotes the ligand (O^{2-} or OH group) on the surface of the supports in this paper). It can therefore by presumed that both 1/TiO_2 and 1/TiO_2(r) have 3 as a minor surface species. P1 can be assigned to free $Co_2(CO)_8$ which was physically deposited on Sample V or the wall of the reactor because of the following reasons. P1 was observed only for

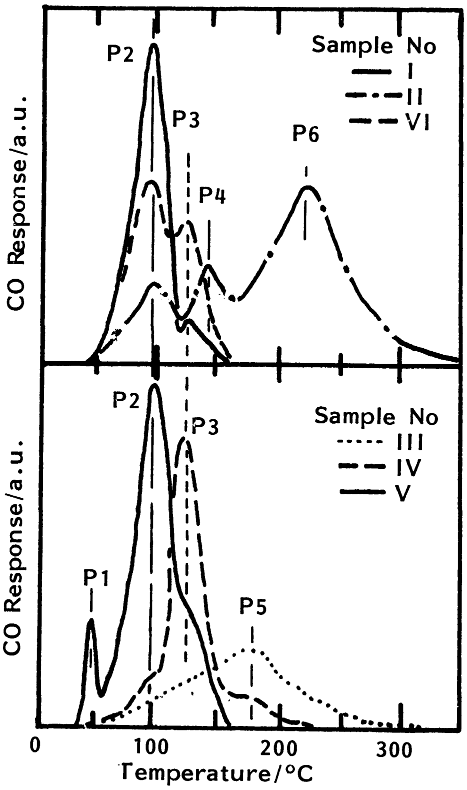

Fig. 1. TPDE Spectra of the $Co_2(CO)_8$/Oxides.

Sample I-V: see Table1, Sample VI: $Co_2(CO)_8$/TiO_2(r), 1.5% Co, Raising rate of the temperature: 2 °C min^{-1}, Flow rate of helium: 20 cm^3min^{-1}

extremely high loading samples such as 4.5% **1**/Al_2O_3(DA) and disappeared when the sample was previously washed with pentane. An IR study showed that the resulting pentane solution contained **1**. One experiment showed that the TPDE spectrum of **1**/silica wool gave a peak P1. The presence of **1** and/or **3** in Samples I and V was confirmed by the IR spectra with a weak band ν_4 around 1865 cm^{-1} which is the characteristic band of μ^2-CO in **1** or **3** (see Fig. 2).

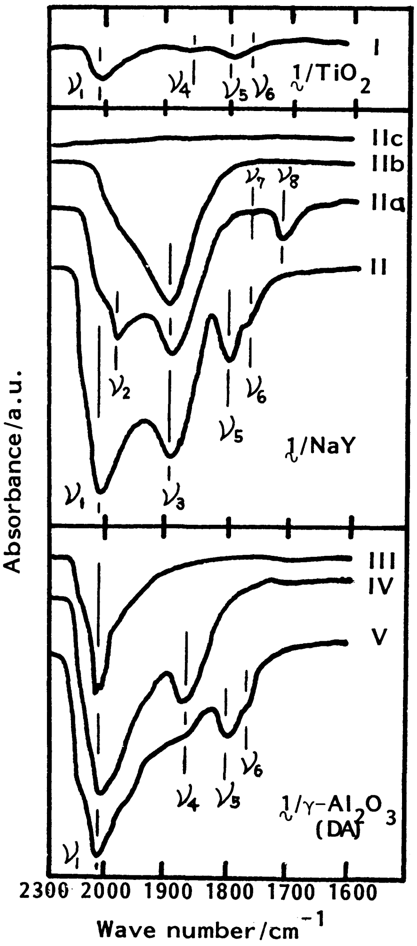

Fig. 2. IR spectra of the $Co_2(CO)_8$/oxides decomposed at 25 °C (I-V), at 100 °C(IIa), at 200 °C (IIb), or above 300 °C (IIc).

The spectra I-V correspond to Samples I-V in Table 1, respectively. The backgrounds or the spectra of the supports were eliminated by a computing system equipped with the spectrometer.

Assignments of the structures of the surface carbonyl species which correspond to the other TPDE peaks, P2, P4, and P6 were attempted to be done mostly by IR studies. The following results and discussion suggest that there is a surface cobalt cluster carbonyl species $[Co_6(CO)_{16}]_{ads}$ (**4**) or $[Co_6(CO)_{16-n}(L_s)_n]$(n=0 or small values) (**5**) in Samples I, II, and V, and that P2 corresponds to the decomposition of the cluster. The IR spectra of Samples I, II, and V which would give the TPDE peak P2 have common absorption bands ν_5 (1807 cm^{-1}), ν_6 (1770 cm^{-1}), and ν_1 (2020-2100 cm^{-1}). The wave numbers of ν_5 and ν_6 are in fair agreement with those of the characteristic bands (1806, 1772 cm^{-1}) of μ^3-CO in $Co_6(CO)_{16}$ (6).13) ν_1 can be ascribed to the band of the terminal CO in neutral cobalt carbonyl compounds such as **1**, **3**, **6**, etc. It is known that 6 decomposes around 100 °C. P2 was observed also around 100 °C. The bands ν_5 and ν_6 completely disappeared when the samples were heated above 100 °C (see the IR spectrum IIa, for example). The chemical results shown in Table 1 indicate that the composition of the surface carbonyl species in Samples I and V which give almost pure P2 in the TPDE spectra is close to that of **6** or $Co(CO)_{2.67}$. However, the chemical results were not accurate enough to determine whether some of the CO ligands in **4** are displaced by the surface ligands L_s(O^{2-} or OH) or not. It may therefore be better to assume that the surface cluster is **5**.

Sample II gives a strong band ν_3(1880-1900 cm^{-1}) which is attributable to the characteristic band of $[Co(CO)_4]^-$ (**7**).13) It has been known that the interaction between **1** and the bases sush as ethanol, pyridine, etc. gives rise to a complex $[Co(B)_x]^{2+}([Co(CO)_4]^-)_2$ (**8**).13) Therefore, we might suggest that Sample II has another surface complex such as $\{[Co(L_s)_y]^{2+}([Co(CO)_4]^-)_2\}$ (**9**) which might be formed by the interaction beteween **1** and the surface basic ligands L_s in the zeolite. The chemical results in Table 1 is not inconsistent with this assumption.

When Sample II was heated at 100 °C,the intensity of ν_3 decreased to some extent and new IR bands ν_2(1980-2000 cm^{-1}), ν_7 (1960-1780 cm^{-1}), and ν_8(1720 cm^{-1}) appeared as Spectrum IIa shows. The adsorption of CO to the resulting sample at 25 °C restored ν_1 and ν_5 bands without any change of the other bands. Chini reported that $\{[Co(B)_x]^{2+}[Co_6(CO)_{15}]^{2-}\}$ (**10**) which has the characteristic IR bands around 1980, 1780, and 1735 cm^{-1} was obtained by pyrolysis of **8** near 60 °C. Therefore, ν_2 and ν_8 (also ν_7) might be ascribed to the bands of the terminal CO and μ^3-CO, respectively, in $[Co_6(CO)_{15}]^{2-}$ (**11**) which was presumably formed from **7** in **9**, probably in the supercage of the zeolite. When Sample II was heated above 160 °C, ν_2, ν_7, and ν_8 disappeared but the intensity of ν_3 remained almost constant. ν_3 vanished above 350 °C. These results suggest that the TPDE peaks P4 and P6 correspond to the decompositions of **11** and **7** in the zeolite, respectively.

Consequently, our results strongly suggest the evidence in the formation of the surface Co_6-cluster, $[Co_6(CO)_{16-n}(L_s)_n]$ and $[Co_6(CO)_{15}]^{2-}$ on the applied oxides under the limited conditions.

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References

1) R.L. Burwell, Jr., and A. Brenner, J. Am. Chem. Soc., 97, 2565 (1975); J. Catal., 52, 364 (1978); F. Correa, R. Nakamura, R.E. Stimon, R.L. Burwell, Jr., and D.F. Shriver, J. Am. Chem. Soc., 102, 5112 (1980).
2) R. Nakamura and R.L. Burwell, Jr., J. Am. Chem. Soc., 103, 673 (1981).
3) M. Ichikawa, Chem. Commun., 1976, 26; 1978, 566; Bull. Chem. Soc. Jpn., 51, 2268 , 2273 (1978); M. Ichikawa and K. Shikakura, Proc. 7th Int. Congr. Catal., B, 1980, 925.
4) A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bilhou-Bougnol, and W.F. Graydon, Inorg, Chem. 18, 3104 (1979); F. Huges, P. Bussiere, J.M. Basset, D. Commereuc, Y. Chauvin, L. Bonneviot, and D. Olivier, Proc. 7th Int. Congr. Catal., A, 1980, 402.
5) A. Kazusaka and R.F. Howe, J. Mol. Catal., 9, 183, 199 (1980).
6) P. Gelin, Y.B. Taarit, and C. Naccache, 59, 357 (1979).
7) H. Knozinger and Y. Zhao, J. Catal., 71, 337 (1981).
8) V.L. Kuznetov, A.T. Bell, and Y.I. Yermakov, J. Catal., 65, 374 (1980); A.S. Lisitsyn, A.V. Golovin, V.O. Kuznetov, and Y.I. Yermakov, React. Kinet. Catal. Lett., 19, 187 (1982).
9) H.E. Ferkul, D.J. Stanton, J.D. McCown, and M.C. Bird, Chem. Commun., 1982, 955.
10) K. Tanaka, K.L. Watters, and R.F. Howe, J. Catal., 75, 23 (1982).
11) Y. Iwasawa, M. Yamada, S. Ogasawara, Y. Sato, and H. Kuroda, Chem. Lett., 1983, 621.
12) R. Nakamura, A. Oomura, N. Okada, and E . Echigoya, Chem. Lett., 1982, 1463.
13) P. Chini, Chem. Commun., 1967, 29, 440.

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