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SURFACE SUBCARBONYLS IMPREGNATED BY THE REACTIONS BETWEEN $Co_2(CO)_8$ AND γ-Al_2O_3 OR SiO_2

Ryuichi NAKAMURA,† Akihiro OOMURA, Norio OKADA, and Etsuro ECHIGOYA
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku , Tokyo 152

Some different surface subcarbonyls such as $[Co_4(CO)_{12}]_{ads.}$, $[Co_2(CO)_6B_2]$, and $[Co(CO)_3B]_2$, ($B = O_2^-$, OH^- on the supports, were observed in the impreganation of $Co_2(CO)_8$ with preheated γ-Al_2O_3 and SiO_2 supports at 298 K. Their relative concentrations distinctly depend on the Co loading as well as the support.

There has been recent interest throughout the world in catalysts derived from the reactions between metal carbonyls and oxides such as alumina, silica, etc., because those catalysts often show conspiciously high catalytic activities and characteristic selectivities in different catalytic reactions.[1-7]

Since Burwell and his co-workers have studied the reactions between the carbonyls such as $Mo(CO)_6$,[3-6] $Ni(CO)_4$[8], etc., and the suitably preheated γ-Al_2O_3 and pointed out the importance in quantitative analysis of gases (CO, CH_4, H_2, etc.) evolved during the preparation of those catalysts, the interest has encompassed not only preparation techniques for various supported metal,[6-10] metal ion[4], and metal carbonyl catalysts,[1-4] but also the chemistry of metal carbonyl compounds on oxide supports.[3,6-8,10-16]

Our interest has been focused on the reactions between $Co_2(CO)_8$ and oxides such as γ-Al_2O_3, SiO_2 and the catalytic properties of the resulting products. It is well known that $Co_2(CO)_8$ is an important catalyst precursor in various homogeneous reactions, while the fixations of the carbonyl on supports have been required to obtain more stable immobilized catalysts. However, studies on the reactions between $Co_2(CO)_8$ and oxides have not been reported although there have been a few reports which have described the outlines on the catalytic properties of some supported $Co_2(CO)_8$ catalysts.[5,12] In this paper we report the chemistry and behaviors in the reactions between $Co_2(CO)_8$ and suitably dehydroxylated γ-Al_2O_3 and SiO_2 supports, which were studied by adsorption experiment, gas-analysis, IR spectroscopy and by applying the TPDE (temperature programmed decomposition) technique, discussing the effects of the Co loading and the sorts of the supports used.

The alumina (60-80 mesh) used as a support was JRC-ALO-4 (a reference catalyst from Catalysis Society of Japan). Before impregnation of $Co_2(CO)_8$ it was preheated *in situ* in flowing helium at 773 K or 1223 K for 1 h to obtain partially dehydroxylated alumina (PDA), or fully dehydroxylated alumina (DA). PDA was γ-Al_2O_3 having roughly 4 OH^-, 5 O^{2-}, and 5 Al^{3+} per nm^2 on its surface. DA was γ-Al_2O_3 containing a small amount of δ-Al_2O_3 and had no OH^-. The specific surface areas of PDA and DA were ca. 175 and 160 m^2g^{-1}, respectively. The silica gel (60-80 mesh) used as a support was prepared by air calcination of Snowtex O (Nissan Chemicals Co., Ltd.) at 773 K for 2 h. It was also preheated *in situ* at 773 K for 1 h to obtain partially dehydroxylated silica gel (PDS). The specific surface area of PDS was ca. 190 m^2g^{-1}. $Co_2(CO)_8$ was obtained from Alfa-Products Co., Ltd.. It was pruified by recrystallizations from its pentane solution and impregnated on the supports from its pentane solution (ca. 10 mol cm^{-3}). The purity of $Co_2(CO)_8$ in the solution used was more than 99 %. The pentane used as the solvent was purified by repeated distribution over Molecular Sieves. Ultra pure helium (O_2 < 0.03 ppm) which was used as a carrier gas was obtained by passing through a column of Molecular Sieves 13X at 77 K, followed by a Mn^{2+}/ SiO_2 trap at room temperature.[8)]

The impregnations of $Co_2(CO)_8$ onto the suitably preheated supports were done at 273 or 298 K by injection of the solution of $Co_2(CO)_8$ with a gas-tight syringe, followed by evaporating the solvent in flowing helium. The resulting solids were decomposed in flowing helium at the same temperatures, and then used in TPDE experiments. The gases evolved during the impregnation and decomposition steps were analyzed by the technique which had been developed by Burwell and his coworkers.[8)] The TPDE experiments were done in flowing helium (20 $cm^3 min^{-1}$), according to a conventional temperature-programmed-desorption technique. In each experiment, 0.25 g of the support was used. The samples used in IR studies were prepared by the same manners described before except that the oxide support was used as a disk (ca. 50 mg). The IR spectra of the samples were recorded on a Hitachi EPI-G3 spectrometer at room temperature.

Table 1 Evolution of CO during $Co_2(CO)_8$ impregnation at 273 or 298 K

loading /wt% Co	time[a)] /min	(CO evolved/$Co_2(CO)_8$ used)[b)] on PDA 273K[f)]	on PDA 298K	on DA 273K	on DA 298K	on PDS[c)] 273K
0.5	30	2.02	2.04	2.00	2.03	1.65
	120	2.03	2.04	2.02	2.03	2.00[e)]
	180	2.03	2.05	2.04	2.05	2.25[e)]
2.0[d)]	30	-	1.90	-	1.85	g
	120	-	2.10	-	2.25	-
	180	-	2.20	-	2.20	-
	300	-	2.23	-	2.25	-

a) start after the solvent was evaporated, b) mol ratios; interactions (see text): c) "WIS", d) "SIS" followed by "WIS", others "SIS"; experimental errors: e) ±0.10, others ±0.05, f) by a single run, others by several runs, g) The sublimation of $Co_2(CO)_8$ was observed. -not measured

Behaviors in adsorption of $Co_2(CO)_8$ onto the supports from the pentane solution

When 1.0 cm^3 of the pentane solution of $Co_2(CO)_8$ was introduced at 298 K onto 0.25 g of PDA or DA the color of the support immediately turned brown, while the solution became clear in several minutes. During this short period, the evolution of CO was observed. We term this fast adsorption as " strong interaction with the support" or "SIS". In similar experiments with 4.0 cm^3 of the solution "SIS" was also observed; however the solution remained orange for several hours, at least. When the unadsorbed $Co_2(CO)_8$ was deposited onto the solid by evaporating the solvent at 298 K the additional evolution of CO was observed. We term the reaction of this type as " weak interaction with support" or "WIS". More detail quantitative adsorption experiments have revealed that the saturation points of "SIS" for PDA and DA are at 1.5±0.2 and 1.3±0.2 wt% Co, or about 0.43 and 0.41 $Co_2(CO)_8$ molecules per nm^2, respecively. It is worth noting that the saturation points hardly depend on the concentration of OH^- on the support. When PDS was used as a support only "WIS" was observed even at low loadings (0.1 - 1.0 wt% Co.), indicating the capacity of PDS for "SIS" is less than 6 x 10^{-3} $Co_2(CO)_8$ molecules per nm^2. An experiment with a high loading PDS (1.5 wt% Co) showed the sublimation of $Co_2(CO)_8$ from the sample during the evaporation of the solvent. Thus, detail experiments on the characterization of these systems were mostly done with 0.5 wt% Co/PDS, /PDA, /DA and 2.0 wt% Co/PDA or /DA.

Characterization of the $Co_2(CO)_8$ impregnated samples

During the impregnation of $Co_2(CO)_8$ and decomposition of the resulting products at 273 or 298 K, the amount of CO evolved was measured. No other gases such as H_2, CH_4, and other hydrocarbons were evolved, although a very small amount of CO_2 was detected for 2.0 wt% Co/PDS and /PDA. The ratios of CO evolved to $Co_2(CO)_8$ used were listed in Table 1. The table shows that almost exactly two CO molecules per one $Co_2(CO)_8$ complex are liberated from 0.5 wt% Co/PDA and /DA, suggesting that "SIS" yields the relatively stable surface subcarbonyl species formally expressed as $[Co(CO)_3]_{n\ ads}$. The table indicates that the average compositions of the subcarbonyl species on 2.0 wt% Co/PDA, /DA and 0.5 wt%

Co/PDS are formally represented by [Co(CO)$_{3-x}$]$_m$ ads. where x is within ± 0.35, gradually increasing with the time course of the decomposition.

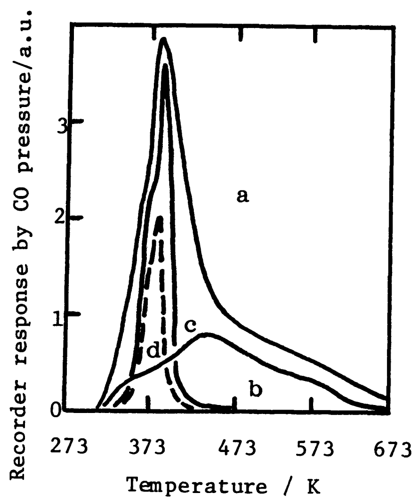


Fig. 1 TPDE spectra of $Co_4(CO)_{12}$ and the $Co_2(CO)_8$ impregnated DA and PDS

a 2.0%Co/DA, b 0.5%Co/DA, c 0.5%Co/PDS, d $Co_4(CO)_{12}$ solid, The impregnated samples were decomposed in flowing helium at 298 K for 2 h, and the temperature was then raised with a rate of 2 deg min^{-1}.

Fig. 1 compares the TPDE spectra of the different samples which have already lost approximately two CO per $Co_2(CO)_8$ by the impregnation at 298 K. 0.5 wt% Co/PDS ([Co(CO)$_{3.05}$]$_m$ /PDS) as well as a reference sample ($Co_4(CO)_{12}$) gives a sharp response around 388 K. This evidence implies the presence of $Co_4(CO)_{12}$ on PDS. Yermakov et al. have studied the IR spectra of different catalysts derived from $Co_2(CO)_8$ and indicated the presence of $Co_4(CO)_{12}$ with a small amount of $Co_2(CO)_8$ on the $Co_2(CO)_8$-impregnated SiO_2 (4.1 wt% Co).[5)] The agreement between our results and Yermakov's result indicates that a major subcarbonyl species on the impregnated PDS (0.5 - 4 wt% Co) is $Co_4(CO)_{12}$ although its concentration slightly varies with the time of the decomposition.

The TPDE spectrum of 0.5 wt% Co/DA ([Co(CO)$_{3.0}$]$_n$/DA) is distinctly different from that of 0.5 wt% Co/PDS or $Co_4(CO)_{12}$ suggesting the absence of $Co_4(CO)_{12}$ on it. A similar result was obtained with 0.5 wt% Co/PDA. Therefore, we assume that n = 2 or that the subcarbonyl species on 0.5 wt% Co/DA and /PDS is [$Co_2(CO)_6B_2$], where B is surface O^{2-} or OH^- on the supports. Interestingly, the TPDE spectrum of 2.0 wt% Co/DA ([$Co_2(CO)_{2.95}$]$_m$/DA) comprizes the response by 0.5 wt% Co/PDA and that by 0.5 wt% Co/DA. These results indicate that 2.0 wt% Co/DA has, at least, two different subcarbonyls; probably, they are adsorbed $Co_4(CO)_{12}$ and ligated [$Co_2(CO)_6B_2$].

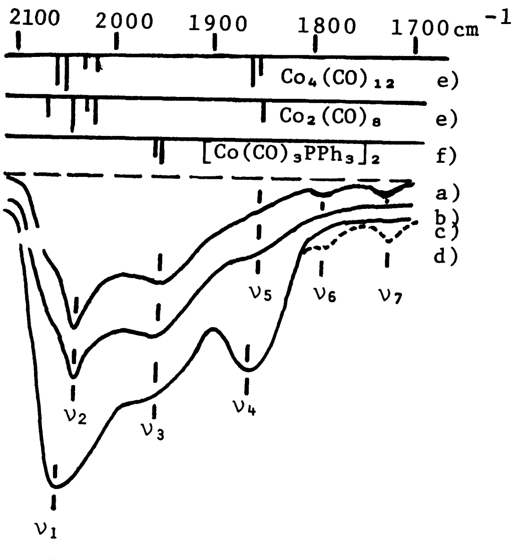


Fig.2 IR spectra of the $Co_2(CO)_8$ impregnated PDA and DA

a 0.5%Co/PDA b 0.5%Co/DA, c 2.0%Co/DA d 2.0%Co/PDA, These samples were decomposed in flowing helium at 298 K for 1 h after the impregnations.
ν_1 2070, ν_2 2050, ν_3 1950, ν_4 1870
ν_5 1855, ν_6 1795, ν_7 1715 cm^{-1}
e) in pentane, f) solid in KBr

Fig. 2 shows the IR spectra of the different impregnated samples. It was confirmed that the spectrum of the impregnated PDS was close to that reported by Yermakov,[5)] which implies that the subcarbonyl species on PDS is $Co_4(CO)_{12}$. From the IR spectroscopical observation, we could suggest on the characterization of the surface subcarbonyls impregnated as follows.

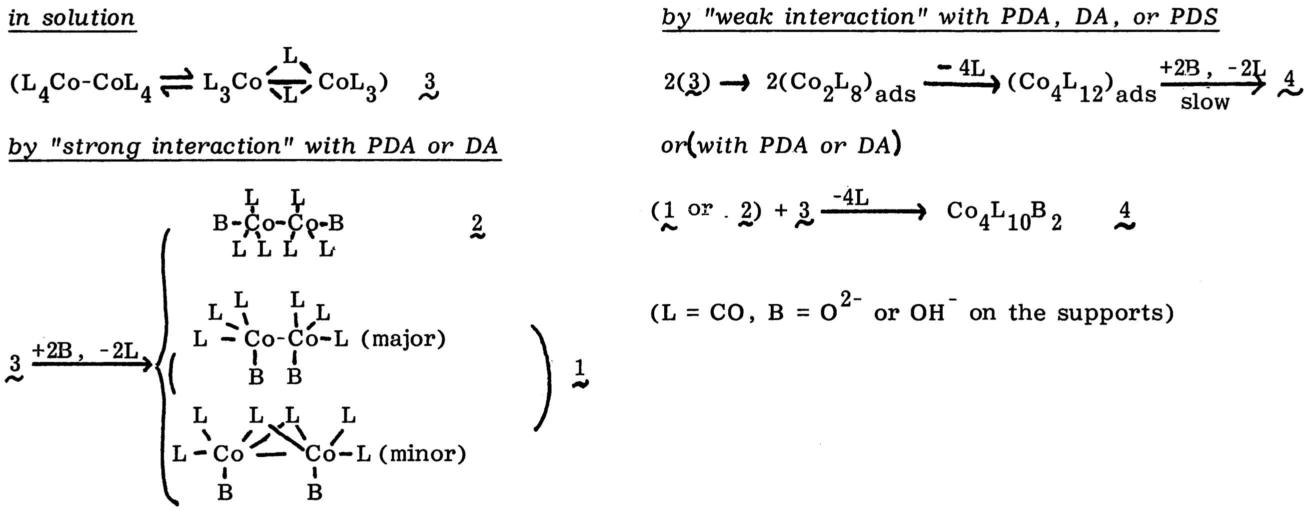
(1) The effect of the Co loading is remarkable. Both 0.5 wt% Co/PDA and / DA have relatively strong ν_2 and ν_3 bands and a weak ν_5 band. The ν_2 and ν_5 bands are attributable to [$Co_2(CO)_6B_2$], **1**, of which structure is similar to that of $Co_2(CO)_8$ although the concentrations of μ^2-CO ligands in these comlexes are different (It has been known that the ratio of μ^2-CO/terminal CO in $Co_2(CO)_8$ is affected by envioroments), while the ν_3 band can be ascribed to [$Co(CO)_3B$]$_2$, **2**, of which structure is analogeous to that of [$Co(CO)_3PPh_3$]$_2$ (see later). On the contraray, the stpectra of the other samples are characterized by a couple of strong bands (ν_1 and ν_4) , indicating the presence of $Co_4(CO)_{12}$

on their surfaces as expected by the results described before.

(2) $[Co(CO)_3PPh_3]_2$ gives a strong absorption band of which frequency is very close to that of the ν_3 band. Vohler has studied the structures of various complexes having $Co(CO)_3$ and/or $Co(CO)_4$ groups by IR spectroscopy and shown that no compounds except $[Co(CO)_3PPh_3]_2$ have absorption bands between 1900 and 2000 cm^{-1}.17) Therefore, we assume that the surface complex giving the ν_3 bands resembles $[Co(CO)_3PPh_3]_2$ whose structure is characterized by point group D_{3h} or D_{3d}.

(3) These are no big differences between the same loading samples from PDA and DA, except that either sample from PDA has a couple of very weak additional new bands (ν_6 and ν_7) which may due to some interaction between some of the surface subcarbonyl species and the OH groups on PDA.

In summary, we suggest that the following reactions are possible during the impregnation of $Co_2(CO)_8$ onto the preheated alumina or silica supports.



in solution

$(L_4Co{-}CoL_4 \rightleftharpoons L_3Co\overset{L}{\underset{L}{\rightleftharpoons}}CoL_3)$ 3

by "strong interaction" with PDA or DA

by "weak interaction" with PDA, DA, or PDS

$2(3) \rightarrow 2(Co_2L_8)_{ads} \xrightarrow{-4L} (Co_4L_{12})_{ads} \xrightarrow[\text{slow}]{+2B,\ -2L} 4$

or (*with PDA or DA*)

$(1 \text{ or } 2) + 3 \xrightarrow{-4L} Co_4L_{10}B_2$ 4

($L = CO$, $B = O^{2-}$ or OH^- on the supports)

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