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SURFACE TRIIRON CARBONYLS SUPPORTED BY THE REACTIONS OF $Fe_3(CO)_{12}$ WITH γ-Al_2O_3 OR SiO_2

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It is shown by means of Extended X-ray Absorption Fine Structure (EXAFS), IR and UV spectroscopies and by temperature programmed decomposition(TPDE) and gas phase analyses that $Fe_3(CO)_{12}$ reacted with the surface OH group of γ-Al_2O_3 to give the surface complex, $Fe_3(CO)_{10}$(H)(OAl<), while $Fe_3(CO)_{12}$ was weakly supported on SiO_2 retaining its original structure and chemical nature.

Supported metal carbonyl clusters have collected much attention from catalytic chemical interests of the assembly of metal atoms highly dispersed on inorganic supports as well as in connection with a new chemistry in the interface between homogeneous and heterogeneous systems.$^{1)}$ In the present paper, in contrast to the behaviour of $Fe_3(CO)_{12}$ on η-Al_2O_3,$^{2)}$ the formation of $Fe_3(CO)_{12}$(H)(OAl<) by the reaction of $Fe_3(CO)_{12}$ with a pretreated γ-Al_2O_3 is reported, while $Fe_3(CO)_{12}$ was weakly supported on SiO_2 keeping its original structure.

The reaction of $Fe_3(CO)_{12}$ with γ-Al_2O_3(surface area: 150 m^2g^{-1}) or SiO_2(500 m^2g^{-1}) was performed by a dry mixing method, followed by 2 h-ageing at 313 K under vacuum. The γ-Al_2O_3 and SiO_2 were pretreated at 573 and 473 K for 2 h in dry air, respectively. The EXAFS spectra were taken in a laboratory system equipped with a high power rotating-anode X-ray generator in a flow of high purity (99.9995 %) N_2 at atmospheric pressure.$^{3)}$ The EXAFS data were analyzed by an empirical curve-fitting method using empirical amplitude and phase shift parameters.$^{4)}$ The UV diffuse reflectance and IR spectra were measured under vacuum in suitable cells combined with a closed circulating system.

When $Fe_3(CO)_{12}$ was supported onto SiO_2, no decarbonylation occurred. The TPDE$^{5)}$ curve of the SiO_2-supported $Fe_3(CO)_{12}$ cluster was much the same as pure $Fe_3(CO)_{12}$ showing a single CO peak at 387 K. IR absorption peaks of 2045, 2025 and 1997 cm^{-1} for terminal CO of $Fe_3(CO)_{12}$ supported on SiO_2 and their relative intensities were very close to those of pure $Fe_3(CO)_{12}$ in Table 1. The similarity of the $Fe_3(CO)_{12}/SiO_2$ and the pure cluster in the $\sigma \longrightarrow \sigma^*$ and $\sigma^{*\prime} \longrightarrow \sigma^*$ transition energies relating to the Fe-Fe bonding,$^{6)}$ 22.2 and $16.3\text{x}10^3 cm^{-1}$, and 22.2 and $16.4\text{x}10^3 cm^{-1}$, respectively, in Table 2, indicates that both clusters have electronically same triangular Fe_3-skeleton. The Fe-Fe bond distance(0.264

Table 1. IR data(ν_{CO}) of supported and pure clusters

carbonyls	ν_{CO} wave number / cm^{-1}
$Fe_3(CO)_{12}$	2047(vs), 2031(vs), 2001(vs), 1856(w-m), 1821(m)
$Fe_3(CO)_{12}/SiO_2$	2045(vs), 2025(vs), 1997(vs)
$Fe_3(CO)_{12}$/Aerosil	2053(vs), 2030(s), 2000(s,sh)
$Fe_3(CO)_{10}(H)(OAl<)^a$	2077(m), 2050(m), 2025(s), 2005(vs), 1955(sh,br)
$Fe_3(CO)_{10}(H)(OAl<)^b$	2088(m), 2063(m), 2020(s,sh), 2005(vs), 1950(sh,br)
$[Fe_3(CO)_{11}H]^-Al(O-)_x^+$ c	2075(w,sh), 2005(s,br)
$Os_3(CO)_{12}$ d	2069(vs), 2035(vs), 2015(m), 2000(m)
$Os_3(CO)_{10}(H)(OAl<)^d$	2107(w), 2068(s), 2056(s), 2023(vs), 2005(m)
$Os_3(CO)_{10}(H)(OSi<)^e$	2122(w), 2088(vs), 2075(s), 2037(vs,br), 1955(w,sh)

a, γ-Al_2O_3; b, ALON-C; c, ref.2); d, ref.10); e, ref.9)

Table 2. Electronic absorption data of pure and supported iron carbonyls under vacuum by means of UV diffuse reflectance spectroscopy

carbonyls	wave number / 10^3cm^{-1}
$Fe_3(CO)_{12}$ a	36.0(vs), 30.8(s,sh), 22.3(ms), 16.5(s)
$Fe_3(CO)_{12}$	28.2(s), 22.2(ms), 16.4(s)
$Fe_2(CO)_9$	33.3(s,sh), 28.0(vs,br), 20.3(m,sh)
$Fe_3(CO)_{12}/SiO_2$	36.9(vs), 28.4(s,sh), 22.2(ms), 16.3(s)
$Fe_3(CO)_{10}(H)(OAl<)$	27.4(s), 23.5(s), 18.3(vs), 14.4(m,sh)

a, sample in pentane; other samples: powder

Table 3. Bond distances for pure and supported carbonyls determined by an in-laboratory EXAFS spectroscopy

carbonyls	bond distances / nm Fe-C	Fe-Fe	R_f
$Fe_3(CO)_{12}$	0.182	0.261	0.505
$Fe_3(CO)_{12}$ a	Fe-C(t) 0.1847(mean) Fe-C(br) 0.180(mean)	0.268(mean) 0.2558	——
$Fe_2(CO)_9$ b	Fe-C(t) 0.1838 Fe-C(br) 0.2016	0.2523	——
$[Fe_3(CO)_{11}H]^-$ c	——	0.2691 0.2577	——
$Fe_3(CO)_{12}/SiO_2$	0.204	0.264	0.208
$Fe_3(CO)_{10}(H)(OAl<)$	0.218	0.247	0.127

a, x-ray, ref.7); b, x-ray, ref.11); c, x-ray, ref.12);

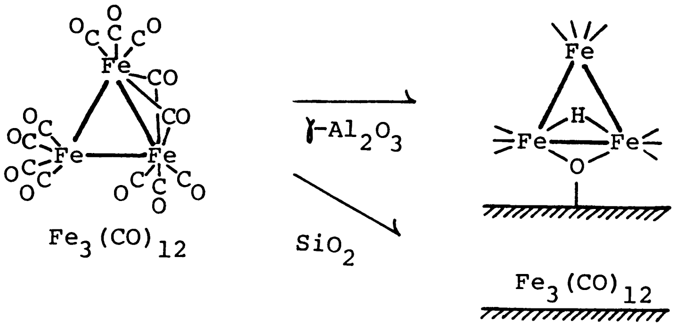
The quality of curve-fitting data was evaluated by the reliability factor(R_f), $R_f = \Sigma((k^3\chi)_{exp} - (k^3\chi)_{calc})^2 / \Sigma((k^3\chi)_{exp})^2$, where $(k^3\chi)_{exp}$ and $(k^3\chi)_{calc}$ are Fourier-filtered and calculated data, respectively.

nm in Table 3) of the SiO_2-supported $Fe_3(CO)_{12}$ cluster was similar to 0.261 nm (0.2558 and 0.268(mean) nm according to XRD7)) for $Fe_3(CO)_{12}$. Thus these results demonstrate that $Fe_3(CO)_{12}$ was weakly supported on the pretreated SiO_2 retaining its original structure and chemical nature.

When $Fe_3(CO)_{12}$ was supported onto the pretreated γ-Al_2O_3, 1.1 CO per a $Fe_3(CO)_{12}$ cluster were evolved. Also the evolution of 1.9 CO molecules were observed over Al_2O_3 powder(ALON-C) which has the less capability for the adsorption of CO formed by decarbonylation. The subcarbonyls formed on both Al_2O_3 showed the similar IR(Table 1) and UV diffuse reflectance spectra, indicating that the same surface subcarbonyl species with the composition of $[Fe_3(CO)_{10}]$ were formed by the reactions of $Fe_3(CO)_{12}$ with two Al_2O_3. No H_2 evolution was observed during the reaction. CO_2-derived surface species like carbonates except for the negligible formation of CO_2(< 0.06 $CO_2/Fe_3(CO)_{12}$) were not detected. It has been reported2) that one CO ligand of $Fe_3(CO)_{12}$ was oxidized to CO_2(or adsorbed carbonates) by the reaction of the cluster with the basic OH group of η-Al_2O_3 leading to the formation of $[Fe_3(CO)_{11}H]^-Al(O-)_x^+$ where no evolution of CO was claimed. The IR spectrum of the surface subcarbonyl on γ-Al_2O_3 was much different from that of the hydrido carbonyl anion as shown in Table 1. The UV spectrum in Table 2 showed a strong band at $18.3\times10^3 cm^{-1}$. The Fe-Fe bond distance of the surface subcarbonyl in Table 3 was much shorter than that of the surface anion. These results exclude the possibility of the formation of $[Fe_3(CO)_{11}H]^-$, the other carbonyl species like $Fe_2(CO)_9$, $[Fe_2(CO)_8H]^-$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$, $[Fe_4(CO)_{13}H]^-$ and $[Fe_4(CO)_{13}]^{2-}$ 8)being also excluded.

The Fe-Fe bond distance, 0.247 nm in Table 3, is remarkably shorter than 0.261 nm of pure $Fe_3(CO)_{12}$ and nearly equal to 0.248 nm of Fe metal. The similar shrinkage of metal-metal bond has also been demonstrated9) with the supported osmium cluster obtained by the reaction of $Os_3(CO)_{12}$ with SiO_2; the mean Os-Os bond length is shortened from 0.288 nm of $Os_3(CO)_{12}$ to 0.268 nm which corresponds to the Os-Os bond length of Os metal. Besson et al.9) suggested the oxidative addition of a silanol group to a Os-Os bond of $Os_3(CO)_{12}$ leading to the formation of $Os_3(CO)_{10}(H)(OSi\leqslant)$ involving μ-H and μ-$OSi\leqslant$ ligands. The γ-Al_2O_3-supported triiron subcarbonyl showed a new distinct band on the higher-ν_{CO} side similarly to $Os_3(CO)_{10}(H)(OSi\leqslant)$9) and $Os_3(CO)_{10}(H)(OAl<)$10)in Table 1; suitable model Fe_3-clusters to be compared seem unknown. The TPDE chromatogram of the surface subcarbonyl showed a CO peak at 413 K higher by 26 K as compared with the SiO_2-supported $Fe_3(CO)_{12}$ cluster and at the same temperature a H_2 peak was observed. The hydrogen is obviously derived from the surface OH groups since the ν_{OH} band intensity of γ-Al_2O_3 was reduced by supporting of $Fe_3(CO)_{12}$ in vapour. The quantity of H_2 desorbed in the temperature range 343-493 K was ca. 0.5 H_2 per a Fe_3-cluster. These results indicate the incorporation of one surface OH group in $[Fe_3(CO)_{10}]$, that is, similarly to the case of $Os_3(CO)_{12}$, the oxidative addition of the surface OH group of γ-Al_2O_3 to a Fe-Fe bond of $Fe_3(CO)_{12}$ leading to the formation of $Fe_3(CO)_{10}(H)(OAl<)$.

Thus it is suggested on the basis of the EXAFS, IR and UV spectra, the TPDE analysis and the chemical composition that a $Fe_3(CO)_{12}$ cluster reacted with a surface OH group of γ-Al_2O_3 at 313 K to form a surface complex, $Fe_3(CO)_{10}(H)(OAl\langle)$, rather than a simple interaction of coordinatively unsaturated unstable $[Fe_3(CO)_{10}]$. with $[HO-Al\langle]_n$. This surface complex was much more sensitive toward dioxygen than the SiO_2-supported $Fe_3(CO)_{10}$ cluster and a $[Fe_3(CO)_{11}H]^-$ anion; the surface complex was almost instantaneously oxidized to Fe(III) ions(by Mössbauer) showing the peaks at 28.1(CT band), 21.3(d-d) and 17.9(d-d)$\times 10^3 cm^{-1}$ by exposing to air at room temperature. The preferential formation of $Fe_3(CO)_{10}(H)(OAl\langle)$ or $[Fe_3(CO)_{11}H]^-Al(O-)_x^+$ may depend upon the electronic character(oxidative or basic) of the surface OH groups of alumina.



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