Surface-supported Metal Carbonyl Clusters: Formation of $[HFe_3(CO)_{11}]^-$ by Interaction of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ with Alumina and Magnesia

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Summary Interaction of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ with the surface of alumina and magnesia results in the formation of the anionic hydrido cluster carbonyl $[HFe_3(CO)_{11}]^- M^+$, $M^+ = Al(O\text{–})_x{}^+$ or $Mg(O\text{–})_y{}^+$, which indicates the basic character of the hydroxy-group of alumina and magnesia towards $Fe(CO)_5$ and $Fe_3(CO)_{12}$; the easy formation of $[HFe_3(CO)_{11}]^- M^+$ may also account for the same selectivities for formation of low molecular weight olefins observed in Fischer–Tropsch synthesis whether starting from $Fe(CO)_5$ or from $Fe_3(CO)_{12}$ adsorbed on alumina or magnesia.

It has been shown[1] that molecular cluster carbonyls, when chemisorbed on inorganic oxides, give rise, upon heating, to the formation of hydrocarbons. Under CO + H_2 or CO + H_2O, hydrocarbon synthesis becomes catalytic with a high selectivity towards the formation of low molecular weight olefins.[2] Among the parameters which influence the product distribution are the basicity of the support and its water content; the latter seems to be a determining factor. Such observations were recently confirmed by Ichikawa[3] in the case of ethanol synthesis with pyrolysed rhodium carbonyl clusters. With $Fe(CO)_5$ and $Fe_3(CO)_{12}$ supported on alumina and magnesia we have recently discovered a very high selectivity towards propene formation from synthesis gas.[2,4] We report here data which indicate that with $Fe(CO)_5$ and $Fe_3(CO)_{12}$, the first step of chemisorption on a basic support such as magnesia or alumina is the nucleophilic attack of a hydroxy-group of the support on a carbonyl ligand co-ordinated to the cluster framework (or monomeric species) leading to the formation of the anionic hydrido cluster (A) linked to the surface.

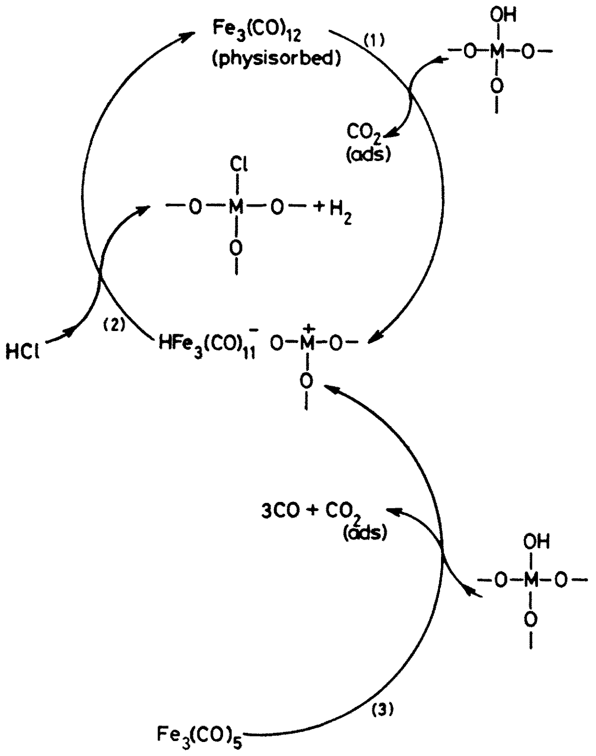
$$[HFe_3(CO)_{11}]^- M^+,\ M^+ = \overset{+}{Al}(O\text{–})_x, \overset{+}{Mg}(O\text{–})_y$$
(A)

In a typical experiment η-alumina (10 g; 300 m^2 g^{-1}) was treated overnight at 150 °C under reduced pressure (10^{-4} Torr). $Fe_3(CO)_{12}$ (1·01 mmol) in degassed dry hexane (50 ml) and the activated alumina were then stirred at room temperature under argon. Within 2 h the initially green solution was colourless and the solid deep red. The i.r. spectrum of the solid showed ν(CO) bands at 2075sh,w and 2005br,s cm^{-1}, and bands at 1470br,m and 1580br,m cm^{-1} indicated the formation of carbonates from the reaction of CO_2 (Scheme) with surface O^{2-} species. No gaseous CO_2 was detected at 25 °C suggesting that the CO_2 had reacted with the carrier to form adsorbed carbonates. The u.v. spectrum of the solid showed a broad band at 540 nm. After removal of hexane, the surface species was extracted into a solution of Et_4NCl (10·9 mmol) in CH_2Cl_2. After stirring for 1 h at 25 °C under argon, the solid became colourless and the solution deep red. The i.r. spectrum of the solution showed ν(CO) bands at 2071w, 2002s, 1970m, 1945w, and 1715m cm^{-1}, and the u.v. spectrum an absorption maximum at 543 nm, in good agreement with the i.r.[5] [ν(CO) 2070w, 2000vs, 1972s, 1946m, and 1718m cm^{-1}] and u.v.[6] spectrum (λ_{max} 540 nm) reported for $Et_4N^+[HFe_3(CO)_{11}]^-$.

None of the following anionic carbonyl species of iron; $[HFe(CO)_4]^-$, $[Fe(CO)_4]^-$, $[HFe_2(CO)_8]^-$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$, $[Fe_4(CO)_{13}]^{2-}$, and $[HFe_4(CO)_{13}]^-$, could account for the i.r. and u.v. bands observed.[6,7] The solid obtained from the red solution was recrystallized from methanol–water and the elemental analyses obtained were consistent with the formulation $Et_4N^+[HFe_3(CO)_{11}]^-$. The ^1H n.m.r. spectrum of this product in CD_2Cl_2 at −60 °C exhibited a high-field proton resonance at δ 15·5 relative to Me_4Si, also in agreement with the spectrum of $Et_4N^+[HFe_3(CO)_{11}]^-$.[8]

Surface $[HFe_3(CO)_{11}]^-$ was also obtained if the η-alumina was pretreated *in vacuo* at other temperatures (25—500 °C), suggesting that hydroxy-groups rather than molecular water are responsible for the formation of the anionic cluster. γ-Alumina and magnesia could be used as well, magnesia being the most reactive support. Silica and silica–alumina did not promote the formation of the anionic hydrido cluster, even under thermal activation, simple physisorption occurring in these cases. Heating the physisorbed cluster under CO at 50 °C resulted in cleavage of the metal–metal bond with formation of $Fe(CO)_5$, a well known reaction.[9]

The formation of surface $[HFe_3(CO)_{11}]^-$ was also observed when $Fe(CO)_5$ was adsorbed on γ-alumina, η-alumina, or magnesia, but at a slower rate than with $Fe_3(CO)_{12}$. In a typical experiment, η-alumina (5 g) was treated overnight at 80 °C and 10^{-4} Torr pressure, and then added to a solution of $Fe(CO)_5$ (2·08 mmol) in dry degassed hexane (25 ml) at room temperature under argon. After 14 h the solution was partially decolourised and the solid was red, as with $Fe_3(CO)_{12}$. Extraction of the surface species with a solution in CH_2Cl_2 of Et_4NCl (2·4 mmol) and recrystallisation from methanol–water led to a compound with i.r., u.v., ^1H n.m.r., and microanalytical data similar to those for $Et_4N^+[HFe_3(CO)_{11}]^-$ formed from $Fe_3(CO)_{12}$.



Scheme. M = Al^{III} or Mg^{II}.

Formation of anionic hydrido iron clusters on the surface of alumina and magnesia can be explained by reactions (1) and (3) in the Scheme. Since alumina pretreated above 300 °C does not contain molecular water it is reasonable to assume that hydroxy-groups rather than molecular water are responsible for the nucleophilic attack on the carbonyls. The hydroxy-groups therefore are highly basic on alumina and magnesia since, in solution, formation of $[HFe_3(CO)_{11}]^-$ from $Fe_3(CO)_{12}$ generally requires basic attack of $Fe_3(CO)_{12}$ by 2 M methanolic-KOH.[9] Similarly, $[HFe_3(CO)_{11}]^-$ can be obtained by basic attack of $Fe(CO)_5$ in water.[10] This nucleophilic character of hydroxy-groups of alumina and magnesia has been recognized recently.[11]

Addition of aqueous HCl (25 mmol) to $[HFe_3(CO)_{11}]^-$ (0·5 mmol) supported on η-alumina and magnesia gave gaseous H_2 (0·45 mmol) and the solid became green. CO or CO_2 were not evolved. After washing with CH_2Cl_2, the solid became colourless and the CH_2Cl_2 solution deep green. The i.r. spectrum of the solution in the ν(CO) region (2045s and 2022m cm^{-1}) indicated the presence of $Fe_3(CO)_{12}$. This reaction [reaction (2) in the Scheme] is known to occur in solution.[12]

These results indicate the basic character of the hydroxy-groups of magnesia and alumina towards $Fe(CO)_5$ or $Fe_3(CO)_{12}$.

The formation of $[HFe_3(CO)_{11}]^- M^+$ may also account for the same selectivities observed in Fischer–Tropsch synthesis starting from either $Fe(CO)_5$ or $Fe_3(CO)_{12}$.[2,4] Studies are in progress to determine the level of nuclearity of metal particles resulting from the thermal decomposition of

$[HFe_3(CO)_{11}]^- M^+$. The low nuclearity expected from the work of Brenner[13] would account for the high selectivity towards low molecular weight olefins if one assumes that the mechanism of carbon bond formation is structure sensitive.[14] Finally the formation of metal hydrides on alumina or magnesia, and probably on ZnO and La_2O_3,† might explain the necessity of a basic support for the easy synthesis of alcohols from synthesis gas with conventional heterogeneous catalysts or with pyrolysed cluster carbonyls.[3] It is possible that this synthesis would imply the nucleophilic attack of a transition metal hydride capable of exhibiting hydridic character towards co-ordinated CO. Such a reaction path has recently been shown to occur in stoicheiometric reactions.[15]

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† Similar results seem to be obtained with ZnO and La_2O_3. However, the low surface area of these oxides did not allow the isolation of $[HFe_3(CO)_{11}]^-$ in a significant amount.

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