

Surface-supported Metal Carbonyl Clusters: Formation of $[\text{HFe}_3(\text{CO})_{11}]^-$ by Interaction of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$ with Alumina and Magnesia

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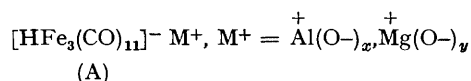
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Summary Interaction of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$ with the surface of alumina and magnesia results in the formation of the anionic hydrido cluster carbonyl $[\text{HFe}_3(\text{CO})_{11}]^- \text{M}^+$, $\text{M}^+ = \text{Al}(\text{O}^-)_x^+$ or $\text{Mg}(\text{O}^-)_y^+$, which indicates the basic character of the hydroxy-group of alumina and magnesia towards $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$; the easy formation of $[\text{HFe}_3(\text{CO})_{11}]^- \text{M}^+$ may also account for the same selectivities for formation of low molecular weight olefins observed in Fischer-Tropsch synthesis whether starting from $\text{Fe}(\text{CO})_5$ or from $\text{Fe}_3(\text{CO})_{12}$ adsorbed on alumina or magnesia.

It has been shown¹ that molecular cluster carbonyls, when chemisorbed on inorganic oxides, give rise, upon heating, to the formation of hydrocarbons. Under $\text{CO} + \text{H}_2$ 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 Ichikawa³ in the case of ethanol synthesis with pyrolysed rhodium carbonyl clusters. With $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ 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 $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$, 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.



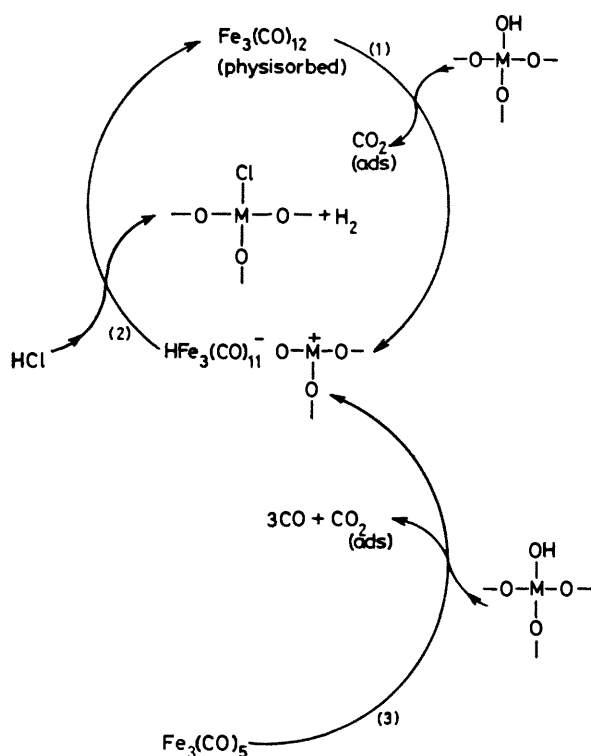
In a typical experiment η -alumina (10 g; 300 m² g⁻¹) was treated overnight at 150 °C under reduced pressure (10⁻⁴ Torr). Fe₃(CO)₁₂ (1.01 mmol) in degassed dry hexane (50 ml) and the activated alumina were then stirred at room temperature under argon. Within 2 h the initially green solution was colourless and the solid deep red. The i.r. spectrum of the solid showed $\nu(\text{CO})$ 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 CO₂ (Scheme) with surface O²⁻ species. No gaseous CO₂ was detected at 25 °C suggesting that the CO₂ 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 Et₄NCl (10.9 mmol) in CH₂Cl₂. 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 $\nu(\text{CO})$ 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 [$\nu(\text{CO})$ 2070w, 2000vs, 1972s, 1946m, and 1718m cm⁻¹] and u.v.⁶ spectrum (λ_{max} 540 nm) reported for Et₄N⁺[HFe₃(CO)₁₁]⁻.

None of the following anionic carbonyl species of iron; [HFe(CO)₄]⁻, [Fe(CO)₄]⁻, [HFe₂(CO)₈]⁻, [Fe₂(CO)₈]²⁻, [Fe₃(CO)₁₁]²⁻, [Fe₄(CO)₁₃]²⁻, and [HFe₄(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 Et₄N⁺[HFe₃(CO)₁₁]⁻. The ¹H n.m.r. spectrum of this product in CD₂Cl₂ at -60 °C exhibited a high-field proton resonance at δ 15.5 relative to Me₄Si, also in agreement with the spectrum of Et₄N⁺[HFe₃(CO)₁₁]⁻.⁸

Surface [HFe₃(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 [HFe₃(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 Fe₃(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 Fe₃(CO)₁₂. Extraction of the surface species with a solution in CH₂Cl₂ of Et₄NCl (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 Et₄N⁺[HFe₃(CO)₁₁]⁻ formed from Fe₃(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 [HFe₃(CO)₁₁]⁻ from Fe₃(CO)₁₂ generally requires basic attack of Fe₃(CO)₁₂ by 2 M methanolic-KOH.⁹ Similarly, [HFe₃(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 [HFe₃(CO)₁₁]⁻ (0.5 mmol) supported on η -alumina and magnesia gave gaseous H₂ (0.45 mmol) and the solid became green. CO or CO₂ were not evolved. After washing with CH₂Cl₂, the solid became colourless and the CH₂Cl₂ solution deep green. The i.r. spectrum of the solution in the $\nu(\text{CO})$ region (2045s and 2022m cm⁻¹) indicated the presence of Fe₃(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 Fe₃(CO)₁₂.

The formation of [HFe₃(CO)₁₁]⁻ M⁺ may also account for the same selectivities observed in Fischer-Tropsch synthesis starting from either Fe(CO)₅ or Fe₃(CO)₁₂.^{2,4} Studies are in progress to determine the level of nuclearity of metal particles resulting from the thermal decomposition of

$[\text{HFe}_3(\text{CO})_{11}]^- \text{M}^+$. The low nuclearity expected from the work of Brenner¹³ 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 stoichiometric 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 $[\text{HFe}_3(\text{CO})_{11}]^-$ in a significant amount.

¹ A. K. Smith, A. Theolier, J. M. Basset, R. Ugo, D. Commereuc, and Y. Chauvin, *J. Amer. Chem. Soc.*, 1978, **100**, 2590.

² Fr. P. 77.16450/1977.

³ M. Ichikawa, *J.C.S. Chem. Comm.*, 1978, 566; *Bull. Chem. Soc. Japan*, 1978, **51**, 2273.

⁴ D. Commereuc, Y. Chauvin, F. Hugues, and J. Basset, to be published.

⁵ J. R. Wilkinson and L. T. Todd, *J. Organometallic Chem.*, 1976, **118**, 199.

⁶ W. Hieber and H. Beutner, *Z. Naturforsch.*, 1962, **17b**, 211.

⁷ K. Farmery, M. Kilner, R. Greatex, and N. W. Greenwood, *J. Chem. Soc. (A)*, 1969, 2339.

⁸ H. A. Hodali, D. F. Schriver, and C. A. Ammlung, *J. Amer. Chem. Soc.*, 1978, **100**, 5239.

⁹ W. Hieber and G. Brendel, *Z. anorg. Chem.*, 1957, **289**, 324.

¹⁰ J. R. Case and M. C. Whiting, *J. Chem. Soc. (A)*, 1960, 4632.

¹¹ H. Knözinger and B. Stubner, *J. Phys. Chem.*, 1978, **82**, 1526; H. Knözinger and P. Ratnasamy, *Catalysis Rev.*, 1978, **17**, 31;

H. Knözinger, *Adv. Catalysis Related Subjects*, 1976, **25**, 184; M. Che, C. Naccache, and B. Imelik, *J. Catalysis*, 1972, **24**, 328; A. J.

Tench and R. L. Nelson, *Trans. Faraday Soc.*, 1967, **63**, 2254.

¹² W. McFarlane and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 181.

¹³ A. Brenner, *J.C.S. Chem. Comm.*, 1979, 251.

¹⁴ M. Boudart, A. G. Aldag, J. E. Benson, N. A. Douhgarty, and C. B. Harwins, *J. Catalysis*, 1966, **6**, 92; M. Boudart, *Adv. Catalysis*, 1965, **20**, 153.

¹⁵ J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1978, **100**, 2716; J. A. Labinger, K. S. Wong, and W. R. Scheidt, *ibid.*, p. 3254; P. T. Wolczawski, R. S. Threlkel, and J. E. Bercaw, *ibid.*, 1979, **101**, 218.