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Attachment and Characterization of Ionic Triiron Carbonyl Clusters onto Functionalized Polystyrene and Silica Supports

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Metal clusters have recently attracted widespread interest as catalysts [1, 3]. One of them, the triiron dodecacarbonyl, was used in phase transfer catalysis for aniline formation from nitroarene [4]. The same cluster was used as precursor for small metal particles which led to very selective catalysts for the Fisher-Tropsch reaction [5]. For both of these works, the compound $(HFe_3(CO)_{11})^-$ was supposed to be a key intermediate.

We report here the fixation and the characterization of clusters analogous to $(HFe_3(CO)_{11})^-(NR_4^+)$ onto functionalized supports.

The fixation of such compounds presenting a well-defined structure offers obvious advantages for catalysis, such as ease of separation, lack of corrosion, and stabilization [2].

Attachments of clusters analogous to $(Ir_4(CO)_{12-x}(PPh_3)_x)$ (x = 1, 2, 3) [6], $(H_2Ru_4(CO)_{12-x}(PPh_3)_x$ (x = 1, 2, 4) [7], $(H_2Os_3(CO)_9PPh_3)$ [8], $(Fe_2Pt(CO)_8(PPh_3)_2)$, $(RuPt_2(CO)_5(PPh_3)_5)$, $(HAuOs_3(CO)_{10}PPh_3)$ [9] on phosphinated poly(styrene-divinylbenzene) have been described. Similar attachments of $(Os_3(CO)_{11}PPh_3)$, $(H_2Os_3(CO)_9PPh_3)$ [10], $(HAuOs_3(CO)_{10}PPh_3)$ [9], and $(Ir_4(CO)_{12-x}(PPh_3)_x)$ (x = 1, 2, 3) [11] on phosphinated silica supports have also been reported. None of the forementioned cluster attachments involved an ionic bonding between the supported ligand and the cluster, similar to the attachment described here.

The poly(styrene-divinylbenzene) support was a commercial resin (DOWEX) incorporating ammonium groups Ⓓ-CH_2-$\overset{+}{N}(CH_3)_3$, Cl^-, or a copolymer of styrene and divinylbenzene (DVB) (Ⓟ). The copolymerization took place in cells previously described [12], producing 11 μ m-thick membranes with an optimal transparence for infrared spectroscopy. The poly(styrene-DVB) membranes Ⓟ were chloromethylated according to a described procedure [13], and the resulting solids Ⓟ-CH_2Cl (30 mg) were treated at 273 K, under N_2 for 48 hours, with triethylamine in dioxane (25/300 ml). Membranes including ammonium chloride groups were obtained: Ⓟ-CH_2-$\overset{+}{N}(Et)_3$, Cl^-.

Ammonium modified silica SIL–$(CH_2)_3$-$\overset{+}{N}Et_3$, Cl^- (SIL = silica) was prepared from the reaction of SIL–$(CH_2)_3Cl$ (5 g), obtained according to a described procedure [14], with triethylamine in DMF (25/200 ml) at 333 K and $P_{N_2} = 5 \times 10^5$ N/m^2 for 12 hours [14].

The cluster $(HFe_3(CO)_{11})^-(HNEt_3)^+$ was prepared according to a described procedure [15].

The two types of solid incorporating ammonium chloride groups were contacted under nitrogen with a CH_2Cl_2 solution of iron cluster at 273 K (Fe_3/N = 3 molar ratio).

Using a ligand exchange between a cationic ammonium ligand on the molecular cluster and an analogous attached ligand led to the formation of solids incorporating iron species (Samples 1–3). The attached species were identified by comparison of their carbonyl stretching spectra with those of analogous molecular clusters [16] (Table I). On the basis of this comparison, the attached species can clearly be identified. To the best of our knowledge, they represented the first clusters supported onto functionalized solid supports via ionic bonds. The iron and nitrogen contents of the solids (samples 1–3) are reported in Table II.

Samples 1–3 showed a very poor stability in presence of oxygen: the supported clusters decom-

TABLE I. Carbonyl Stretching Frequencies of Molecular and Supported Triiron Clusters.

Sample number or ref.	Solvent or support	Cation	ν_{CO} terminal	ν_{CO} bridge
[16]	CH_2Cl_2	NEt_4^+	2070w, 2000vs, 1972s, 1946m	1718m
[16]	CH_3NO_2	NEt_4^+	2075w, 2000vs, 1976s, 1949m	1733m
1[a]	Ⓓ-CH_2-	NEt_3^+	2055w, 2010m, 1985s, 1955m	
2[a]	Ⓟ-CH_2-	NEt_3^+	2065w, 2000vs, 1970s, 1945m	1720m
3[a]	SIL-$(CH_2)_3$	NEt_3^+	2055w, 2010m, 1987s	

[a] As expected, the custom-made membrane (Sample 2), a nearly transparent support, is optimal for infrared transmission spectroscopy. The other supports contain impurities or interact more strongly with the cluster, leading to poorly-defined spectra.

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TABLE II. Iron and Nitrogen Contents of the Solids Incorporating Clusters Analogous to $(HFe_3(CO)_{11})^-(HNEt_3)^+$.

Sample	Sample number	N % wt	Fe % wt
Ⓓ-$CH_2-\overset{+}{N}Me_3$, $HFe_3(CO)_{11}^-$	1	3.9	1.8
Ⓟ-$CH_2-\overset{+}{N}Et_3$, $HFe_3(CO)_{11}^-$	2	1.1	0.02
SIL-$(CH_2)_3-\overset{+}{N}Et_3$, $HFe_3(CO)_{11}^-$	3	3.3	1.1

posed after 10 min as indicated by the disappearance of the CO infrared bands. A similar decomposition occurred when the samples were heated at 363 K under inert atmosphere. In both cases, flowing CO at 298 K and $P_{CO} = 10^5$ N/m^2 did not regenerate the initial infrared spectrum. A purple color was indicative of the presente of $(HFe_3(CO)_{11})^-$ clusters (which could not be detected by electron microscopy), whereas a brown color was indicative of the presence of decomposition products. In this case, an electron micrograph showed the presence of iron crystallites (20 to 100 Å).

Samples 1–3 were stabilized under a CO or Ar atmosphere ($P_{total} = 10^5$ N/m^2) and could be kept for days without any change in the infrared spectrum. Samples 1 and 2 allowed the transformation under mild conditions of nitrobenzene into aniline. Studies are in progress to determine if this transformation is catalytic. Sample 3 is being tested as a CO hydrogenation catalyst.

References

1 J. Haggin, *Chem. Eng. News*, *13*, Feb. 8, (1982)
2 B. C. Gates and J. Lieto, *Chemtech*, March (1980).
3 D. C. Bailey and S. H. Langer, *Chem. Rev.*, *81*, 109 (1981).
4 H. Alper and M. Gopal, *J. Chem. Soc*, *Chem. Comm.*, 821 (1980).
5 F. Hugues, A. K. Smith, Y. Ben Taarit, J M. Basset, D. Commereuc and Y. Chauvin, *J. Chem. Soc.*, *Chem. Comm.*, 68 (1980).
6 J. Lieto, J. J. Rafalko and B. C. Gates, *J. Catal.*, *62*, 149 (1980).
7 Z. Otero-Schipper, J. Lieto and B. C. Gates, *J. Catal.*, *63*, 175 (1980).
8 J. B. N'Guini Effa, J. Lieto and J. P. Aune, *J. Mol Catal.*, in press.
9 R. Pierantozzi, K J. McQuade, B. C. Gates, M. Wolf, H. Knözinger and W. Ruhman, *J. Am. Chem. Soc.*, *101*, 5436 (1979).
10 S. C. Brown and J. Evans, *J. Mol. Catal.*, *11*, 143 (1981).
11 T. Castrillo, H Knozinger, J. Lieto and M. Wolf, *Inorg Chim. Acta*, *44*, L239 (1980).
12 G. Zundel, 'Hydratation and Intermolecular Interactions. Infrared Investigations with Polyelectrolyte Membranes', Academic Press, New York (1969).
13 K. W. Pepper, H. M. Paisley and M. A. Young, *J. Chem. Soc.*, 4097 (1953).
14 K. G. Allumn, R. D. Hancock, I. V. Howell, S. McKenzie, R. C. Pitkethly and P. J. Robinson, *J. Organometal. Chem.*, *87*, 203 (1975).
15 W. McFarlane and G. Wilkinson, *Inorg Synth.*, *8*, 185 (1965)
16 J. R. Wilkinson and L. J. Todd, *J. Organometal. Chem.*, *118*, 199 (1976).