Supported Anionic Tri-iron Clusters as Agents for Nitrobenzene Reduction

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Anionic tri-iron clusters supported on functionalized polymers reduce nitrobenzene to aniline; a reaction intermediate has been identified by i.r. spectroscopy.

Tri-iron clusters are reducing agents for the reduction of $-NO_2$ to $-NH_2$ groups.[1,2] When a solution of $Fe_3(CO)_{12}$ is brought in contact with alumina, the supported anionic cluster $HFe_3(CO)_{11}^-$ (**1**) is obtained; it is a reducing agent for the transformation of nitrobenzene into aniline,[2] and a precursor for small aggregates which are catalysts for the Fisher–Tropsch reaction.[3] We have prepared polymers incorporating anionic tri-iron clusters[4] (**1**), and describe here the trapping of a nitrene intermediate in the polymers when they were used as reducing agents for nitrobenzene, equation (1).

The supports (polym) were commercial anion exchange resin beads (Dowex) or poly(styrene–divinylbenzene) membranes (11×10^{-6} m thick) functionalized with $-NR_3^+$ groups. When these solids were brought into contact with a solution of (**1**), samples (A) and (B) were obtained, respectively. A flow reactor system[5] was used, the reactor being either a small tube packed with (A) or an i.r. cell containing (B). Helium was bubbled into purified nitrobenzene and the resulting saturated vapour flowed to the reactor. The design allowed the simultaneous recording of the conversion of the organic reagent and the i.r. spectrum of the supported reagent.

The % conversion of nitrobenzene into aniline was recorded by on-stream gas chromatography. The number of moles of aniline produced was computed and compared to the number of moles of (**1**) incorporated in (A): a stoicheiometric transformation of nitrobenzene into aniline was observed. Identical results were obtained in the presence of H_2. The converted solid was heated to 348 K, but no further reaction was observed. A colour change was observed (red–purple to brown), pointing to the cluster decomposition. The reaction could not be made catalytic with $p(CO) = 3 \times 10^5$ Pa and $p(H_2) = 5 \times 10^5$ Pa at 333 K.

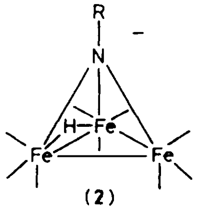
The experiments demonstrated that $HFe_3(CO)_{11}^-$ supported on functionalized polymers was responsible for the stoicheiometric reduction of nitrobenzene to aniline, unknown support impurities being the proton source. They also raised a question about the nature of intermediate products involved in the reduction. In an attempt to answer this question, the same reaction was carried out with (B) held in a cell which allowed the monitoring of the clusters, during the reaction, by i.r. spectroscopy.[5] When nitrobenzene was brought into contact with the membrane, a change in the i.r. spectrum was

$$PhNO_2 \xrightarrow{i} PhNH_2 \qquad (1)$$

i, polym–$CH_2{}^+NEt_3$, $HFe_3(CO)_{11}^-$, He, room temp.

$HFe_3(CO)_{11}^-$

(**1**)



(**2**)

Table 1. Characterization of polymer-bound tri-iron clusters and molecular analogues.

Sample[a]	Ref.	Sample	Solvent	$\nu(CO)/cm^{-1}$
$HFe_3(CO)_{11}^- \ Y^+$	4	(**1**)	CH_2Cl_2	2070w, 2000vs, 1972s, 1946m, 1718m
polym–$CH_2{}^+NEt_3$, $HFe_3(CO)_{11}^-$	4	(B)	—	2060w, 2000vs, 1970s, 1945m, 1720m
$HFe_3(CO)_9NPh^- \ Y^+$		(**2**)	CH_2Cl_2	2047vw, 2005s, 1972vs, 1966m, 1939w
polym–$CH_2{}^+NEt_3$, $HFe_3(CO)_9NPh^-$		(C)	—	2045vw, 2005s, 1972vs, 1968m, 1942w

[a] polym = poly(styrene–divinylbenzene), 11×10^{-6} m-thick membrane. $Y^+ = HNEt_3^+$.

observed, leading to (C) (Table 1). The resulting spectrum could not be assigned to anions coming from the tri-iron cluster decomposition.[6] Literature[7] indicated that a probable intermediate in the reduction of nitro-compounds to amines is the anion (**2**).

We prepared (**2**; R = Ph) and obtained its i.r. spectrum which is comparable, in the carbonyl region, to that of the species (C) on the membranes (Table 1), pointing to the presence of an attached compound analogous to (**2**) in the reaction chain from nitrobenzene to aniline.

In summary, we have demonstrated that polymeric solids incorporating tri-iron clusters reduce $PhNO_2$ to $PhNH_2$. An intermediate in the transformation is identified. This work illustrates the value of a spectroscopic reactor when used with a matrix-isolated reagent and vapour-phase reactants.

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