Synthesis of Highly Dispersed Catalysts of Supported Iron

By Alan Brenner

(*Department of Chemistry, Wayne State University, Detroit, Michigan,* 48202)

Summary Iron carbonyls are used to synthesize catalysts of Fe supported on Al_2O_3 which are more than an order of magnitude more dispersed than those that have been obtained by the traditional techniques of catalyst synthesis.

Catalysts of supported iron are among the oldest and most studied heterogeneous catalysts, being used in a variety of hydrogenation type reactions. Recently, the development of highly dispersed catalysts of supported metals has been investigated extensively.[1] Fe catalysts have been particularly challenging because at loadings of *ca.* 10% (on Al_2O_3 or SiO_2) they typically have a dispersion of only *ca.* 1%, about an order of magnitude lower than for most of the other group 8B metals.[2,3] At low loadings, where many of the other metals can be prepared in close to 100% dispersion, the dispersion of Fe catalysts is essentially zero because interaction with the support prevents reduction of Fe^{3+} below Fe^{2+}.[4] [The catalysts are usually made by impregnation with $Fe(NO_3)_3$ followed by calcination and reduction.] These results suggest that zero-valent catalyst precursors may provide a route to highly dispersed, supported Fe. This note reports the use of Fe carbonyls to synthesize such catalysts with dispersions $>50\%$.

$Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ were physisorbed on γ-Al_2O_3 (previously calcined in O_2 at 500 °C) under rigorously air-free conditions using the high purity system and techniques already described.[5,6] Previous temperature programmed decomposition (TPDE) studies of $Fe_3(CO)_{12}$–Al_2O_3 in flowing He had revealed that above 250 °C decarbonylation of the complex is accompanied by partial oxidation of the Fe by H^+ in the surface hydroxy groups of the Al_2O_3 [H_2(g) is evolved].[7] More sensitive TPDE experiments with the three carbonyls establish that activation near 200 °C results in the Fe being oxidized to an average oxidation number of *ca.* 0·2, but oxidation is negligible at 120 °C even though *ca.* 40% of the carbonyl ligands are evolved. Therefore, the catalysts were activated at 120 °C for 30 min in flowing He prior to having their dispersions measured.

The Table contains the dispersions of the carbonyl catalysts as well as the dispersions of classically prepared Fe–Al_2O_3 for comparison. Dispersions were obtained in the standard manner by measuring the adsorption isotherm at 0 °C, evacuating for 15 min, repeating the isotherm, and using the difference as the amount of chemisorption. Corrections have been made for the small amount of CO chemisorbed on the Al_2O_3 as found in separate blank experiments. The chemisorption stoicheiometry for Fe–Al_2O_3 is 1 CO per 2 surface Fe,[8] and the same stoicheiometry has been assumed for the carbonyl catalysts.† It is clear that the use of zero-valent complexes has led to a nearly two orders of magnitude increase in dispersion, and the dispersion is now in line with values for the other group 8B metals. The high dispersion is effected by eliminating the high temperature calcination and reduction of Fe^{3+} which can lead to sintering (high loadings) or poor reducibility (low loadings). Consistent with this, oxidation and reduction of $Fe(CO)_5$–Al_2O_3 lowers its dispersion 13 fold.

Table. The dispersion of supported Fe catalysts. The chemisorption was measured at P_{CO} 1200 Torr on 0·50 g of catalyst.

Catalyst	Loading (% Fe)	Net chemisorption/ cm³ (S.T.P.)	Fe dispersion/ %
$Fe_3(CO)_{12}$	0·51	0·234	46
$Fe_2(CO)_9$	0·50	0·235	47
$Fe(CO)_5$	0·48	0·345	71
$Fe(CO)_5$ [a]	0·48	0·027	5·6
Fe [a]	0·33	0·000	0·0
Fe [a]	3·6	0·030	0·83
Fe [a]	8·5	0·029	0·34

[a] Calcined in flowing O_2 at 400 °C for 30 min followed by reduction in flowing H_2 for 1h at 500 °C and cooling in He.

The species present on the carbonyl catalysts after activation at low temperatures are probably best described as subcarbonyl species[5] and may resemble (albeit at much higher dispersion) CO adsorbed on classical catalysts of supported Fe. An interesting difference between the two types of catalysts is that chemisorption continues to high pressures on the carbonyl catalysts (at 200 Torr the amount of chemisorption is 69% of the value at 1200 Torr) whereas the surface becomes saturated at $<$ 20 Torr for each of the classical Fe catalysts,[3] indicative of weaker bonding on the former catalysts. The ready, reversible adsorption of CO on the carbonyl catalysts suggests they are co-ordinatively unsaturated.

Preliminary experiments show that the carbonyl catalysts can be quite active for olefin hydrogenation and methanation.

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† A chemisorption stoicheiometry of 1 CO per surface Fe for the carbonyl catalysts would not materially change the results.

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