Oxidation of Iron in Titania-supported Iron–Ruthenium under Reducing Conditions: *In Situ* Evidence from ^{57}Fe Mössbauer Spectroscopy

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In situ studies of ruthenium-rich iron–ruthenium clusters supported on titania of differing surface areas by ^{57}Fe Mössbauer spectroscopy show that the pre-reduced bimetallic phase undergoes partial oxidation when treated in atmospheres of hydrogen or hydrogen and carbon monoxide.

Titania-supported metal systems have recently attracted considerable interest because of their adsorption properties, the possibility of electron transfer between the metal and titania, and their catalytic behaviour.[1—3] We report here on evidence recorded *in situ* by ^{57}Fe Mössbauer spectroscopy for the unprecedented oxidation of titania-supported iron–ruthenium when heated under reducing conditions. Such behaviour is distinctly different from that observed during recent studies[4] of iron–ruthenium supported on alumina and silica where treatment in hydrogen and in carbon monoxide and hydrogen was accompanied by reduction.

Titania with surface areas of 11, 50, and 237 m^2 g^{-1} was impregnated with aqueous solutions of iron(III) nitrate and ruthenium(III) chloride by methods identical to those used

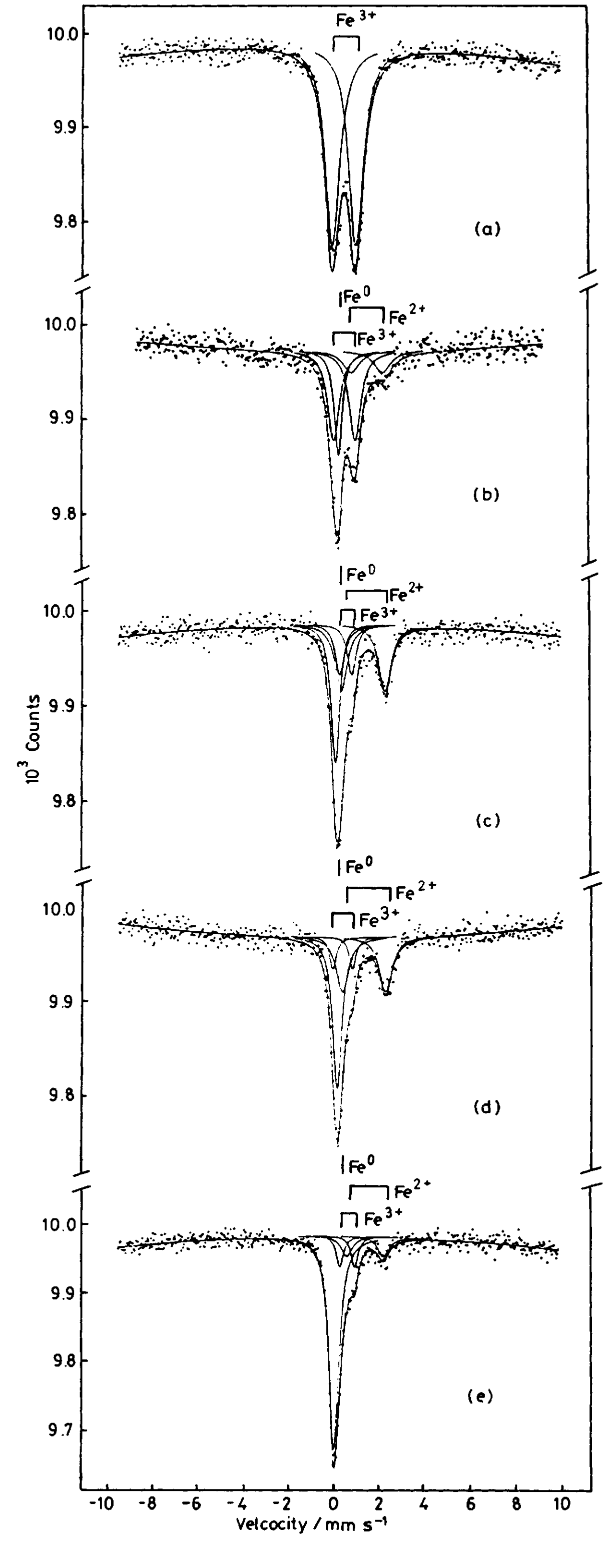

Figure 1. ^{57}Fe Mössbauer spectra recorded *in situ* from 1% Fe–5% Ru–TiO_2 (50 m^2 g^{-1}) following treatment at (a) 480 °C, 4 h, air; (b) 235 °C, 4 h, hydrogen; (c) 450 °C, 4 h, hydrogen; (d) 500 °C, 4 h, hydrogen; (e) 600 °C, 4 h, hydrogen.

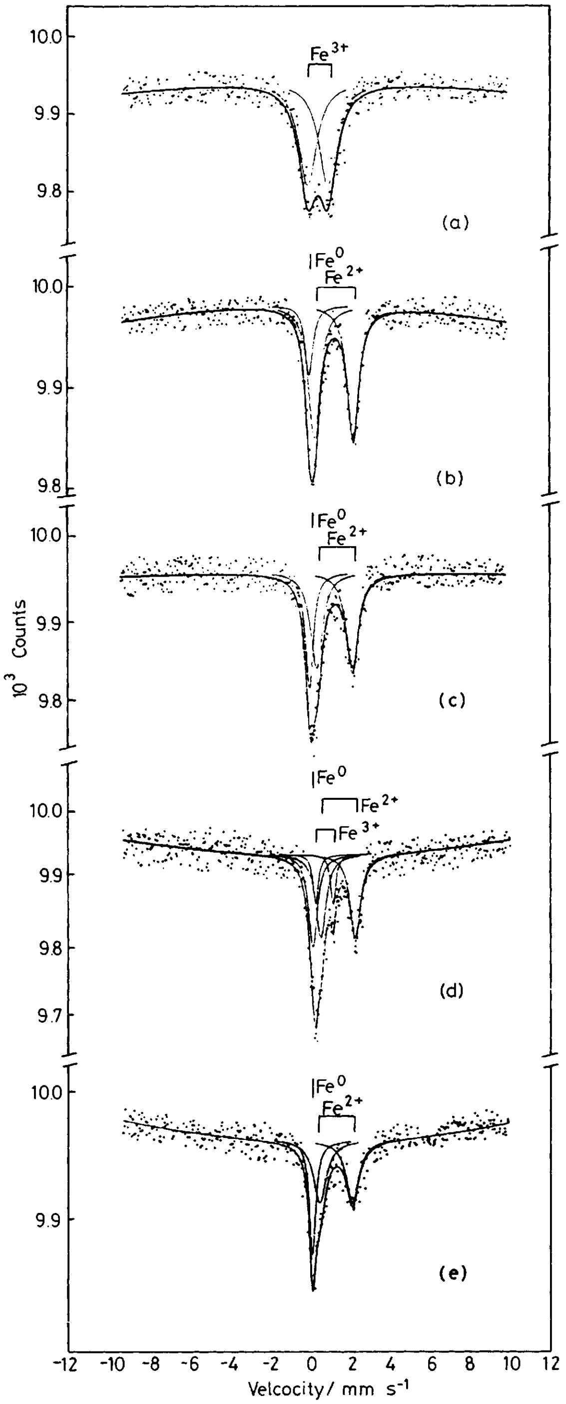

Figure 2. ^{57}Fe Mössbauer spectra recorded *in situ* from 0.2% Fe–1% Ru–TiO_2 (50 m^2 g^{-1}) following treatment at (a) 480 °C, 4 h, air; (b) 235 °C, 4 h, hydrogen; (c) 450 °C, 4 h, hydrogen; (d) 500 °C, 4 h, hydrogen; (e) 600 °C, 4 h, hydrogen.

previously[4] to give metal loadings of 0.2% Fe, 1% Fe, 0.2% Fe–1% Ru, 1% Fe–1% Ru, and 1% Fe–5% Ru. The materials were dried in air at 60 °C (12 h) and at 110 °C (1 h) before calcination in air at 480 °C (4 h). Samples for examination by ^{57}Fe Mössbauer spectroscopy were prepared with 50% of the total iron content being composed of isotopically pure ^{57}Fe. The Mössbauer spectra were recorded at 298 K in a quartz *in situ* cell as previously described.[4]

All samples, except those composed of 0.2% Fe–1% Ru, underwent progressive reduction when treated in hydrogen (66 ml min^{-1}) at increasing temperatures. A typical set of results recorded from the 1% Fe–5% Ru–TiO_2 (50 m^2 g^{-1}) sample is depicted in Figure 1 and shows that the initial

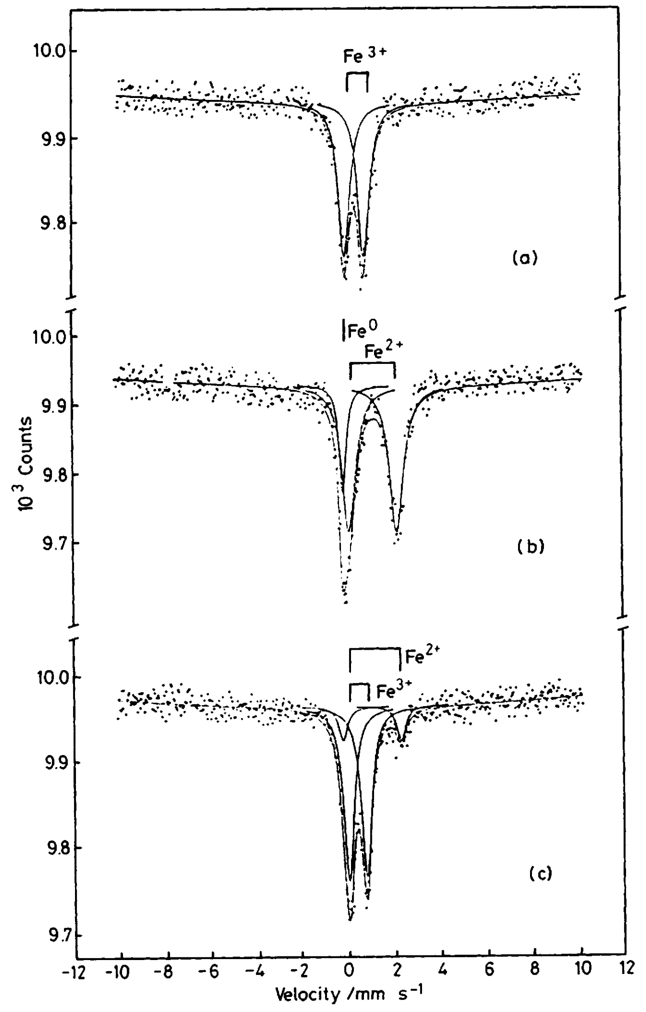

Figure 3. ^{57}Fe Mössbauer spectra recorded *in situ* from 0.2% Fe–1% Ru–TiO_2 (11 m^2 g^{-1}) following treatment at (a) 480 °C, 4 h, air; (b) 235 °C, 4 h, hydrogen; (c) 235 °C, 2 h, carbon monoxide and hydrogen.

material prepared by calcination in air gives a quadrupole split Mössbauer spectrum characteristic of iron(III) in an oxygen environment and very similar to those reported[4—9] for iron oxide supported on alumina and other data which have been associated with supported small particle superparamagnetic α-Fe_2O_3. The iron component was partially reduced at 235 °C in hydrogen to a mixture of iron(III), iron(II), and iron(0) in the form of an iron–ruthenium alloy.[4] Subsequent treatment in hydrogen at 450 °C and 500 °C gave further reduction of the iron(III) species to iron(II) and iron(0) and at 600 °C some of the iron(II) was reduced to the iron–ruthenium alloy.

The behaviour of the samples composed of 0.2% Fe–1% Ru when treated in hydrogen at temperatures exceeding 450 °C was distinctly different. For example, the spectra recorded from 0.2% Fe–1% Ru–TiO_2 (50 m^2 g^{-1}) (Figure 2) showed that exposure to hydrogen at 235 °C and 450 °C gave reduction of iron(III) to iron(II) and the iron–ruthenium alloy but that further treatment in hydrogen at 500 °C was accompanied by partial oxidation of the iron(II) to iron(III). Subsequent treatment in hydrogen at 600 °C was accompanied by reduction of iron(III) to iron(II).

Similar results were recorded when the titania-supported 0.2% Fe–1% Ru samples which had been pre-reduced in hydrogen at 235 °C for 4 h were treated in a 1:2 mixture of flowing carbon monoxide and hydrogen (100 ml min^{-1}). For example 0.2% Fe–1% Ru–TiO_2 (11 m^2 g^{-1}) (Figure 3) which had been pre-reduced to iron(II) and an iron–ruthenium alloy by treatment in hydrogen at 235 °C underwent partial oxidation to iron(III) when treated in carbon monoxide and hydrogen at 235 °C for 2 h.

It appears significant that the formation of iron(III) species from iron(II) during treatment in hydrogen is a feature of low metal loaded, low iron content iron–ruthenium (0.2% Fe) on all three titania supports and is not observed in the bimetallic materials supported on silica and alumina. It is also pertinent to note that the oxidized iron is reduced when the treatments under hydrogen are continued at 600 °C and it seems unlikely that the oxidation is a result of the thermally induced loss of oxygen from the titania support. However, it would be reasonable to assume that the initial treatment of the bimetallic materials containing 0.2% iron in hydrogen at temperatures not exceeding 450 °C gives small particles of iron(II) which may be in contact with the excess of non-alloyed ruthenium which was shown by *X*-ray photoelectron spectroscopy to be present as ruthenium metal. A comparison of the ^{57}Fe Mössbauer data recorded from hydrogen-reduced low metal-loaded titania with that on alumina and silica[4] shows that iron interacts weakly with titania and, given the capacity of group 8 metals to transfer electrons to titania,[3] it seems possible that at 500 °C electron transfer from iron(II) to ruthenium and thence to the titania support gives rise to the formation of iron(III), perhaps as a superficial layer on the iron(II) species, which is amenable to reduction to iron(II) when treated in hydrogen at higher temperatures. In support of this mechanism we would mention that the titania-supported 0.2% Fe–1% Ru materials which had been reduced at 450 °C in hydrogen also underwent oxidation when heated in oxygen-free argon at 500 °C but were not re-reduced by subsequent treatment in the inert atmosphere. Furthermore, a titania-supported 0.2% Fe material which had been reduced at 450 °C for 4 h in hydrogen was unchanged by treatment in argon at higher temperatures.

It is interesting to note the amenability to oxidation of the pre-reduced titania-supported 0.2% Fe–1% Ru materials at a lower temperature in carbon monoxide and hydrogen than in pure hydrogen. The result may be indicative of the dissociative chemisorption of carbon monoxide on iron and the consequent generation of oxygen which enhances the anaerobic conversion of iron(II) into iron(III). The iron carbide formed by the dissociative chemisorption of carbon monoxide may be hydrogenerated by hydrogen adsorbed on the excess of ruthenium.

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