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Iron-57 Mössbauer Spectra of Supported Iron Oxides and Hydroxides

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Supported α-Fe_2O_3 is readily obtained by heating microgram quantities of iron-57 on magnesium oxide in vacuo. *Treatments which produce heavier iron coatings give hydrolysed iron(III) species which may be difficult to distinguish and which dehydrate less readily. Thin layers of supported α-Fe_2O_3 are reduced by hydrogen to an iron(II) species whereas materials containing thicker layers of hydrolysed iron(III) are partially converted to metallic iron.*
iron.

Introduction

Mössbauer spectroscopy is in principle a favourable technique for the study of catalysts and solid surfaces. The adsorption of microcrystallites onto high area inert supports produces materials in which a large proportion of the atoms are at surface sites. Such materials are well suited to examination by transmission Mössbauer spectroscopy and the materials often resemble catalysts which are used in large scale processes. It is unfortunate that many of the initial Mössbauer studies have reported contradictory data [1] which may reflect differences in coverage of the supporting material and the number of surface Mössbauer nuclei. It is also possible that reactions between the support and the adsorbed species have lead to confusion over the nature of the supported material.

This work compares iron-57 Mössbauer spectra recorded from samples bearing a heavy loading of iron on magnesium oxide with spectra from samples prepared with microgram quantities of iron-57. The reduction of these materials with hydrogen has also been investigated.

Experimental

The supported iron oxides and hydroxides were prepared by adsorbing iron onto finely divided magnesium oxide (4×10^{-8} m particle diameter) from aqueous solutions of iron(III) salts, separating the product and drying in air.

Iron-57 Mössbauer spectra were recorded in the transmission mode with a conventional constant acceleration spectrometer using a $^{57}Co/Rh$ source.

Results and Discussion

The iron-57 Mössbauer parameters of the materials investigated are recorded in Tables I, III, IV and V.

Iron Oxides and Hydroxides

Contrary to some reports [2] the iron-57 Mössbauer parameters of samples heated in air were independent of the anion characterising the impregnating iron(III) solution.

Samples containing more than 4% by weight of iron and dried at 473 K in air gave quadrupole split absorptions at 298 K and 77 K, $\delta \sim 0.30$ mm s^{-1}; $\Delta \sim 0.72$ mm s^{-1}, which were similar to those reported [2–6] for small particle [5] (<180 Å) superparamagnetic α-Fe_2O_3 when supported on silica gel or alumina. A summary of these data are given in Table II.

It is significant that these Mössbauer parameters resemble those reported for hydrolysed iron(III) species [7], δ 0.35 mm s^{-1}; Δ 0.72 mm s^{-1}, iron(III) hydroxides [8] and thin layers [9] (<50 Å) of γ-FeOOH, $\Delta \sim 0.73$ mm s^{-1}.

Samples containing more than 20% by weight of iron gave quadrupole split Mössbauer spectra until calcined at 873 K when six line patterns typical [10] of bulk antiferromagnetic α-Fe_2O_3 were recorded. A sample containing 19% by weight of iron calcined at 873 K gave a spectrum showing the superimposition of a doublet on a six line pattern similar to that obtained [11] when non magnetic marine nodules which initially gave quadrupole split spectra attributable to an iron(III) hydroxide were heated at 923 K. Similar composite spectra were recorded from samples containing 1–2% by weight of iron and dried at 473 K.

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TABLE I. Iron-57 Mössbauer Parameters for Iron Oxides Supported on Magnesium Oxide and Heated in Air.

% by weight adsorbed	Impregnating solution	Dried at K	Spectrum at K	Mössbauer Parameters			
				Doublet		Magnetic Splitting	
				$\delta(\pm0.03)^a$/mm s^{-1}	$\Delta(\pm0.05)$/mm s^{-1}	$\delta(\pm0.05)^a$/mm s^{-1}	H/kG
34	$Fe(NO_3)_3$	473	298	0.29	0.70		
		473	77	0.31	0.74		
		823	298	0.30	0.74		
		873	298			0.33	482
		873	77			0.38	496
27	$Fe(NO_3)_3$	473	298	0.29	0.70		
		473	77	0.31	0.72		
	$FeCl_3$	473	298	0.28	0.73		
		473	77	0.30	0.75		
19	$Fe(NO_3)_3$	473	298	0.29	0.71		
		473	77	0.31	0.75		
		873	298	0.28	0.73	0.34	467
		873	77	0.31	0.76	0.36	477
4	$Fe(NO_3)_3$	473	298	0.29	0.73		
2	$Fe(NO_3)_3$	473	298	0.29	0.69	0.28	464
		473	77	0.38	0.68	0.36	472
	$FeCl_3$	473	298	0.34	0.69	0.28	474
1	$Fe(NO_3)_3$	473	298	0.33	0.76	0.29	461

[a] δ relative to iron metal.

TABLE II. Iron-57 Mössbauer Parameters for Quadrupole Split Spectra of Supported Iron Oxide Microcrystallites.

Support	δ/mm s^{-1}	δ(Fe)/mm s^{-1}	Δ/mm s^{-1}	Ref.
Silica	0.13^a	0.31	0.60	2
Silica	0.16^a	0.34	0.75	2
Silica	0.62^b	0.37	0.84	3
Silica	0.63^b	0.38	0.73	3
α-alumina	0.58^b	0.33	0.71	3
α-alumina	0.63^b	0.38	0.72	3
η-alumina	0.58^b	0.33	0.95	3
η-alumina	0.64^b	0.39	0.82	3
γ-alumina	0.59^b	0.34	0.99	3
γ-alumina	0.60^b	0.35	0.87	3
Silica	0.56^b	0.31	0.69	4
Silica	0.65^b	0.40	0.74	4
Silica	0.60^b	0.35	0.77	4
Silica	0.56^b	0.31	0.71	4
Silica		0.38	0.44	6
Silica		0.32	0.57	6
Silica		0.32	0.98	6

[a] δ relative to Co/Pd. [b] δ relative to sodium nitroprusside.

It is clearly difficult to distinguish the hydrolysed species referred to above from the superparamagnetic α-Fe_2O_3 by Mössbauer spectroscopy and it seems possible that the materials in which the iron content would be unlikely to give small particle superparamagnetic α-Fe_2O_3 may contain an iron(III) hydroxide, possibly γ-FeOOH, which is paramagnetic at 77 K.

It is interesting to note [12] that X-ray techniques are not always capable of distinguishing different surface species and it is also significant that the possibility of compound formation between the support and the supported material cannot be ignored.

Materials containing 2% by weight of iron, when heated between 473 K and 873 K *in vacuo*, gave quadrupole splittings (Table III) which were larger than those of the materials calcined in air. The quadrupole splittings decreased ($\Delta \sim 0.70$ mm s^{-1}) on adsorption of water vapour but were recovered by subsequent heating *in vacuo* suggesting that dehydration processes are as likely to cause larger quadrupole splittings in supported iron oxides as are superficial iron(III) ions or decreasing α-Fe_2O_3 particle size [3].

It would seem reasonable to expect that authentic small particle supported α-Fe_2O_3 may be best prepared by heating materials bearing microgram quantities of iron-57 *in vacuo*. The examination of enriched iron oxides containing 10 μg of ^{57}Fe which

TABLE III. Iron-57 Mössbauer Parameters at 298 K for Iron Oxide Supported on Magnesium Oxide Containing 2% by Weight of Iron and Heated *in vacuo.*

Temperature K	Time hours	Mössbauer Parameters	
		$\delta(\pm0.03)^a$/ mm s^{-1}	$\Delta(\pm0.05)$/ mm s^{-1}
473	4	0.31	0.92
673	4	0.31	0.89
873	4	0.30	0.81

[a] δ relative to iron metal.

TABLE IV. Iron-57 Mössbauer Parameters at 298 K for Iron Oxides Supported on Magnesium Oxide Containing 10 μg of ^{57}Fe and Heated *in vacuo.*

Temperature K	Time hours	Mössbauer Parameters	
		$\delta(\pm0.03)^a$/ mm s^{-1}	$\Delta(\pm0.05)$/ mm s^{-1}
298	16	0.37	0.65
373	4	0.37	0.65
573	4	0.37	0.71
873	4	0.36	0.83

[a] δ relative to iron metal.

occupies an area of 300 cm^2 gave, when heated *in vacuo,* Mössbauer spectra (Table IV) showing the typical chemical isomer shifts of high spin iron(III) ions and quadrupole splittings which gradually increased with temperature. No transition to a species showing magnetic ordering was observed even when the materials were heated to 873 K in air. The line widths were larger than those expected for iron in well crystallised materials and were consistent with the presence of iron(III) ions in a heterogenity of sites producing a range of superimposed quadrupole split Mössbauer absorptions.

Reduction of These Materials

Hydrogen reduction of samples containing more than 2% by weight of iron oxide or hydroxide at 873 K gave spectra at 298 K (Table V) which were similar to those previously interpreted [13–17] in terms of the superposition of an iron(II) doublet on a six line metallic iron pattern. The Mössbauer parameters resembled those recorded for other specimens containing more than 10% of iron [13] where the less intimate metal-support interaction seems to facilitate reduction to metallic iron. Reports of the reduction of a 3 wt% sample of iron oxide on silica gel to a high spin iron(II)–iron(III) mixture [18] which was further reduced on adsorption of ammonia [19] could not be confirmed.

The materials prepared from the separated iron-57 were reduced at 873 K to a species with Mössbauer parameters, δ 1.12 mm s^{-1}; Δ 0.31 mm s^{-1}. The spectrum although typical of an iron(II) species was not unlike that reported [20] for the iron oxide called 'wustite' formed during the reduction of α-Fe$_2$O$_3$. Reactions at lower temperatures gave incomplete conversion to the reduced form. Heating the reduced materials in air returned all the samples to the original iron(III) species.

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TABLE V. Iron-57 Mössbauer Parameters at 298 K for Iron Oxide Supported on Magnesium Oxide Reduced with Hydrogen.

% by weight of iron adsorbed	Reduction temp/time K/hours	Mössbauer Parameters			
		Doublet		Magnetic Splitting	
		δ $(\pm0.03)^a$/mm s^{-1}	Δ (±0.05)/mm s^{-1}	δ $(\pm0.03)^a$/mm s^{-1}	H/kG
34	873/4	0.94	0.81	0.08	124
	873/6	0.91	0.87	0.05	118
27	873/4	0.99	0.84	0.02	119
	873/6	1.01	0.74	0.10	122
17	873/4	1.01	0.81	0.01	114
	873/6	1.01	0.77	0.02	122
2	873/4	0.99	0.90	0.01	118
	873/6	0.97	0.76	0.02	119

[a] δ relative to iron metal.

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