MAGNETIC HYPERFINE FIELD STRUCTURE OF IRON URUSHIBARA TYPE CATALYSTS

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ABSTRACT

We have utilized the Mössbauer effect to study the hyperfine field structure of iron Urushibara catalysts. The Mössbauer spectra of those catalysts prepared using zinc show that they consist of a mixture of magnetic and non-magnetic Fe-Zn alloys. Both the magnetic field distribution in the magnetic phase and the relative amounts of magnetic and non-magnetic phases depend on the Fe-Zn ratio used in the preparation of the catalyst. This dependence on Fe-Zn ratio is in contrast to iron Urushibara catalysts prepared using aluminum (and Raney iron type catalysts) in which the active phase is almost pure α-Fe, irrespective of the Fe-Al ratio. The activity of zinc prepared iron Urushibara catalysts for certain hydrogenation reactions is known to be greater than that of aluminum prepared iron Urushibara catalysts and the above results suggest a relationship between activity and the modification of the iron catalyst by alloyed zinc. The alloying behavior of the Fe-Zn particles may be analogous to that of the so-called bimetallic clusters observed in other alloy systems.

INTRODUCTION

Relationships between the electronic and magnetic properties of solids and their activity as heterogeneous catalysts have been the subject of considerable discussion and controversy.[1] In particular, the fact that many transition metals and their alloys have high activity as hydrogenation catalysts is well known and yet the development of an unambiguous relationship between electronic properties and catalytic activity has been elusive. Most catalysts are prepared by techniques which give a material with high surface area. These preparation techniques also give a material with a complex structure which is difficult to determine due largely to the fact that the active material is in the form of small particles. One of the most difficult parameters to determine, and one which is of great importance in investigating relationships between electronic structure and catalytic properties, is the extent to which the metals used in preparing the catalysts are alloyed together. In this paper we utilize the ^{57}Fe Mössbauer effect to study the effect of preparation technique on the alloying and magnetic behavior of Urushibara type iron hydrogenation catalysts.

Urushibara Fe can be prepared[2] from either a ferrous chloride or ferric chloride solution. The resulting catalysts are denoted Urushibara-Fe(II) and Urushibara-Fe(III), respectively. Here we consider catalysts of the Urushibara-Fe(III) type prepared utilizing both Al and Zn and denoted Urushibara-Fe(III)-Al and Urushibara-Fe(III)-Zn, respectively. In the course of this study it has been discovered that those prepared using Zn form multi-phase Fe-Zn alloys in which the total Zn can be varied considerably. There appears to be very little alloying behavior for those prepared using aluminum. This is in contrast to previous work in which it was believed[2] that both were nearly pure α-Fe.
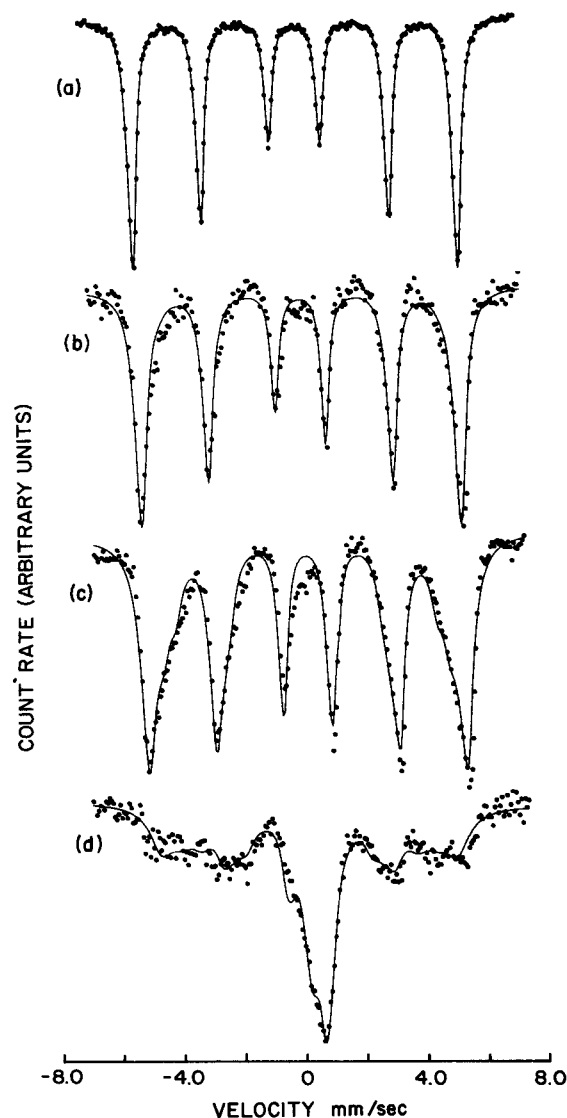

Fig. 1 Mössbauer spectra from catalysts prepared as described in the text. Circles are data points and solid line is the least squares fit. Zero velocity represents the center of a pure Fe spectrum. All spectra were taken at 298±2K. (a) Urushibara-Fe(III)-Al, (b) Urushibara-Fe(III)-Zn1, (c) Urushibara-Fe(III)-Zn2, (d) Urushibara-Fe(III)-Zn3.

EXPERIMENTAL

Samples were prepared according to the methods given in detail by Hata.[2] Hata[2] also gives a detailed discussion of chemical reactions, particle sizes, x-ray diffraction, etc. Urushibara-Fe(III)-Zn was prepared by adding iron chloride (FeCl$_3$·6HO) to a mixture of 25g zinc dust in 8 ml water. The product was washed with water and the solid recovered by filtering. This material was then treated with acetic acid and the resulting catalyst collected on a sintered glass filter and washed with ethyl alcohol. A small amount of the catalyst was mounted in amyl acetate and Mössbauer spectra obtained at room temperature. Four samples are reported on in

Table I

Parameters obtained from least squares fitting the spectra of Fig. 1. Spectra were obtained and 298±2K and isomer shifts are relative to α-Fe at that temperature.

Parameter	Al	SAMPLE U-Fe(III)- Zn1	Zn2	Zn3
$\langle H_1 \rangle$,kG	329	325	324	300
σ_{H_1},kG	-	12	16	39
H_1 rel. intensity	1.0	0.96	0.61	0.30
$\langle H_2 \rangle$,kG	-	285	290	260
σ_{H_2},kG	-	12	24	40
H_2 rel. intensity	0	0.02	0.27	0.15
$\langle H_3 \rangle$,kG	-	-	265	220
σ_{H_3},kG	-	-	35	40
H_3 rel. intensity	0	0	0.10	0.18
Line 1 Isomer Shift, mm/s	-	+0.82	+0.85	+0.60
Width, mm/s	-	0.30	0.28	0.57
relative intensity	-	0.02	0.02	0.17
Line 2 Isomer Shift	-	-	-	+0.12
Width	-	-	-	0.73
relative intensity	-	-	-	0.20

spectrum from Urushibara-Fe(III)-Al (Fig. 1a) was fitted to a single six-line magnetic hyperfine field pattern. The spectra from the Urushibara-Fe(III)-Zn samples (Figs. 1b, 1c, and 1d) were fitted to three separate six-line magnetic hyperfine field patterns with average field <H>. Each of the three six-line patterns was constrained to have a 3:2:1:1:2:3 line intensity ratio and each was assumed to be broadened by a hyperfine field distribution with width σ_H. For Urushibara-Fe(III)-Zn1 and Urushibara-Fe(III)-Zn2 (Figs. 1b and 1c), one additional line was assumed responsible for the increased intensity evident in detail here: for Urushibara-Fe(III)-Zn1, 20 g of iron chloride were added to the zinc dust-water mixture; for Urushibara-Fe(III)-Zn2, 7.5 g were added; and for Urushibara-Fe(III)-Zn3, 2.5 g were added; a sample of Urushibara-Fe(III)-Al was prepared utilizing 10 g of iron chloride and 20 g of Al powder.

RESULTS

Mössbauer spectra from the four samples are shown in Fig. 1. The spectra were least squares fitted using a program described previously.[3] The

one of the inner two lines of the magnetic pattern and was included in the least squares fit. For Urushibara-Fe(III)-Zn3 (Fig. 1d) two additional central lines were included in the fit. As can be seen from the Figure, this fitting procedure gave reasonable fits. These fits are considered adequate to reveal the main features of the spectra. Numerical results are displayed in Table I.

DISCUSSION

The spectrum for Urushibara-Fe(III)-Al (Fig. 1a) is, within our experimental error, indistinguishable from that obtained for pure α-Fe. For Urushibara-Fe(III)-Zn (Figs. 1b, 1c, and 1d) a two phase material is indicated, one phase being magnetic and the other non-magnetic. The possibility of incipient superparamagnetism was ruled out by applying a 1 kG field. This produced no detectable change in the observed spectra. The presence of iron oxides, hydroxides, etc. can be ruled out on the basis of known hyperfine fields and isomer shifts. For the magnetic phase, both the hyperfine field value and the broadened lines indicate an alloy which is a primary solid solution of Zn in α-Fe. Currently, no information concerning the Mössbauer spectra of iron-rich Fe-Zn alloys is available. However, in analogy with disordered Fe-Al, Fe-V, etc., one expects the hyperfine field, H_n, for an Fe atom surrounded by n nearest-neighbor Zn atoms to be given approximately by

$$H_n \approx H_o - n\Delta H. \qquad (1)$$

The effect of second, third, etc., nearest neighbor Zn atoms is, in first approximation, a reduction in hyperfine field value and a broadening of each line.

Using these simple considerations and assuming randomness, one can make a rough estimate of the concentration of Zn in the magnetic phase. These estimates are: 1/2% for Urushibara-Fe(III)-Zn1, 6% for Urushibara-Fe(III)-Zn2; and 8% for Urushibara-Fe(III)-Zn3. The accuracy of these results depend on the validity of the model used (especially the assumption of randomness) and, considering the rather large value of 40 kG found for ΔH, probably represent lower limits. The six and eight percent values are considerably in excess of the equilibrium solid solubility at room temperature (~4%).

Both the considerable alloying of Fe and Zn and the absence of alloying of Fe and Al in these catalysts are contrary to what one might expect if only the bulk phase diagram were considered. It is possible that the thermodynamic stability of the small metallic particles is such than an Fe-Zn alloy is more stable than separate Fe and Zn particles, as has been demonstrated theoretically and experimentally in a number of other alloy systems.[4] For example, systems such as Cu-Os, which are almost immiscible in the bulk, have been shown to exhibit a much enhanced miscibility when in the form of extremely small particles, forming so-called[5] "bimetallic clusters." The enchanced solid solution of Zn in Fe observed in the present study may be due to a similar phenomenon.

The possibility of high local temperatures in the region of the embryonic Fe particles might also be considered as a source of the high degree of Fe-Zn alloying. However, magnetic iron oxides would also be expected to form under these conditions and we have no evidence for a magnetic Fe oxide being present. In addition, such local heating would also be present in the preparation of Urushibara-Fe(III)-Al, and Fe-Al alloys would also be expected to form, but there is no evi-

dence for these alloys. The alloying that takes place thus appears due to chemical driving forces during the catalyst preparation.

The catalytic activities of Urushibara iron prepared using Zn or Al are known to be considerably different. For example, Urushibara-Fe(III)-Zn is active for the partial hydrogenation of 2-butyne-1,4-diol, whereas Urushibara-Fe(III)-Al is entirely inactive.[6] The Mössbauer results presented here suggest that this promotion effect of Zn could be due to the formation of Fe-Zn alloys. If this is the case, then there should be an optimum value of Zn content which maximizes the reaction rate.

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SIZE EFFECT ON THE SPIN WAVE RESONANCE SPECTRA
OF HEISENBERG ANTIFERROMAGNETIC FILMS*

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The spin wave resonance absorption spectra in simple cubic Heisenberg antiferromagnetic films of different thicknesses are calculated, the surfaces being (111) planes. By using spin wave theory, we obtain one surface spin wave resonance absorption line and a series of bulk spin wave resonance absorption lines. We find that the intensity of the surface spin wave line relative to those of the bulk increases as the film becomes thinner. For very thin films, the spectrum is quite sensitive to whether the number of layers is even or odd. For thick films, if the anisotropy field is much smaller than the exchange field, the surface spin wave frequency is lower than that of the lowest bulk spin wave frequency by approximately a factor of $\sqrt{2}$. The bulk spin wave frequencies obey the n^2 law and the intensities vary as $1/n^2$; this agrees with the work of Orbach and Pincus.[1]

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