

acid-Lewis base reactions and the one-electron redox processes or whether different surface sites are responsible remains uncertain.

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Mossbauer Effect Spectra of a Supported Iron Catalyst*

The Mossbauer effect spectra of silica gel and alumina impregnated with iron and calcined in air have been reported by several authors (1-3). These samples were studied "as prepared" without any control of the environment. We wish to report some initial work on the application of the Mossbauer effect to the study of the structure of an iron-on-silica-gel catalyst in both the oxidized and reduced state.

A catalyst was prepared by impregnating Davison 923 silica gel with sufficient ferric nitrate solution enriched in iron-57 to produce a 3 wt % iron-on-silica-gel sample. This catalyst was placed in a thin-window glass cell and calcined in oxygen at 500°C

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for 16 hr. The Mossbauer effect spectrum after outgassing the calcined sample is shown in Fig. 1. It is similar to spectra reported by others, except for an unusually large quadrupole splitting of 1.87 mm/sec. Kündig *et al.* (3) prepared a series of iron-on-silica-gel samples in a manner similar to ours, but varied the crystallite size of the ferric oxide on the surface by varying the concentration of the impregnating solution. They found that the quadrupole splitting increased from 0.44 mm/sec for α -Fe₂O₃ crystallites with an average diameter of 180 Å to 0.57 mm/sec for those with an average diameter of 135 Å. A rough extrapolation of their data suggests that the α -Fe₂O₃ crystallites are about 20 Å in diameter in this sample. However, the electric field gradient responsible for the quadrupole splitting is sensitive to the geometrical and defect structure of the crys-

tallites, and the extrapolation is subject to very large error. At most, the crystallites are small enough to escape measurement by X-ray line-broadening, which means they are less than 100 Å in diameter. It is interesting to note that the quadrupole splitting for this sample is greater than the value calculated by Flinn *et al.* (1) for a

this with the results of Kündig *et al.* (3) we find that very small crystallite size is indicated. The shift decreases with decreasing size, and Kündig reported values going from +0.63 to +0.57 mm/sec for the samples described above. The cause of these changes in the differential chemical shift and quadrupole splitting as a function of

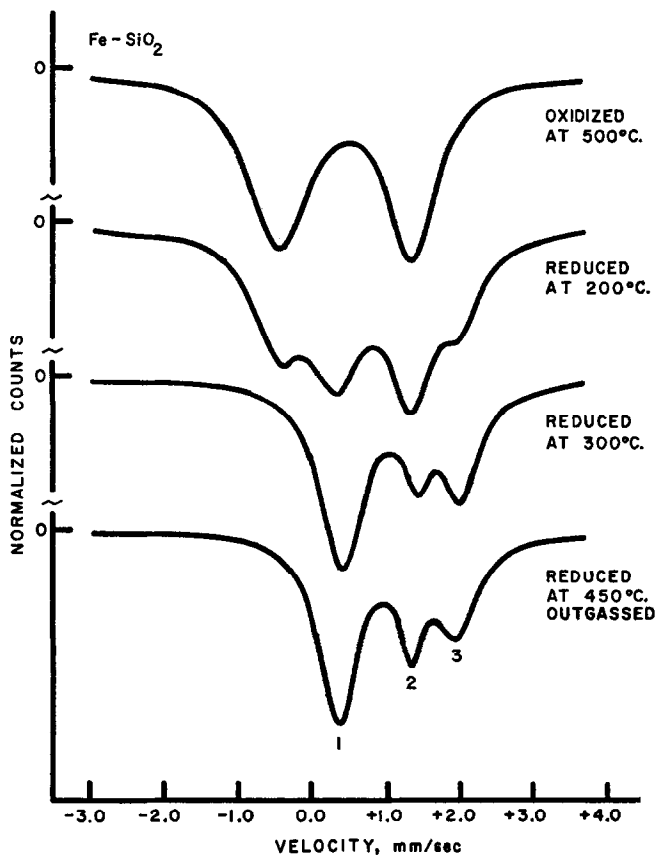


FIG. 1. Mossbauer absorption spectra of a 3 wt % iron-on-silica-gel sample undergoing progressive reduction with hydrogen.

ferric ion in an octahedral environment with one oxygen missing, but it is less than the calculated value of 2.26 mm/sec obtained for this model using the more recent value of -9.14 for the Sternheimer anti-shielding factor (4).

We found a differential chemical shift, defined as the position of the centroid of the sample spectrum relative to the centroid of the spectrum of a sodium nitroprusside standard reference crystal (5), of $+0.543$ mm/sec for this sample. Again comparing

crystallite size is not known, but it is reasonable to assume that there is an increasing number of defects in the structure as the crystals become smaller which produces a gradual change in the average coordination number for the iron site. The same type of change in these two parameters has been observed for ferric ions going from octahedral to tetrahedral sites in spinel structures (4, 6).

Both the quadrupole splitting and the differential chemical shift are temperature-

dependent, as shown in Table 1. Similar results were obtained by Flinn, Ruby, and Kehl (1). In fact, the change in differential chemical shift, $\delta_0 = 5 \times 10^{-4}$ mm/sec $^{\circ}$ K, is almost an exact match, but the change in the quadrupole splitting of our sample with temperature is much larger than theirs.

The asymmetry seen in the two peaks is commonly observed and may arise from either the Goldanskii effect or relaxation phenomena. The Goldanskii effect is the result of anisotropy in the recoil-free fraction in the gamma ray emission. It would

TABLE 1
DIFFERENTIAL CHEMICAL SHIFTS AND
QUADRUPOLE SPLITTINGS FOR IRON ON SILICA
GEL CALCINED AT 500 $^{\circ}$ C AS A FUNCTION
OF SAMPLE TEMPERATURE

| Temperature ($^{\circ}$ C) | Differential chemical shift (mm/sec) | Quadrupole splitting (mm/sec) |
|--|---|-------------------------------------|
| 26.0 $^{\circ}$ \pm 1.0 $^{\circ}$ | +0.543 \pm 0.005 | 1.876 \pm 0.017 |
| 25.0 $^{\circ}$ \pm 1.0 $^{\circ}$ | +0.548 \pm 0.005 | 1.868 \pm 0.017 |
| -91.0 $^{\circ}$ \pm 1.0 $^{\circ}$ | +0.602 \pm 0.005 | 1.907 \pm 0.016 |
| -101.0 $^{\circ}$ \pm 1.0 $^{\circ}$ | +0.611 \pm 0.005 | 1.923 \pm 0.017 |

be expected to be present in highly dispersed catalyst samples since the vibrational amplitude of the iron nucleus normal to and parallel to the surface would not be expected to be the same. Superimposed on this may be an asymmetry produced by relaxation effects. Blume (7) has shown for ferric ions that, as the spin-lattice relaxation time of the 3d electrons approaches the Larmor precessional frequency of the nucleus when the temperature is lowered, the $\frac{1}{2} \rightarrow \frac{3}{2}$ transition begins to broaden before the $\frac{1}{2} \rightarrow \frac{1}{2}$ transition. Then, as the temperature decreases, the two peaks become more asymmetric, which is just the reverse of the temperature dependence of the Goldanskii effect. The asymmetry in the spectrum of our sample is temperature-independent. The recoil-free fraction increases with decreasing temperature as expected, but the relative peak heights remain constant. It may be that the two effects are operative and cancel each

other out over the limited temperature range we have covered.

Following calcination the oxide was progressively reduced by heating in hydrogen at 200 $^{\circ}$, 300 $^{\circ}$, and 450 $^{\circ}$ C. The resulting spectra are shown below the oxide spectrum in Fig. 1. In each case, except the last, the sample was cooled in its hydrogen atmosphere to room temperature before it was pumped out. Thus, each spectrum represents a reduced state, or partially reduced state, with hydrogen chemisorbed on it. The bottom spectrum resulted from outgassing the sample for 12 hr at 450 $^{\circ}$ C after reduction at that temperature. The quadrupole splitting of the oxide disappears and is replaced by a spectrum which contains three peaks and is shifted toward more positive velocities. The middle peak appears to be most sensitive to adsorption. Its size relative to the other two peaks increases with the degree of outgassing. The spectrum of the reduced and outgassed catalyst must be representative of iron atoms in at least two different states on the surface. The half-width at half-maximum is much smaller for the middle peak than for the other two, which is a strong indication of two states. Numbered from left to right peaks 1 and 3 appear to constitute a doublet caused by quadrupole splitting at one iron site. The values at room temperature for the differential chemical shift, +1.36 mm/sec., and the quadrupole splitting, 1.65 mm/sec., are typical of a high-spin ferrous state. The middle peak presents a problem. It appears to be a singlet, but it is difficult to imagine an atom on, or just in the surface, as having a symmetrical electrical field gradient surrounding the nucleus. If an asymmetric electrical field gradient obtains at the nuclei of the iron atoms producing peak 2, then peak 2 is half of a doublet with the other half superimposed on either peak 1 or peak 3. The fraction of the total area under the peaks varies with hydrogen coverage for peaks 2 and 3, but the fraction under peak 1 remains constant. This suggests that peaks 1 and 2 constitute a second doublet caused by quadrupole splitting.

In Table 2 the differential chemical

shifts and the quadrupole splittings are given for superimposed doublets consisting of peaks 1 and 2 and peaks 1 and 3 as a function of the temperature of the sample. Also, the differential chemical shift of peak 2 is given as a function of sample temperature. The temperature dependence of the 1-2 doublet is small and linear. This is characteristic of the ferric state in which the $3d$ orbitals are just half-filled. Changes in the electric field gradient are dependent only on expansion and contraction of the lattice. On the other hand, the temperature dependence of the 1-3 doublet is much

cating a ferric state, but $\delta_0 = +1.513$ mm/sec for peak 2, which is much too large for a ferric ion. Thus, peak 2 must be part of a doublet.

Two iron sites have been tentatively identified in the spectrum of the reduced catalyst; one, a ferric ion with a room-temperature differential chemical shift and quadrupole splitting of $+1.023$ mm/sec and 0.980 mm/sec, respectively, and, two, a ferrous ion with a room-temperature differential chemical shift and quadrupole splitting of $+1.357$ mm/sec and 1.649 mm/sec, respectively. Extensive literature on the preparation of iron catalysts (δ) show that the initial reduction of iron oxide produces magnetite followed by a slow and difficult reduction to the metal. No Mossbauer spectra of very small particles of magnetite are available for comparison, but the areas under the two small peaks in our spectra are both about 25% of the total and vary relative to each other by only a few percent during final reduction and outgassing steps. In a magnetite structure the area under the spectrum produced by the ferric ion should be twice as large as the area produced by the ferrous ion. Therefore, the probable state of the reduced form of this catalyst is a 1-to-1 mixture of ferrous and ferric oxide of very small particle size on the surface of the silica gel.

Further Mossbauer effect measurements are being made on supported iron catalysts as a function of catalyst preparation, support material, and chemisorption of various compounds in hopes of defining more precisely the nature of the active sites.

TABLE 2
DIFFERENTIAL CHEMICAL SHIFTS AND
QUADRUPOLE SPLITTINGS FOR IRON ON SILICA
GEL REDUCED AND OUTGASSED AT 450°C AS A
FUNCTION OF SAMPLE TEMPERATURE

| Temperature (°C) | Peak | Differential chemical shift (mm/sec) | Quadrupole splitting (mm/sec) |
|-------------------------|------|---|-------------------------------------|
| $26^\circ \pm 1^\circ$ | 1-2 | $+1.023 \pm 0.005$ | 0.980 ± 0.013 |
| | 1-3 | $+1.357 \pm 0.010$ | 1.649 ± 0.024 |
| | 2 | $+1.513 \pm 0.005$ | |
| $-26^\circ \pm 1^\circ$ | 1-2 | $+1.043 \pm 0.005$ | 0.996 ± 0.014 |
| | 1-3 | $+1.361 \pm 0.011$ | 1.633 ± 0.027 |
| | 2 | $+1.540 \pm 0.005$ | |
| $-87^\circ \pm 1^\circ$ | 1-2 | $+1.076 \pm 0.005$ | 1.013 ± 0.011 |
| | 1-3 | $+1.428 \pm 0.008$ | 1.719 ± 0.020 |
| | 2 | $+1.582 \pm 0.005$ | |

larger and the slope increases with a decrease in the temperature. This is characteristic of the ferrous state with its additional $3d$ electron distributed between all of the $3d$ orbitals in the high-temperature limit. As the temperature is lowered the population by the sixth electron of the lowest level of the $3d$ orbitals increases relative to the upper levels, and this has a larger effect on the electric field gradient than the expansion and contraction of the lattice. Now consider the possibility of peak 2 being a singlet. The temperature dependence of the differential chemical shift for peak 2 is small and linear, indi-

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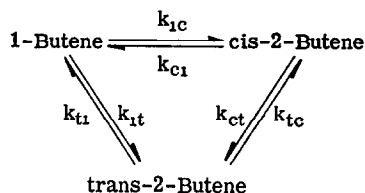
Selective Poisoning of Al_2O_3 Catalysts

In two recent Notes, Medema and Houtman (1, 2) reported evidence for two types of active centers for *n*-butene isomerization over gamma alumina. They based their claims on abrupt changes in certain product curves and on different cutoff points as reactions of each of the isomers were progressively poisoned with triethylamine in a microcatalytic reactor. It is the purpose of this communication to point out possible dangers in applying this technique and to offer an alternative explanation for their results.

Several investigators (3-9) have shown that *n*-butene isomerization reactions follow first order kinetics over acidic oxide catalysts. By making one of the reactants radioactive, it was possible for us (9) to follow to equilibrium simultaneously the conversion of *two* isomers over alumina in a static reactor, and these results could be quantitatively reproduced with a mathematical model based entirely on first order kinetics. All six relative rate constants, and also their temperature dependencies, were determined. Furthermore, neither poisoning nor selectivity changes with time, such as those reported by Medema and Houtman (1) in their Fig. 3, were observed with our alumina, which was prepared from the neutral hydrolysis of aluminum isopropoxide and was probably a mixture of eta and gamma alumina.

Although the two aluminas may be different, it is possible to use data from our catalyst to calculate reaction distribution patterns (Fig. 2) which have shapes very similar to those presented by these authors

(Fig. 1), *without assuming different numbers and/or types of active sites*. In our case the initial cis/trans ratio from 1-butene, i.e., the ratio of first order rate constants k_{1c}/k_{1t} in the reaction scheme



was 6.25 ± 0.2 at 23°C , and the difference in activation energy for the two paths was -1.8 ± 0.2 kcal/mole. (The "significant figures" given are those actually used in the calculations.) Correcting this value for the temperature difference would lead to a k_{1c}/k_{1t} ratio of 1.67 ± 0.4 at 250°C ; this value is almost within the limit of error in agreement with the low conversion cis/trans ratio (about 2.2) observed by Medema and Houtman (1) in their Fig. 1a. Considering the different sources of the two aluminas and the long temperature extrapolation for the cis/trans ratio, this is quite good agreement.

This value ($k_{1c}/k_{1t} = 1.67$), together with the cis/1-butene ratio from trans isomerization taken from Medema and Houtman's Fig. 1c ($k_{2c}/k_{2t} = 2.29$) and the three equilibrium constants of Benson *et al.* (10) at 250°C ($k_{c1}/k_{1c} = 0.55$, $k_{t1}/k_{1t} = 0.31$, and $k_{tc}/k_{ct} = 0.57$), provide five equations relating the six rate constants. Defining k_{1c} as 100 gives the sixth equation required to