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A Mössbauer Effect Study on Crystallites of Supported Ferric Oxide

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Crystallite size measurements and interaction with the support material of ferric oxide with silica gel and alumina have been studied using Mössbauer spectroscopy and x-ray diffraction techniques. No compound formation from reaction of the ferric oxide with the silica gel was detected, but changes in size distribution of the microcrystalline ferric oxide with the extent of calcination and type of silica gel used were observed. Similar results were obtained for alumina supported samples calcined for a prolonged period of time.

Reoxidation of alumina-supported ferric oxide reduced in flowing hydrogen at 500–600°C, unlike the silica gel samples, did not result in a Mössbauer spectrum identical to that of the sample in its initial state. Reaction of the support with the iron in its reduced state is indicated by a temperature study of the reoxidized samples. The data may be interpreted as reaction with the alumina, or bimodal size distribution of the microcrystalline ferric oxide, or both.

Common to both the silica gel and alumina supported samples was the observation of the existence of a ferric oxide phase that was either amorphous or consisted of crystallites too small to be detected by x-ray diffraction.

INTRODUCTION

The size and size distribution of microcrystallites of metals supported on the surface of high area oxides are important physical properties of supported metal catalysts. In order to make valid comparisons between metallic catalysts on "inert" supports, it is necessary to know the metallic surface area rather than the total surface area found by the usual BET method. Probably the most reliable method at present for this is the measurement of the chemisorption of hydrogen or carbon monoxide. This method has been carefully evaluated recently for some of the transition metal catalysts (*1–4*).

In some cases the activity of a particular type of catalyst for a given reaction has been found to be directly proportional to the metallic surface area (*1, 4–7*). On the other hand, the activity of some catalytic systems appears to be a function of the size, or a variation in the type of site, of the supported crystallites (*3, 8, 9*). Boudart and co-workers (*9*) have suggested that these results can be classified into two groups represented by "facile reactions," which are not sensitive to the heterogeneity of the active surface, and "demanding reactions," which are. Recently, Bond (*10*) has described a model for estimating the number of B_5 sites on a metallic surface as a function of crystallite size. These B_5 sites may be significant in the study of "demanding reactions" where multiple-bonded species occur. Thus, it has become increasingly evident that a knowledge of crystallite size and size distribution is quite important in catalytic studies involving supported metals.

The direct measurement of metallic surface area by chemisorption is the preferred technique when determining specific rate constants of reactions on supported metal catalysts, but obtaining reproducible results has been troublesome for the first row transition metals. This is particularly true in the case of iron, and is probably the consequence of the difficulty in completely reducing iron to its metallic state. The alternative is the use of some other method that can measure the average size of the microcrystallites from which the surface area can be calculated. A particularly attractive method of this type has been developed for ferric oxide microcrystallites by Kündig and co-workers (*11, 12*) using parameters derived from the Mössbauer spectra of α-Fe_2O_3 on silica gel. From such data an estimate of the metallic surface area of reduced samples may be made. In this method one takes advantage of the fact that α-Fe_2O_3 is weakly ferromagnetic. The magnetic ordering of this structure causes the Mössbauer spectrum to split into six lines. However, the magnetic ordering is volume and temperature dependent. When the crystallites are small enough to be in the superparamagnetic state the six line spectrum collapses into a doublet. This is a result of thermal energy overcoming the energy barrier of the crystal field that otherwise holds the magnetic moment in an easy direction in the larger crystals. Thus, at a given temperature there will be a crystallite size below which the magnetic moment changes from one easy direction to another rapidly enough to average to zero during the time of the measurement. The theory of this transition was developed by Neel in studies of the thermal fluctuations in ferromagnetic (*13*) and antiferromagnetic (*14*) particles the size of a single magnetic domain. Bean and Livingston (*15*) have discussed in detail the concept of superparamagnetism and the transition to stable single domain behavior. The relaxation time, τ, for the spontaneous change in direction of the magnetic moment in single domain crystallites with uniaxial anisotropy is usually written

$$\tau = \frac{1}{f} e^{\frac{Kv}{kt}}.$$

The energy barrier, Kv, contains the magnetocrystalline anisotropy constant, K, and the volume, v. T is the temperature, k is Boltzmann's constant, and f is usually set equal to the gyromagnetic precessional frequency of the magnetization vector about the effective field. This equation is valid for high energy barriers, and Aharoni (*16, 17*) has shown that it is still a good approximation for barriers as low as $2kT$. Aharoni (*17*) also points out that the frequency factor, f, is not a constant but is proportional to the reduced energy barrier, $(Kv/kT)^{1/2}$; however, in the absence of an applied magnetic field the error is no more than 10%.

In a single domain particle of α-Fe_2O_3 the magnetization vector is held in the c-plane perpendicular to the c-axis by the magnetocrystalline field. In Mössbauer effect studies, the measuring device or "observer" is the Fe-57 nucleus. Therefore, the six line Mössbauer spectrum collapses into a doublet when the relaxation time, τ, is shorter than the period for the precession of the nuclear spin about the direction of the effective magnetic field. Kündig (*11, 12*) has calculated a Larmor frequency for the Fe-57 nucleus in α-Fe_2O_3 of 4×10^7 sec^{-1}, or an "observer" relaxation time of 2.5×10^{-8} sec. On substituting this and an expression for the frequency factor proportional to the specific volume and anisotropy constant of the oxide into the above equation for relaxation, Kündig obtains the following relationship;

$$\ln(2 \times 10^{-4} K) = \frac{Kv}{kT}$$

The anisotropy constant, K, may be evaluated by obtaining spectra of a series of samples having known average particle sizes at constant temperature, or from spectra as a function of temperature of a sample having a known particle size. K is then evaluated at the point where half the total area under the spectrum results from the Zeeman pattern and the other half from the superparamagnetic spectrum. If K is independent of temperature and particle size, the method can be used to determine both size and size distribution in appropriate samples. An example of the type of

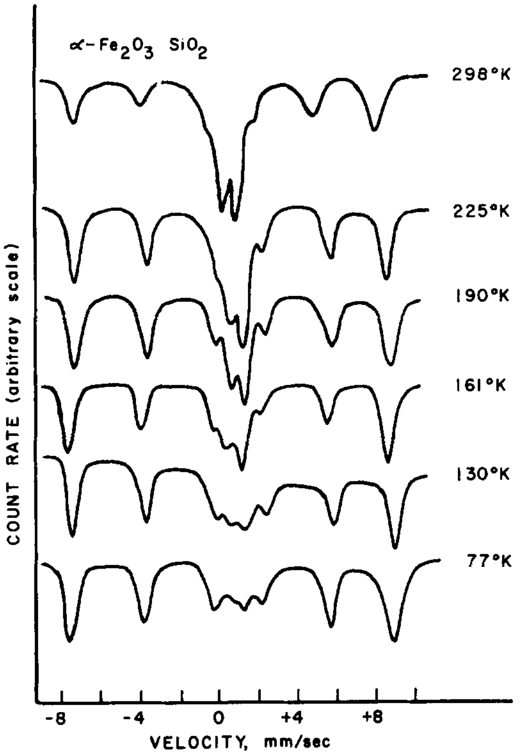

FIG. 1. Mössbauer spectra of α-Fe_2O_3 supported on silica gel as a function of temperature of the sample.

spectra from which these parameters are derived is shown in Fig. 1.

EXPERIMENTAL

Mössbauer spectrometer. The spectrometer was built in this laboratory following the design by Ruegg, Spijkerman, and De Voe (*18*). It was operated at constant acceleration using an RIDL Model 34-27 series multichannel analyzer operating in the multiscaler mode. The spectrometer drive was synchronized with the analyzer by using the channel address signal to power the drive and resetting the analyzer with a pulse from a photocell-slit system which triggered at the end of a drive cycle. The drive cycle has a period of about 1 second. The velocity range can be continuously varied from 0 to 20 cm/sec. The spectrometer is capable of 0.1% precision and normally uses 200 channels or half the capacity of the memory. The ratio of peak height to the standard deviation of the counts off resonance was about 14:1 for the samples used in this study. The source, Co-57 in palladium, was calibrated with a National Bureau of Standards sodium nitroprusside standard, and all chemical shifts and velocity scales are given with reference to this standard.

Materials. Davison silica gel Grades 923 and 70 and Davison eta-alumina Grade 992-F were used as support materials. These supports were impregnated with aqueous solutions of Fisher Reagent grade $Fe(NO_3)_3 \cdot 9H_2O$. The incipient wetness method was used to impregnate the supports followed by either oven drying or freeze drying before calcining in air to the oxide. The average crystallite size was determined by x-ray line broadening using Warren's correction as described in Alexander and Klug (*19*). Surface area measurements were made on some of the calcined samples using the flow method of Nelsen and Eggertsen (*20*). The results are shown in Table 1.

TABLE 1
SOME PHYSICAL PROPERTIES OF THE SUPPORTED α-Fe_2O_3 SAMPLES IN THEIR INITIAL STATE

Sample No.	Support	Wt. % Fe_2O_3	Area (m^2/g)	Av. diam. (Å)	Hyperfine field (kOe)	X-ray ident.
1	SiO_2	12	—	158	496	α-Fe_2O_3
2	SiO_2	15	—	—	—	—
3	SiO_2	16	—	145	515	α-Fe_2O_3
4	SiO_2	17	362	650	516	α-Fe_2O_3
5	η-Al_2O_3	17	153	100	506	α-Fe_2O_3
6	η-Al_2O_3	28	109	300	512	α-Fe_2O_3
7	η-Al_2O_3	28	—	230	506	α-Fe_2O_3
8	η-Al_2O_3	28	—	—	508	α-Fe_2O_3

For those samples which were taken through one or more oxidation-reduction cycles, the hydrogen was purified by passing successively through a Deoxo unit, 13X molecular sieve, and a liquid nitrogen trap or liquid nitrogen cooled charcoal trap. Reoxidation was carried out either in air or in flowing oxygen taken directly from the tank. Samples subjected to this treatment were contained in quartz cells with thin windows and vacuum stopcocks attached for inlet and outlet of the gases. The sample temperature was controlled within 0.5°C during the course of a run by a gas flow cryostat designed to accommodate the quartz cells. The calcined samples were held in plastic envelopes or encapsulated in epoxy resin.

Results and Discussion

The samples listed in Table 1 may be classified into two categories according to treatment following impregnation and initial calcination. With the exception of No. 1, one group was calcined at higher and higher temperatures, and Mössbauer spectra at room temperature were taken as a function of the temperature of heat treatment. The other samples were placed in the quartz cells and attached to a typical vacuum and gas handling system. These samples were reduced in flowing hydrogen at temperatures as high as 600°C and outgassed for use in other chemisorption and catalytic reaction experiments (*21*). Following this, the samples were reoxidized in air or flowing oxygen to determine if the reduction treatment had affected the original structure of the ferric oxide crystallites.

X-ray diffraction patterns were made of several of the samples in Table 1. The patterns of samples, Nos. 1, 3, 4, 5, 6, 7, and 8, consisted of lines for the support and α-Fe_2O_3. The Mössbauer spectrum of each of these samples exhibited a six line Zeeman spectrum characteristic of bulk α-Fe_2O_3 with a doublet superimposed on the center of it. In no case, either before or after extensive calcining or reduction-reoxidation treatments, were there any lines observed in the x-ray diffraction patterns that could be identified with compound formation between the iron species and the support.

The hyperfine fields observed in the initial state are generally lower than the 515-520 kOe value reported for bulk α-Fe_2O_3. This was also observed by Kündig (*11*) and Nakamura and Shimizu (*22*), who studied ultrafine particles of unsupported α-Fe_2O_3. The latter attributed this observation to a decrease in the molecular field acting on the spins in the smaller crystallites, but it is not clear whether it is an effect of size or of defect structures in the microcrystallites that might be annealed out without a change in the size.

Silica Gel Support

Sample 1 was prepared by impregnating Davison Grade 70 silica gel, drying at 200°C, and calcining at 500°C for 2 hours as described by Kündig (*11*). The percent Fe_2O_3 content and the Mössbauer spectrum at room temperature of this sample were very similar to his sample C (*11*). The spectra as a function of temperature, as shown in Fig. 1 for this sample, were resolved into their Zeeman and doublet components and the relative areas of each determined. That fraction of the total area under the absorption peaks which was produced by the superparamagnetic state is plotted versus the temperature in Fig. 2, curve A. The average crystallite size is assumed to be measured at that point on the curve where 50% of the crystallites are in the superparamagnetic state. This point is at 304 ± 10°K for this sample. Using the value obtained by Kündig of 7.6×10^4 ergs/cm^3 for the anisotropy constant, one finds a value of 140 ± 10 Å for the average diameter of the crystallites. This compares favorably with the x-ray line broadening figure of 158 ± 10 Å. However, this calcination treatment does not appear to have produced an "equilibrium" or stable state. Another sample from the same batch of impregnated silica gel was calcined in a muffle furnace at 500°C overnight and its Mössbauer spectrum was found to have almost all of its area under the doublet,

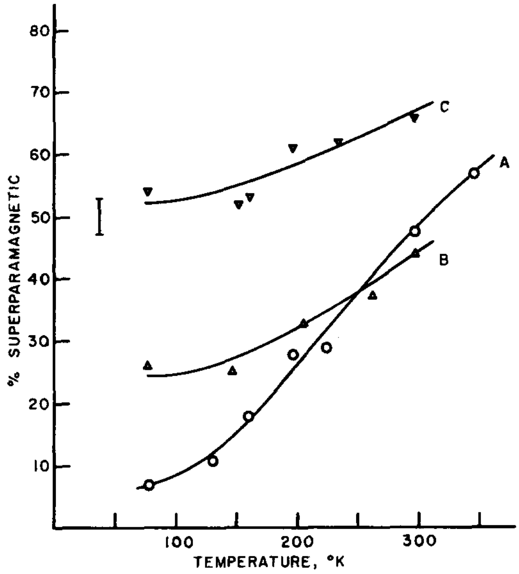

FIG. 2. Fraction of α-Fe_2O_3 in the superparamagnetic state as a function of temperature. ○ = 12% α-Fe_2O_3 on silica gel; △ = 17% α-Fe_2O_3 on η-Al_2O_3 in its initial state; ▽ = 17% α-Fe_2O_3 on η-Al_2O_3 after a redox cycle.

with the Zeeman pattern just detectable above the background.

Other impregnated samples using Davison Grade 923 silica gel were found to behave in a similar fashion. The data for sample 2 in Table 2 show that prolonged calcination following an initial overnight treatment in a muffle furnace does not result in any further changes in the Mössbauer spectrum of the sample. Samples 3 and 4 were initially calcined in the same manner as sample 2, but they were then reduced in flowing hydrogen overnight at 500°C. The Mössbauer spectra of the samples in the reduced state consisted of a Zeeman pattern characteristic of metallic iron and a superimposed doublet with a chemical shift of $+1.33 \pm 0.05$ mm/sec, and a quadrupole splitting of 2.20 ± 0.10 mm/sec characteristic of high spin ferrous ion. It appears that only crystallites sufficiently large to produce a Zeeman pattern in the spectrum are reduced to the metallic state while the superparamagnetic fraction reduces to a ferrous state. This may account, in part, for the discrepancies found in previous studies of the metallic surface areas of supported iron catalysts.

These two samples were then reoxidized. The data in Table 3 show that the initial state of the sample is recovered, with the exception of an unexplained increase in the quadrupole splitting of the doublet for sample 3. No permanent changes have resulted, at least as far as the physical properties measured by these Mössbauer parameters are concerned. However, we note that 70% of each spectrum is a doublet produced by ferric oxide in the superparamagnetic state: crystallites less than about 100 Å in diameter. The remainder of each spectrum is produced by crystallites with an average diameter much

TABLE 2

CHEMICAL SHIFTS, QUADRUPOLE SPLITTINGS, AND PERCENT DOUBLET AT ROOM TEMPERATURE FOR SUPPORTED FERRIC OXIDE AS A FUNCTION OF CALCINATION

Sample No.	Treatment Time (hr.)	Treatment Temp. (°C)	Chemical shift (mm/sec)	Quadrupole splitting (mm/sec)	% doublet
1	2	500	$+0.60 \pm 0.05$	0.68 ± 0.10	45
2	18	540	$+0.56 \pm 0.05$	0.69 ± 0.10	70
	138	540	$+0.65 \pm 0.05$	0.74 ± 0.10	70
8	20	450	$+0.65 \pm 0.05$	0.82 ± 0.10	48
	70	540	$+0.57 \pm 0.05$	0.83 ± 0.10	15
	190	540	$+0.65 \pm 0.05$	0.83 ± 0.10	21
	12	700	$+0.60 \pm 0.05$	0.89 ± 0.10	15
	52	700	$+0.62 \pm 0.05$	0.90 ± 0.10	14
	96	750	$+0.55 \pm 0.05$	0.65 ± 0.10	15
	6	1100	$+0.58 \pm 0.05$	0.46 ± 0.10	27

TABLE 3

Chemical Shift, Quadrupole Splittings and Percent Doublet at Room Temperature for Supported Ferric Oxide Before and After a Reduction-Reoxidation Treatment

Sample No.	Chemical shift (mm/sec)	Quadrupole splitting (mm/sec)	% doublet
3, Initial	+0.60 ± 0.05	0.77 ± 0.10	72
Final	+0.61 ± 0.05	0.94 ± 0.10	70
4, Initial	+0.56 ± 0.05	0.71 ± 0.10	70
Final	+0.59 ± 0.05	0.77 ± 0.10	70
5, Initial	+0.69 ± 0.05	0.79 ± 0.10	44
Final	+0.66 ± 0.05	0.98 ± 0.10	66
6, Initial	+0.62 ± 0.05	0.89 ± 0.10	19
Final	+0.53 ± 0.05	0.95 ± 0.10	48
7, Initial	+0.59 ± 0.05	1.01 ± 0.10	28
Final	+0.54 ± 0.05	0.93 ± 0.10	48

larger than this because each sample was found to undergo a Morin transition, a flip of the spin alignment from the c-plane to the c-axis, on observing the Mössbauer spectrum of the sample cooled to liquid nitrogen temperatures. This transition was not observed for sample 1 or the samples used by Kündig. According to Takada *et al.* (*23*) the Morin transition in α-Fe_2O_3 is observed above liquid nitrogen temperatures only for crystallites larger than 250 Å in diameter. Furthermore, x-ray line broadening data give an average crystallite size of 650 Å for sample 4. The large differences in size indicated by these measurements suggest that the size distribution is very wide and skewed, or possibly is bimodal. The existence of crystallites large enough to undergo a Morin transition, an observation more common than not with extensively calcined samples, complicates the analysis by Kündig's method. In principle, the fraction of the spectrum produced by crystallites undergoing a Morin transition as a function of temperature could be used to obtain further information on size distribution. The Morin transition temperature for bulk α-Fe_2O_3 is 260°K and decreases with decreasing crystallite size, but the size dependence on transition temperature has not yet been thoroughly studied. Regardless of the qualitative interpretation, the fact remains that one of the objectives of these Mössbauer measurements, namely, the determination of an average crystallite size, cannot be easily achieved with such samples.

Alumina Support

Ferric ions can replace aluminum ions in an alumina lattice, and some Mössbauer studies have been made by Wertheim and Remeika (*24*) and by Bhide and Date (*25*) on dilute solutions of ferric ions in alumina. The more favorable conditions for reaction of the iron catalyst with the support present an added complication in the determination of crystallite size and size distribution. To investigate the nature and consequences of this possible reaction with the support, several samples of η-alumina were impregnated with ferric solution and treated in a manner similar to the silica gel samples.

Sample 8 appears to reach a stable state after calcining above 500°C. The data in Table 2 show that prolonged calcination at higher and higher temperatures does not result in any significant changes in the Mössbauer parameters until phase changes in the support begin at 750°C. At this point, x-ray diffraction indicates that the eta form has partly converted to the theta and alpha forms of alumina, and the quadrupole splitting of the central doublet decreases significantly. Finally, at 1100°C the quadrupole splitting decreases further and the percent doublet increases. At such high temperatures one would expect that at least part of the doublet represented ferric ions that had diffused into the alumina lattice. However, no compound formation could be detected by x-ray diffraction, nor were there any new features in the Mössbauer spectrum to indicate compound formation.

Under the usual pretreatment conditions the data show that interaction with the support is negligible except for producing a degree of stability to sintering. If one assumes that the difference between the Debye-Waller factors of the structure that produces the doublet and the ferric oxide that produces the hyperfine pattern is small, then the 15% area under the doublet represents 0.037 g-atom of ferric ion per gram-atom of aluminum ion. This ion ratio falls in the same region where Levy and Bauer (*26*) found the greatest stability to sintering for aluminas doped with lithium, potassium, and magnesium. In 1 g of this catalyst sample, the total amount of iron represented by the doublet is approximately 3×10^{20} atoms. This is more than enough to fill lattice vacancies on the surface and increase the energy of activation for surface diffusion and sintering (*26*).

Reduction of alumina supported samples followed by a reoxidation did not result in a room temperature spectrum identical with the one obtained for the initial state of the sample, in contrast with the results found for the silica gel samples. Spectra as a function of temperature of sample 5 in its initially calcined state were very similar to the silica gel example in Fig. 1 except for peak splitting in the Zeeman pattern with peak position changes that indicated part of the sample had undergone a Morin transition. The change in the fraction of the oxide in the superparamagnetic state with temperature is plotted in Fig. 2, curve B. The sample was then reduced in flowing hydrogen at 525°C for 24 hours and recalcined in air at 540°C for 24 hours. Again spectra as a function of temperature were recorded, and the temperature dependence is shown by curve C of Fig. 2. The change in the doublet area with temperature is only about 10% compared with a 20% change observed with the sample in its initial state. The Mössbauer parameters for the doublet portion of the spectrum are given in Table 3. Samples 6 and 7 behaved in a similar fashion, and this is illustrated in Fig. 3 with a before, spectrum A, and an after, spectrum B, plot of results for sample 7 in its oxidized state at room temperature. One observes that the really significant change in each of these samples is the large increase in the percent area of the doublet. A second reduction-reoxidation cycle did not produce any further changes in the spectrum. Apparently a stability has been achieved similar to the stability found on calcining the sample at higher and higher temperatures; however, there has been an increase instead of a decrease in the area under the doublet from the initial to the stable state.

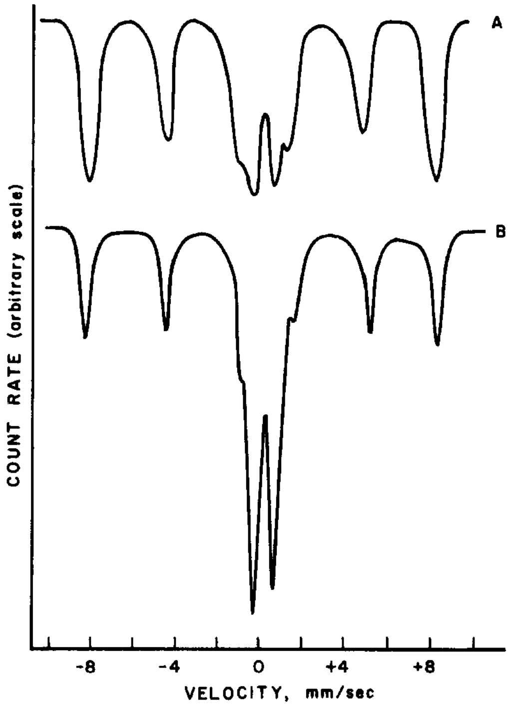

Fig. 3. Mössbauer spectra of α-Fe_2O_3 on η-Al_2O_3 before (top) and after (bottom) a redox cycle.

If one is to use the Mössbauer spectra of these catalysts to determine the average size of the iron oxide crystallites during the life of the catalysts, it is necessary to assume that the doublet represents crystallites of ferric oxide in a superparamagnetic state. Based on this assumption, the growth of the doublet means that the processes of reduction and reoxidation cause some of the larger crystallites to break up into smaller crystallites. This is not supported by x-ray line broadening evidence. The average crystallite diameter for sample 6 measured by x-ray line broadening was 300 Å in its initial state and 400 Å after reduction and reoxidation. Since the superparamagnetic state is temperature dependent, a decrease in the temperature of the sample should cause a decrease in the relative area under the doublet. For several alumina-supported samples that had undergone a reduction and reoxidation cycle, the relative areas did not change by more than 10% between spectra run at room temperature and liquid nitrogen temperature. Furthermore, the decrease in the doublet area with decreasing temperature tends to level out below 150°K, as indicated in Fig. 2. These observations suggest two possible models for the catalysts. Either the doublet represents a compound formed between the iron species and the alumina support and not superparamagnetic α-Fe_2O_3, or the size distribution is bimodal with one fraction much less than 100 Å, another fraction larger than 200 Å, and only a small fraction of the crystallites between 100 and 200 Å in diameter.

Mössbauer spectra have been reported for two compounds of alumina containing iron (*27, 28*). In one, $FeAl_2O_4$, the iron exists in the ferrous state and the Mössbauer spectrum is a composite of two superimposed doublets. This compound has a normal spinel structure with partial inversion. Thus, one of the doublets is produced by Fe^{2+} in tetrahedral sites as in a normal spinel, and the other by Fe^{2+} in octahedral sites with chemical shifts of +1.28 and +1.70 mm/sec, respectively. Such large positive shifts eliminate this compound from contributing to the area under the doublet.

In the other compound, $FeAlO_3$ the iron is in a ferric state and has been found to be ferrimagnetic below 220°K with a hyperfine field of 450 kOe. At room temperature, Trooster and Dymanus (*28*) observed a doublet with a chemical shift, $\delta = +0.597 \pm 0.01$ mm/sec and a quadrupole splitting, $\Delta E_Q = 0.635 \pm 0.015$ mm/sec. This compares favorably with the doublet of the catalyst samples which have chemical shifts of $+0.60 \pm 0.05$ mm/sec and quadrupole splitting of 0.95 ± 0.10 mm/sec. However, the spectra of these samples at liquid nitrogen temperatures did not contain any evidence of the hyperfine field that should be present below 220°K. The larger quadrupole splitting found for the catalyst samples may be a qualitative indication that very small crystallites of $FeAlO_3$ have formed on the alumina surface and that they remain superparamagnetic down as low as 77°K. X-Ray analysis does not show the formation of any iron compounds other than the α-Fe_2O_3 that was present in the initial state of the sample. Thus, any new compound that might produce the doublet in the Mössbauer spectrum must be present in an amorphous phase or as such small crystallites that the x-ray lines are broadened beyond detection.

CONCLUSIONS

This study has shown that there are several limiting factors to the determination of microcrystallite size of supported ferric oxide catalysts from Mössbauer spectra. Obviously, reaction with the support, such as the reaction of the alumina suggested by the reduction-reoxidation data, complicates the analysis. The method depends critically on the superparamagnetic state of ferric oxide to produce the doublet in the spectrum. Any compound formation with the support that contributes to the doublet must be stripped out of the spectrum, and this is a difficult task.

The range of crystallite sizes is limited at the low end by the requirement that some of the crystallites must be large enough to produce a Zeeman pattern over at least a part of the temperature range capabilities of the spectrometer. On the other hand, the upper limit is governed by the size of the crystallites large enough to undergo a Morin transition in the temperature range needed to make the measurements.

The stable state, which appears to be achieved by typical calcining treatments, is encouraging. The physical state of the catalyst does not seem to change during typical reaction conditions, at least for the silica gel supports where no reaction between the ferric oxide and the support is observed. But there is some question of interpretation of the Mössbauer data. For example, sample 5 has 70% of the spectrum area under the central doublet which decreases to about 40% on cooling from room temperature to liquid nitrogen temperature. Assuming no compound formation with the support, this portion of the spectrum then is ferric oxide in the superparamagnetic state meaning that 70% of the ferric oxide is present as crystallites with diameters less than about 100 Å. However, x-ray line broadening measurements indicate an average crystallite size of 650 Å both before and after a reduction-reoxidation cycle. The size distribution must be either highly skewed or bimodal. A bimodal distribution could result from diffusion of the iron into the pores of the support. Following the initial thermal decomposition of the impregnated sample the ferric oxide may diffuse into the micropores of the support until they are completely filled. The size distribution of this portion of the ferric oxide would conform to that of the micropores of the support. The remaining ferric oxide would sinter to larger crystallites in the macrostructure of the support. One immediately recognizes that this model is too simple. There is just not enough ferric oxide present even in the most concentrated samples to fill the micropore volume much less have some left over to sinter into larger crystals on the macropore surface. A number of modifications of the basic idea may be envisioned, such as, the sealing of the mouths of bottle-necked pores by microcrystallites or the sintering of a large fraction of the micropore volume before the ferric ions diffuse into it. The present data cannot distinguish among the various possibilities. Further studies are needed using a variety of experimental techniques to establish a consistent model.

Thus, the method of crystallite size determination by Mössbauer spectroscopy will provide detailed information on the physical state of ferric oxide catalysts, but must be used with care. Pretreatment and reaction conditions may drastically change the catalyst during its life through surface diffusion and sintering and by reaction with the support. Furthermore, these changes may not be readily detected by many of the methods used to determine the physical state of the material, but in combination with other experimental techniques the method promises to yield more details of the structure of supported catalysts than has been attainable before.

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