Small-particle effects in Mössbauer spectra of a carbon-supported iron catalyst

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which is bonding relative to C and Li but antibonding relative to Li₂. This picture of the tetrahedral singlet is of course equivalent to the conventional model involving a substituted sp³ carbon atom.

The planar triplet has one electron in the carbon pₓ orbital (bₓ) and its triplet coupled companion in a very diffuse orbital of a₁ symmetry localized on the side of Li₂ away from the carbon atom. Rotating the Li₂ group about the C₁ axis of CH₂ has little effect on the electron distribution.

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Small-Particle Effects in Mössbauer Spectra of a Carbon-Supported Iron Catalyst

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Highly dispersed iron catalysts, consisting of 5 wt % Fe on high-purity carbon black (Carbolac-1), have been studied by in situ Mössbauer spectroscopy at 295, 77, and 4 K. About 75–80% of the iron in the Fe/C-1 catalyst is reduced to α-Fe in H₂ at 740 K, whereas the remaining iron is present as Fe⁺. The α-Fe particles in reduced Fe/C-1 exhibit behavior characteristic of very small (2–5 nm) particles. First, the most interesting feature of this work is the occurrence of substantial contributions of superparamagnetic α-Fe in the Mössbauer spectra at 295 and 77 K. Second, the magnetic hyperfine fields of the α-Fe in the spectra at 4 K are enhanced by about 7 kOe, due to the influence of the demagnetizing field in the particle. Third, the effective Debye temperatures of the Fe/C-1 catalysts are much smaller than in iron bulk compounds. Exposure of reduced Fe/C-1 to air results in the oxidation of all iron to Fe²⁺. Carburization in syngas (H₂/CO = 3) converts all α-Fe in the reduced catalyst to iron carbides, whereas the Fe⁺ remains unaffected. Conversion of the Fe²⁺ spectrum from a singlet at room temperature to a doublet at 77 K shows that the unusual ferrous singlet is caused by cancellation of electron and lattice field gradients of opposite sign. The work illustrates the usefulness of in situ Mössbauer spectroscopy at cryogenic temperatures in the investigation of highly dispersed systems.

Introduction

Carbon has recently attracted attention as a support material for iron catalysts in CO hydrogenation¹ ¹⁴ and for metal sulfide catalysts in hydrodesulfurization.⁵ Jung et al.¹ reported that iron supported on the porous carbon black Carbolac-1 (C-1) shows excellent retention of catalytic activity in the CO hydrogenation reaction at 508 K and atmospheric pressure, whereas Fe/Al₂O₃ catalysts deactivated severely under these conditions. Characterization by means of CO chemisorption, magnetization, and Mössbauer spectroscopy at room temperature revealed that the iron in these Fe/C-1 catalysts was highly dispersed (average diameters between 2 and 3 nm) and that the degree of reduction was much higher than is usually observed in silica- or alumina-supported iron catalysts with comparable dispersion.⁶ Obviously, the Fe/C-1 catalyst is a potentially interesting system for studying magnetism and lattice dynamics in small metallic iron particles.

In investigating highly dispersed iron systems with their characteristic low effective Debye temperatures, application of Mössbauer spectroscopy at cryogenic temperatures is often advantageous.⁷ At liquid nitrogen or liquid helium temperatures the recoilless fraction increases significantly and hence the quality of the spectra may improve considerably. Moreover, when components which are paramagnetic or superparamagnetic at 295 K become magnetically split at low temperature, identification of iron phases in the spectrum can be greatly facilitated.

Small particles often exhibit different magnetic properties than bulk materials. Superparamagnetism and decreased magnetic splitting due to thermal excitations of the magnetization (collective magnetic excitations) are often observed in supported iron catalysts.⁸ In single-domain ferromagnetic particles yet another effect may be observed: the influence of the demagnetizing field on the magnetic hyperfine splitting, caused by the magnetic poles at the surface of the particle.⁹ ¹⁰ At 295 or 77 K the influence of the demagnetizing field may be obscured by thermal excitations, which decrease the magnetic splitting. At 4 K, however, thermal excitations are virtually absent and at this temperature the influence of the demagnetizing field should be discernable. When several particles stick together in a "grape cluster" type of arrangement, dipole interactions between the magnetic moments of neighboring particles can partially compensate the demagnetizing field and also prevent superparamagnetism. However, when the iron particles are sufficiently separated from each other, one approach is to use in situ Mössbauer spectroscopy at cryogenic temperatures for the study of iron catalysts.¹¹

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TABLE I: Mössbauer Parameters of Unreduced Fe/C-1

<table>
<thead>
<tr>
<th>Parameters*</th>
<th>T = 295 K</th>
<th>T = 77 K</th>
<th>T = 4 K doublet</th>
<th>sextet</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS, mm/s</td>
<td>0.64 ± 0.02</td>
<td>0.77 ± 0.02</td>
<td>0.80 ± 0.02</td>
<td>0.80 ± 0.02</td>
</tr>
<tr>
<td>QS, mm/s</td>
<td>0.75 ± 0.03</td>
<td>0.91 ± 0.04</td>
<td>1.00 ± 0.06</td>
<td>0</td>
</tr>
<tr>
<td>LW, mm/s</td>
<td>0.50 ± 0.05</td>
<td>0.60 ± 0.06</td>
<td>0.72 ± 0.08</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>A, au</td>
<td>0.35 ± 0.01</td>
<td>0.85 ± 0.02</td>
<td>0.56 ± 0.02</td>
<td>0.44 ± 0.02</td>
</tr>
</tbody>
</table>

*IS relative to SNP.

as for example in supported catalysts of low metal loading, one may expect that dipole interactions between the magnetic moments of the particles will be negligible.

Here we report Mössbauer spectra, recorded in situ at 4, 77, and 295 K, of a Carbolac-supported iron catalyst before and after reduction in H2, and after carburization in synthesis gas. The α-Fe particles in the reduced catalyst exhibit superparamagnetism at 295 and 77 K, whereas their magnetic hyperfine splitting at 4 K is enhanced by the demagnetizing field. The investigation illustrates that Mössbauer spectra at 295 K are less informative in the study of well-dispersed particles and that application of the technique at cryogenic temperatures is essential.

Experimental Section

The Fe/C-1 catalyst was prepared by an incipient wetness technique and contained 5 wt % iron on a Carbolac-1 (Cabot, 950 m²/g) support. For Mössbauer experiments quantities of about 200 mg were pressed into a wafer, using a pressure of about 100 atm.

Reduction and carburization experiments were carried out in a cell which can be closed vacuum tight inside a chemical reactor. This cell permits the measurements of Mössbauer spectra of the catalyst under the desired gaseous environment, at temperatures down to 4 K. Reduction occurred in flowing H2 (100 mL/min) for 0.5 h at 400 °C, followed by 17 h at 675 or 740 K. The catalyst reduced at 740 K was treated with synthesis gas (CO:H2 = 1:3; 140 mL/min) at 510 °C for 18 h. The gases H2 (Hoekloos, purity >99.9%) and CO (Hoekloos, >99.5%) were purified separately over a Cu catalyst (BASF, R3-11) and a molecular sieve (Union Carbide, 5A).

Mössbauer spectra were taken with a constant acceleration spectrometer, using an ⁵⁷Fe in Rh source. Isomer shifts (IS) are reported with respect to the NBS standard sodium nitroprusside (SNP). Magnetic hyperfine fields (H) were calibrated with the 515-kOe field of α-Fe₂O₃ at room temperature. The spectra were not corrected for the varying distance between source and absorber. Hence, the spectra show a curved background of instrumental origin. After recording spectra at 295, 77, and 4 K with the vacuum-tight absorber holder in a bath cryostat, another room temperature spectrum was measured in order to verify that the absorber holder had not leaked at cryogenic temperatures. Mössbauer spectra were fitted by computer using a least-squares program of Lorentzian-shaped lines, whereas the curved background was accounted for by a parabola. Total resonant absorption areas were calculated independently by integrating the spectra after correction for the background parabola.

Results

Unreduced Fe/C-1. The Mössbauer spectra of the unreduced catalyst at 295 and 77 K (Figure 1) consist of doublets with parameters characteristic of high-spin Fe³⁺ compounds (Table I). At 4 K about 40% of the spectrum has become magnetically split. The broad lines indicate the presence of a distribution in hyperfine fields, H. This distribution has been calculated with the method proposed by Wivel and Morup. The H distribution contains contributions from fields between about 370 and 530 kOe, with a weighted average of about 450 kOe. The Mössbauer parameters in Table I indicate that both the magnetically split pattern and the doublet correspond to Fe³⁺, most probably in an iron(III) oxide. The temperature dependence of the isomer shift indicates that the effective Debye temperature, θD, of the iron(III) compound is 200 ± 50 K.

The small, magnetically split contributions of $\alpha$-Fe in the room temperature spectra have been ignored in the fit. Within the accuracies, the isomer shifts and resonant absorption areas of all components satisfy the requirement of the theory of lattice dynamics, that they increase with decreasing temperature.\textsuperscript{13} Unfortunately, the isomer shifts are not sufficiently accurate to permit calculation of Debye temperatures from the second-order Doppler shift.

Note that the magnetic hyperfine field of the $\alpha$-Fe at 4 K is $0.75 \pm 0.05$ mm/s in the Mossbauer spectrum of the reduced Fe/C-1 catalyst after exposure to air at 295 K. The spectra of the same samples at 77 and 4 K show very similar features. The main difference appears at 4 K, where it is seen that reduction at 740 K yields more metallic iron (77% of the spectral area) than reduction at 675 K.

Exposure of the reduced Fe/C-1 catalyst to air at 295 K causes the oxidation of all iron to Fe$^3+$, which appears as a doublet with $H = 345 \pm 3$ kOe, which is significantly higher than the 338-kOe field of bulk $\alpha$-Fe at 4 K.\textsuperscript{14} The spectra of the Fe/C-1 catalyst after the two reduction treatments show very similar features. The main difference appears at 4 K, where it is seen that reduction at 740 K yields more metallic iron (77% of the spectral area) than reduction at 675 K.

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the temperature dependence of the isomer shift. We note, for comparison, that the Debye temperatures for bulk $\alpha$-Fe or $\alpha$-Fe$_2$O$_3$ are in the order of 450–500 K. 

**Discussion**

The Mössbauer spectra of the Fe/C-1 catalysts before and after reduction exhibit various features which are characteristic of small-particle behavior. The unreduced catalysts contain iron(III) oxide, which is superparamagnetic at 295 and 77 K. Even at 4 K more than half of the Fe$^{2+}$ in the sample is in a superparamagnetic state. For comparison, all bulk iron(III) oxides show full magnetic splitting at room temperature. The value of the quadrupole splitting at 295 K is 0.75 mm/s, considerably higher than the 0.52 mm/s of $\alpha$-Fe$_2$O$_3$ bulk material. According to van der Kraan, the quadrupole splitting of small particles of $\alpha$-Fe$_2$O$_3$ can be described in terms of a central core which corresponds to a doublet with $Q_S = 0.52$ mm/s, the bulk value, and a surface shell with a doublet characterized by $Q_S = 0.9$ mm/s. The observed $Q_S$ is an average of these two limiting values, depending on the relative fraction of surface atoms in the particle. For comparison, unsupported $\alpha$-Fe$_2$O$_3$ particles with an average diameter of 4 nm have $Q_S = 0.64$ mm/s at 295 K and show partial magnetic splitting at 77 K and full magnetic splitting at 4 K. 

The large quadrupole splitting at 295 K and the absence of magnetic splitting at 77 K in the spectra of unreduced Fe/C-1 indicate that the iron oxide in these catalysts is highly dispersed, probably with particle dimensions well below 4 nm.

The investigation of the reduced Fe/C-1 catalysts illustrates that Mössbauer spectra of highly dispersed systems taken only at room temperature are not sufficient to identify all iron phases present. After the reduced catalysts was cooled in situ to liquid helium temperature, 4 K, the presence of metallic iron could be established without doubt and this knowledge allows the assignment of single-line contributions in the spectra at 77 and 295 K to superparamagnetic metallic iron. Similar considerations facilitate the identification of the Fe$^{2+}$ component in the spectra of reduced Fe/C-1. Since the liquid nitrogen spectra contain a doublet of Fe$^{2+}$, one of the singlets contributing the broad composite peak in the spectrum at 295 K can be attributed to the Fe$^{2+}$ component.

Usually, ferrous compounds exhibit quadrupole-split Mössbauer spectra at room temperature. To explain why the Fe$^{2+}$ component in Fe/C-1 catalysts appears as a singlet, Jung et al. suggested that the environment of the Fe$^{2+}$ ions is unusually symmetric. This interpretation, however, is contradicted by the results reported here, which indicate that the Fe$^{2+}$ contribution is a doublet at 77 K. We propose the following explanation, based on a discussion of quadrupole splittings in iron compounds by Travis. In the case of Fe$^{2+}$ ions, the electric field gradient (EFG) contains two contributions, one from the asymmetric distribution of the six 3d electrons over their energy levels, and one from the lattice when the symmetry is noncubic. The former depends on temperature, the latter almost not. When the electron and lattice contribution to the EFG have opposite signs, they may compensate each other to the EFG have opposite signs, they may compensate each other to the EFG have opposite signs, they may compensate each other to the EFG have opposite signs, they may compensate each other.

Assignment of the Fe$^{2+}$ contribution to a certain phase is not possible yet. The parameters of the Fe$^{2+}$ at 77 and 295 K do not belong to known compounds as, for example, FeO. It seems likely that the Fe$^{2+}$ subspectrum corresponds to ferrous oxide coordinated to adsorption sites on the Carbolac support.

The $\alpha$-Fe in the reduced Fe/C-1 catalysts exhibits interesting magnetic behavior, with the occurrence of superparamagnetic $\alpha$-Fe in the spectra at liquid nitrogen temperature as the most remarkable feature. Obviously, the $\alpha$-Fe particles must be very small, in qualitative agreement with the diameter of about 2 nm which follows from CO chemisorption experiments. Superpara-

magnetism has not been observed very often in metallic iron. Sometimes small contributions of a superparamagnetic $\alpha$-Fe peak occur in Mössbauer spectra at 295 K of reduced Fe/SiO$_2$ catalysts. The Fe/C-1 catalysts, however, show superparamagnetic iron even at 77 K. In general, the occurrence of superparamagnetism in an isolated particle is determined by its magnetic anisotropy energy. When the energy, kT, of thermal excitations is sufficiently high to overcome the anisotropy barrier, the magnetic moment of the particle will fluctuate rapidly between the easy directions of the lattice, and magnetic splitting is not observed. In iron oxides such as Fe$_2$O$_3$ and FeOOH, the magnetocrystalline anisotropy per unit volume is high, and it is by far the dominating contribution to the anisotropy energy. In metallic iron, however, the magnetocrystalline contribution is much smaller and the magnetic anisotropy is largely determined by the shape and the fraction of surface atoms of the particle, and by the influence of neighboring particles. When ferro- or ferrimagnetic particles are close together, dipole interactions occur between their magnetic moments. The moments of neighboring particles tend to align each other in their dipole fields. This dipole interaction is the origin of interaction anisotropy, with an easy direction depending on the relative positions of the particles. Moreover, when neighboring particles are in contact, exchange anisotropy is determined by an exchange interaction at the interface between the particles. A recent study by Tamura and Hayashi showed that the influence of exchange interaction on the total magnetic anisotropy in 10-nm $\alpha$-Fe particles can be considerable. In short, whether or not a metallic iron particle is superparamagnetic depends not only on its size and shape but also on the proximity of other iron particles. We regard the fact that the $\alpha$-Fe particles in the reduced Fe/C-1 catalysts exhibit superparamagnetism at 77 K as strong evidence that the particles are not in contact and, moreover, are sufficiently separated from each other to make the influence of dipole interactions and exchange anisotropy negligible. Apparently, the sum of magnetocrystalline, surface, and shape anisotropy has a value such that superparamagnetism can occur already at 77 K.

The particle size of the $\alpha$-Fe particles in the reduced Fe/C-1 catalyst is about 2 nm. Another investigation of iron particles of comparable small size has been described by Boudart et al. These authors report that Mössbauer spectra of 1.5-nm $\alpha$-Fe particles in Fe/MgO catalysts are magnetically split at room temperature, and their superparamagnetic transition temperature, $T_B$, is estimated to be about 800 K. Figures 2 and 3 show that in our Fe/C-1 catalysts $T_B$ is even lower than 77 K. As $T_B$ and the total magnetic anisotropy energy are proportional, we conclude that the magnetic anisotropy energy in the 1.5-nm $\alpha$-Fe particles in Fe/MgO catalysts is more than 10 times higher than that in the 2-nm iron particles in Fe/C-1 catalysts. A quantitative comparison of the anisotropy energies in the two catalyst systems would require precise knowledge of the shape and dimensions of the iron particles and cannot be made. Whatever the correct explanation of the difference between the two systems may be, comparison of the Mössbauer spectra of Fe/MgO in and Fe/C-1 presented here illustrates clearly that the occurrence of superparamagnetism at a certain temperature is not governed by particle size only, and that differences in morphology, which can be caused by different metal-support interactions, may play an important role as well.

The magnetic hyperfine field of the metallic iron in the reduced Fe/C-1 catalysts at 4 K is 345 ± 3 kOe, whereas in bulk $\alpha$-Fe at 4 K it is 338 kOe. We attribute this difference to the demagnetizing field, caused by the poles of the magnetization vector at the surface of the single-domain particles. In metallic iron, the magnetic hyperfine field is oriented antiparallel with respect to the magnetization, and therefore the demagnetizing field increases the magnetic splitting. The enhancement of $H$ in small iron particles has been observed before in unsupported iron particles with diameters in the range of 6.6 to 10 mm. The magnetic hyperfine field can be written as

$$H = H_{\text{bulk}} + H_{\text{dem}} - H_{\text{gap}}$$

(1)

in which $H_{\text{bulk}}$ is the magnetic hyperfine field of nonmagnetized $\alpha$-Fe bulk material, $H_{\text{dem}}$ the demagnetizing field, and $H_{\text{gap}}$ the magnetic field of neighboring particles. The demagnetizing field of spherical, single-domain $\alpha$-Fe particles is about 7 kOe. As we discussed above, the occurrence of superparamagnetism at relatively low temperatures suggests that the particles are at a distance such that $H_{\text{gap}} = 0$. If we assume approximately spherical particle shape for the iron particles and we use $H_{\text{dem}} = 7$ kOe and $H_{\text{gap}} = 345$ kOe, then eq 1 predicts a magnetic hyperfine field of 345 kOe, in excellent agreement with the observed values of 345 ± 3 and 347 ± 3 kOe for $\alpha$-Fe in the Fe/C-1 catalysts after reduction at 675 and 740 K, respectively (Table II).

The Mössbauer spectra of Fe/C-1 after carburization in CO and H$_2$ at 510 K for 18 h indicate that all metallic iron originally present in the reduced catalyst has been converted into carbides, whereas the Fe$^{2+}$ contribution is hardly or not affected by this treatment. Unfortunately, identification of the carbides formed is impossible and has not offered an explanation of the remarkably high resistance of the Fe/C-1 catalyst to deactivation at reaction conditions.

The effective Debye temperatures, $\theta_D$, of the iron in the Fe/C-1 catalysts, determined from the temperature dependence of the spectral areas, $A(T)$, are in the order of 150-200 K, whereas $\theta_D$ of the corresponding bulk materials is between 450 and 500 K. In general, two reasons can be given for low $\theta_D$ values. First, according to Somorjai, $\theta_D$ of atoms at the surface is about half that of atoms in the bulk. As a large fraction of the atoms in 2-nm particles are at the surface, one expects a $\theta_D$ which is lower than in bulk material. Second, it is not certain whether the $\alpha$-Fe particles in reduced Fe/C-1 are bound to the carbon support or loosely contained in the pores of the support. In the latter case, thermal motion of the particles causes the recoilless fraction of such particles to decrease more rapidly with temperature than is expected on the base of lattice vibrations alone. This effect can mistakenly be interpreted in terms of a decreased Debye temperature and can be recognized from the temperature dependence of the isomer shift, IS(T), which yields a $\theta_D$ independent of particle motion. For unreduced Fe/C-1 the Debye temperature from $A(T)$ and IS(T) are equal, indicating that particle motion plays no role. For the reduced catalysts the IS(T) values are not accurate enough to determine $\theta_D$. We suggest that both the large fraction of surface atoms (near 1/3) and thermal motion of particles inside the pores of the support are responsible for the low value of $\theta_D$.

It is interesting to note that the effective Debye temperature decreases somewhat upon reduction. This is in contrast to our experience with SiO$_2$- and Al$_2$O$_3$-supported iron catalysts where $\theta_D$ is always found to increase as a result of reduction. The interpretation in the case of oxide-supported catalysts is that after impregnation and drying, a highly dispersed metal oxide layer is formed on the support, whereas after reduction metal particles of lower dispersion have formed, bound to the support. The decrease in $\theta_D$ of the Fe/C-1 catalysts upon reduction may indicate that the iron particles formed after reduction are not tightly bound to the support. However, further investigation will be necessary before firm conclusions concerning this point can be drawn.

**Conclusions**

1. The Fe/C-1 catalysts after impregnation and drying contain iron as Fe$^{2+}$ in an iron(III) oxide. The large quadrupole splitting at room temperature, the fact that magnetic splitting sets in below

References:


77 K, and the low effective Debye temperature all indicate that the iron(III) oxide is highly dispersed.

(2) After reduction in H₂ at 675 or 740 K the Fe/C-1 catalysts contain about 60 and 77% metallic iron, respectively. At 295 and 77 K this a-Fe is predominantly in a superparamagnetic state. At 4 K, however, all the a-Fe exhibits magnetic splitting, with a magnetic hyperfine field which is about 7 kOe larger than the 338-kOe field of bulk a-Fe. The difference is in agreement with the influence expected from the demagnetizing field in singledomain a-Fe particles.

(3) The occurrence of superparamagnetic a-Fe in Mössbauer spectra at 77 K indicates that the distance between the a-Fe particles is such that dipole–dipole interactions between the magnetic moments of the particles are negligible. Also, the total magnetic anisotropy energy of the particles must be small.

(4) The reduced Fe/C-1 catalysts contain an Fe²⁺ phase which in the Mössbauer spectra appears as a broadened magnetic sextet at 4 K, a doublet at 77 K, and an unresolved doublet at 295 K. The unusual occurrence of a single line for Fe²⁺ is explained by electronic and lattice contributions to the electric field gradient which are opposite in sign and compensate each other at 295 K.

(5) All iron in the reduced Fe/C-1 catalyst becomes oxidized upon exposing the Fe/C-1 catalyst to air at 295 K, in agreement with the small particle size (2 nm) which follows from CO chemisorption, and the occurrence of superparamagnetism at relatively low temperatures.

(6) Treatment of reduced Fe/C-1 catalysts at 510 K in CO and H₂ converts all a-Fe into iron carbides which are superparamagnetic at 295 K, whereas the Fe²⁺ phase remains unaffected.

The various interesting aspects of small-particle behavior could only be revealed after application of Mössbauer spectroscopy in situ at liquid nitrogen and helium temperatures. The present investigation illustrates that equipment which permits measurement of spectra in situ at cryogenic temperatures is an absolute necessity for complete Mössbauer studies of highly dispersed catalysts.

Registry No. Fe, 7439-89-6.

**Intracrystalline Site Preference of Hydrogen Isotopes in Borax**

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The total hydrogen involved in borax synthesized at 25 °C in aqueous solution is enriched in deuterium by 5.3% compared with the mother liquor. The fractional dehydration factor between the hydrogen in borax and those in the mother liquor with changes in the degree of supersaturation. The fractionation factor changes slightly with a change in the crystallization temperature of borax in the range from 5 to 25 °C. The D/H ratio in the different sites of borax was estimated by a fractional dehydration technique. The results show that hydrogen atoms of the polymeric group [BO₄(OH)₄] are much more enriched in deuterium than those of the cationic group [Na₂·8H₂O]. The D/H values, referred to the mother liquor from which the borax was crystallized, for the cationic group (site A) and the polymeric group (site B) are -35 ± 3 and 167 ± 13%, respectively, based on the fractional dehydration results obtained at -21 °C. At -21 °C, isotopic exchange between different sites during dehydration is assumed not to occur. The mechanism for dehydration of borax is discussed.

**Introduction**

The difference in the isotopic composition of oxygen between free water and water molecules in the hydration sphere of cations and anions in aqueous salt solutions was first discussed by Taube.¹ The effects of ions on the isotopic fractionation between aqueous solutions were investigated and expanded by a number of researchers.²⁻⁴ In addition, information on the fractionation of hydrogen and/or oxygen isotopes between crystals and their saturated solutions has also been accumulated.⁵⁻¹⁰ Bigeleisen¹¹ and Matsuo et al.¹² advocated that the temperature dependence of the hydrogen isotope fractionation factor between hydrates and aqueous solution can be used as a geothermometer. However, the water of crystallization in a hydrate crystal is not always in the same geometric and/or energetic site, so that there should be an isotopic site preference in the crystal of hydrates as was pointed out by Heinzinger and Rao.¹³ Heinzinger and Maiwald¹⁴ conducted a fractional dehydration experiment on CuSO₄·5H₂O and verified such a site preference for this compound. Heinzinger and Götz¹⁵ further estimated a temperature dependence for the site preference. Based on their results, Heinzinger¹⁶ suggested that even a single mineral with isotopic site preference can be used as a geothermometer. Kita and Matsuo¹⁷ concluded that water molecules in the coordination sphere of Cu²⁺ were depleted in deuterium by 32% and water molecules bound to SO₄²⁻ through hydrogen bonding were enriched by 22.6% compared with the mother liquor. Hamza and Epstein¹⁸ found that there is a significant difference in the ¹⁸O/¹⁶O ratio between the OH groups

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