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The Effect of Preparation Method on the Acidic and Catalytic Properties of Iron Oxide

ATSUSHI KAYO, TSUTOMU YAMAGUCHI,[1] AND KOZO TANABE

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

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Five kinds of iron oxides (Fe_2O_3) were prepared from iron alum and iron nitrate by using aqueous ammonia or urea; the surface and catalytic properties were studied. Iron oxide prepared from iron alum with urea exhibited pronounced catalytic activities for the ring-opening isomerization of cyclopropane and the dehydration of 2-butanol; the activity for the dehydration was about 100–400 times higher than those of the other iron oxides. The differences in the catalytic activity of those catalysts were attributed to the changes of acidic properties of the catalysts by different preparation methods. The preparation from iron alum with urea retained sulfate ion in the resulting oxide, while the other methods gave the pure iron oxide. This sulfate ion strongly enhances the acidic properties of the oxide. Infrared study revealed that sulfate ion interacts with iron oxide by a state different from iron sulfate. A model of active sites created by the interaction is proposed.

INTRODUCTION

It is known that the acidic and basic properties as well as the catalytic activity of some oxides and mixed oxides are varied by employing different preparation methods (*1–3*). Iron oxide is a popular catalyst for the oxidative dehydrogenation of butene and the water–gas shift reaction. However, little work has been reported on the acidic and basic properties of the oxide and the variation of those properties by different preparation methods. Recently, the catalytic activities of TiO_2 (*3, 4*), ZrO_2 (*5*), and Fe_2O_3 (*6*) were found to be enhanced remarkably by the addition of a small amount of sulfate ion. Thus, the present work has been done to learn systematically about the influence of the preparation methods on the acidic and catalytic properties of iron oxide and, in particular, to elucidate the role of sulfate ion in connection with the preparation methods. For this purpose, X-ray diffraction, sulfate ion content, surface area, adsorbed amounts of pyridine, NH_3, and CO_2, and infrared spectra of adsorbed species and sulfate ion included in iron oxide have been measured. The dehydration of 2-butanol and the coisomerizations of 1-butene-d_0/$-d_8$ and cyclopropane-d_0/$-d_6$ have been also studied as model reactions.

EXPERIMENTAL

Catalyst Preparation

Fe_2O_3(I). An aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ and excess urea was boiled at about 95°C. Precipitation takes place slowly as urea decomposes. The precipitate was washed repeatedly by hot water, filtered, dried at 100°C, and finally calcined at 500°C for 3 hr.

Fe_2O_3(II). An aqueous solution of iron alum ($Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$) and excess urea was boiled at about 95°C. The resulted precipitate was washed repeatedly by hot water until no SO_4^{2-} ion was detected with $BaCl_2$ in supernatant, filtered, dried at 100°C, and calcined at 500°C for 3 hr.

Fe_2O_3(III). Ammonia water was added to an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ to yield precipitation. The following procedure was similar to the preparation of Fe_2O_3(I).

Fe_2O_3(IV). Ammonia water was added to an aqueous solution of iron alum. The fol-

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[1] To whom all correspondence should be addressed.

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lowing procedure was similar to the preparation of Fe_2O_3(II).

Fe_2O_3(V). Ammonia water was added to an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ to yield precipitation. The precipitate was washed repeatedly by hot water. After the supernatant was removed by decantation, an aqueous solution of $(NH_4)_2SO_4$ was added, followed by evaporation to dryness and calcination at 500°C. The amount of $(NH_4)_2SO_4$ added was adjusted to yield iron oxide containing 2wt% of SO_4^{2-} ion.

Designation of the oxides, the starting materials, the surface areas, and the phase detected by X-ray diffraction of the oxides are summarized in Table 1. Commercial $SiO_2 \cdot Al_2O_3$ (Nikki N631-L) was used for comparison.

Quantitative Analysis of Sulfate Ion

Iron oxide was dissolved into an aqueous HCl solution. An aqueous solution of $BaCl_2$ was added to the solution to precipitate SO_4^{2-} as $BaSO_4$, which was analyzed gravimetrically.

X-Ray, Infrared, and Surface Area

X-Ray diffraction patterns were obtained by using a Toshiba GD-3 diffractometer for the powdered sample that had been calcined at 500°C in air. Infrared spectra were recorded at room temperature by a JASCO DS-701G spectrometer. Infrared spectra were recorded at room temperature by a JASCO DS-701G spectrometer. A disc sample was calcined in air at 500°C for 3 hr and then evacuated at various temperatures. The ir measurements of pyridine or nitric oxide adsorbed on the disc samples were performed by admitting 10 Torr of pyridine or nitric oxide at room temperature and evacuated at various temperatures. Specific surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at −196°C.

Amount of NH_3 and CO_2 Adsorbed

Irreversibly adsorbed amounts of NH_3 and CO_2 were measured gravimetrically by using Cahn-2000 electrobalance at 30°C.

Reaction

The dehydration of 7.5 Torr of 2-butanol and the isomerizations of 50 Torr of 1-butene and cyclopropane were carried out at 100 or 200°C by using a closed recirculation reactor. Prior to reaction, the catalyst was evacuated at 500°C for 2 hr. The products were analyzed by a gas chromatograph which was equipped with a 5-m column of VZ-7 or a 1-m column of TPC. The reaction products of a coisomerization of 1-butene-$d_0/-d_8$ mixture or cyclopropane-$d_0/-d_6$ mixture were separated gas chromatographically and subjected to a mass spectrometric analysis.

TABLE 1

Catalysts, Surface Area, and Crystallographic Phase

Catalyst	Starting materials	Precipitating reagent	Surface area (m^2/g)	Phase by XRD	SO_4^{2-} content (wt%)
Fe_2O_3(I)	Nitrate	Urea	18.0	α-Fe_2O_3	0
Fe_2O_3(II)	Alum	Urea	53.5	Amorphous	2
Fe_2O_3(III)	Nitrate	Ammonia	13.0	α-Fe_2O_3	0
Fe_2O_3(IV)	Alum	Ammonia	11.3	α-Fe_2O_3	0
$SiO_2 \cdot Al_2O_3$	Commercial		350	—	0

RESULTS AND DISCUSSION

i. Adsorption of Pyridine, Carbon Dioxide, Nitric Oxide, and Ammonia

The infrared spectra of pyridine adsorbed on Fe_2O_3(II) and (III) showed four bands at 1605, 1570, 1485, and 1445 cm^{-1}. During evacuation at temperatures up to 200°C, these bands decreased in intensity, although their relative intensities remained constant. Thus the bands were assigned to pyridine coordinatively bonded to Lewis acid sites. No band corresponding to pyridinium ion was found and it has been concluded that only Lewis acid sites exist on the surface on both iron oxides. Evacuation at 300°C after the adsorption of pyridine brought complex spectra for both oxide samples and transmission of infrared beam decreased considerably. Adsorbed pyridine may react with the oxide surface and transform or decompose to different species. Thus it was difficult to compare which oxide held pyridine more strongly on the surface.

Carbon dioxide was not adsorbed on Fe_2O_3(II), while Fe_2O_3(III) adsorbed CO_2 so long as CO_2 was present in a gas phase; evacuation at room temperature brought about the complete disappearance of the corresponding band. This indicates that both Fe_2O_3(II) and (III) have almost no basic property.

Adsorption of NO gave a band at 1880 cm^{-1} on Fe_2O_3(II) and at 1790 cm^{-1} on Fe_2O_3(III) after the evacuation of gas phase at room temperature. These bands disappeared completely after evacuation at 100°C. Higher frequency observed on Fe_2O_3(II) seems to indicate the higher acid strength of this oxide than that of Fe_2O_3(III) (*7*).

The amounts of ammonia irreversibly adsorbed at 30°C are shown in Table 2. Among four ferric oxides, Fe_2O_3(II) showed highest acidity per unit weight of catalyst. However, since the surface area of Fe_2O_3(II) was largest, the acidity per unit surface area of all Fe_2O_3 was almost the same.

TABLE 2

Amounts of NH_3 Irreversibly Adsorbed at 30°C

Catalyst	Amount of NH_3 adsorbed	
	mmol/g	mmol/m^2
Fe_2O_3(I)	0.033	0.0018
Fe_2O_3(II)	0.136	0.0025
Fe_2O_3(III)	0.052	0.0040
Fe_2O_3(IV)	0.029	0.0027
$SiO_2 \cdot Al_2O_3$	0.279	0.0008

ii. Isomerization of 1-Butene

The activity per unit surface area of Fe_2O_3(II) was higher than those of other ferric oxides and even $SiO_2 \cdot Al_2O_3$. However, it seems difficult to correlate the catalytic activity to the acidity per unit surface area (shown in Table 2).

The ratios of *cis-/trans*-2-butene, which were obtained by extrapolating to zero conversion, vary from 1.6 to 2.6. Except over Fe_2O_3(II), the ratios are within the value which is typically found on acidic catalysts (*8, 9*).

Figures 1 and 2 show the results of the coisomerization of 1-butene-d_0/$-d_8$ over Fe_2O_3(II) and (III), respectively. The number of H (or D) atoms exchanged per molecule (AEM value) was calculated from the equation (*9*),

$$\mathrm{AEM} = \sum_{i=0}^{4} \cdot N_i + \sum_{i=5}^{8} (8 - i) \cdot N_i,$$

where N_i is the fraction of isotopic species containing i D atoms and the isotope effect (IE value) was calculated from the equation (*9*),

$$\mathrm{IE} = \left(\sum_{i=0}^{3} N_i + 0.5N_4\right) \Big/ \left(\sum_{i=5}^{8} N_i + 0.5N_4\right).$$

Over Fe_2O_3(II), the isotope effect is small and normalized intercepts of 1.4 for double bond migration and the intercepts of the AEM value near 0.5 clearly show that one

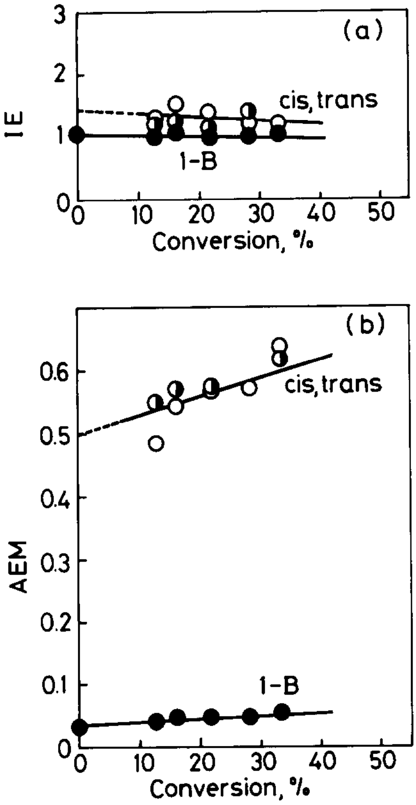


FIG. 1. Coisomerization of 1-butene-d_0/$-d_8$ over Fe_2O_3(II) at 100°C. Total pressure = 50 Torr. (a) Isotope effect, (b) hydrogen atoms exchanged per molecule: ●, 1-butene; ○, *trans*-2-butene; ◑, *cis*-2-butene.

H (or D) atom is exchanged intermolecularly per molecule isomerized. This type of reaction has been typically found on solid acid catalysts, such as $SiO_2 \cdot Al_2O_3$ (*9*, *10*).

The situation is apparently different on Fe_2O_3(III). The AEM value was low enough to show that the exchange does not take place during the reaction and the large primary isotope effect (IE = 5.4) indicates that C–H bond cleavage is probably involved in the rate-determining step. This type of reaction was typically found on Al_2O_3 (*9*).

iii. Ring-Opening Isomerization of Cyclopropane

This reaction took place only on Fe_2O_3(II) and $SiO_2 \cdot Al_2O_3$. The ring-opening isomerization of cyclopropane is known to be catalyzed by Brønsted acids (*11*). The coisomerization of cyclopropane-d_0/$-d_6$ over Fe_2O_3(II) revealed that the reaction proceeds via a hydrogen addition process (see Fig. 3). The small isotope effect indicates that C–H bond cleavage is not involved in the rate-determining step. The AEM value of 0.44 suggests that one H (or D) atom is exchanged intermolecularly per molecule isomerized. A slight shift from 0.5, whose value is expected in a typical intermolecular hydrogen exchange, to 0.44 will be interpreted by assuming that removal of a hydrogen or a deuterium atom from a protonated cyclopropane molecule takes place in an equal probability. Thus the isomerization of cyclopropane to propylene proceeds via a protonated cyclopro-

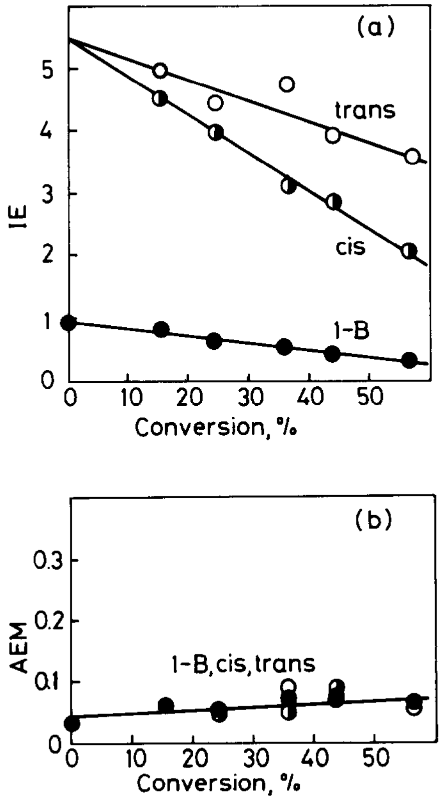


FIG. 2. Coisomerization of 1-butene-d_0/$-d_8$ over Fe_2O_3(III) at 100°C. Total pressure = 50 Torr. (a) Isotope effect, (b) hydrogen atoms exchanged per molecule: ●, 1-butene; ○, *trans*-2-butene; ◑, *cis*-2-butene.

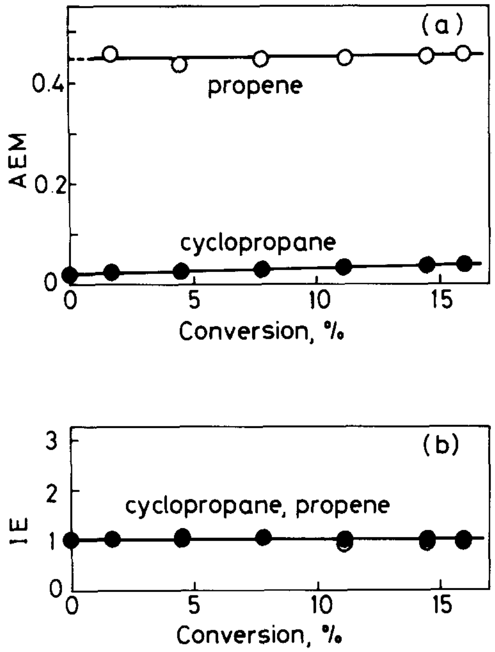


FIG. 3. Coisomerization of cyclopropane-d_0/$-d_6$ over Fe_2O_3(II) at 100°C. Total pressure = 50 Torr. (a) Hydrogen atoms exchanged per molecule, (b) isotope effect: ●, cyclopropane; ○, propene.

pane intermediate over protonic acid sites on both Fe_2O_3(II) and $SiO_2 \cdot Al_2O_3$.

Isotopic studies on the isomerization of 1-butene and cyclopropane revealed that the reaction proceeds apparently via a carbenium ion mechanism, in which a proton addition to hydrocarbon molecules was involved, while infrared spectrometric analysis of the catalysts showed the catalyst has only Lewis acid sites as described in Section i). Therefore, the Brønsted acid (or protonic) sites which played as active sites would be generated by the interaction of hydrocarbon molecules and Lewis acid sites.

iv. Dehydration of 2-Butanol

The reaction rates and the product distributions are summarized in Table 3. Again Fe_2O_3(II) showed the highest activity of the iron oxide catalysts. The activity of Fe_2O_3(II) was about 400 times higher than that of Fe_2O_3(IV) prepared from the same starting material (iron alum) with aqueous ammonia and about 100 times higher than that of Fe_2O_3(I) prepared from iron nitrate and urea. The most active $SiO_2 \cdot Al_2O_3$ gave a thermodynamically equilibrated product distribution, while Fe_2O_3(II) yielded *cis*-2-butene preferentially. The catalysts which exhibit lower activity gave 1-butene preferentially.

The extremely high activity of Fe_2O_3(II) among the four ferric oxides for this reaction and the isomerization of cyclopropane is considered to be caused by the difference in the kinds of precursors and precipitating

TABLE 3

Catalytic Properties

Catalyst	Isomerization of 1-butene			Isomerization of cyclopropane		Dehydration of 2-butanol		
	T (°C)[a]	Rate[b]	*c*/*t*[c]	*T* (°C)[a]	Rate[b]	*T* (°C)[a]	Rate[b]	1 : t : c[d]
Fe_2O_3(I)	100	31	1.6	200	0	200	0.4	1 : 0 : 0
Fe_2O_3(II)	100	189	2.6	100	152	200	40	1 : 1 : 3
Fe_2O_3(III)	100	9.5	1.6	200	0	200	0.2	1 : 0 : 0
Fe_2O_3(IV)	100	90	1.6	200	0	200	0.1	1 : 0 : 0
$SiO_2 \cdot Al_2O_3$	100	88	1.0	100	2	200	11	1 : 7 : 3

[a] Reaction temperature.

[b] 10^{-1} μmol/m² · min.

[c] *cis*-/*trans*-2-butene.

[d] 1- : *trans*- : *cis*-2-butene (ratio obtained by extrapolating to zero conversion).

reagents whose effects will be discussed in more detail in the next section.

v. The Effect of Preparation Method on Catalytic Activity

According to a gravimetric analysis, Fe_2O_3(II) contains 2 wt% of sulfate ion. To elucidate the effect of sulfate ion and the preparation method on the catalytic activity, Fe_2O_3(V) which contains the same amount of sulfate ion was prepared by a different method and the catalytic activity was examined. The results are shown in Table 4. Fe_2O_3(V) containing sulfate ion was much more active for the three reactions than Fe_2O_3(I), (III), and (IV) which do not contain sulfate ion. Thus, it can be concluded that the role of sulfate ion for the catalytic activity is vitally important.

For the dehydration of 2-butanol, the activity per unit surface area of Fe_2O_3(II) was four times higher than that of Fe_2O_3(V) which contained the same amount of sulfate ion. Therefore, it should be realized that not only the content of sulfate ion, but also the use of urea as a precipitating reagent is important for the preparation of highly active iron oxide catalyst for particular reactions.

Origin of Enhanced Acid Strength and Activity by SO_4^{2-} Inclusion in Fe_2O_3

As seen in the preceding sections, the acidic properties and the catalytic activity for the acid-catalyzed reactions of Fe_2O_3(II) and (V) are much higher than those of the other iron oxides. As mentioned in Section v, such an enhancement is primarily brought about by a small amount (2 wt%) of sulfate ion included in the iron oxides. To elucidate the mechanism of the enhancement, the following infrared study of Fe_2O_3(II) itself has been performed.

The spectral changes were measured for the samples which were evacuated at room temperature to 500°C. The results are shown in Fig. 4. Drastic spectral changes are seen at 1400 ~ 1200 cm^{-1} region and the bands can be assigned to sulfate species be-

TABLE 4

Surface and Catalytic Properties of Fe_2O_3(V)

Isomerization of 1-butene			Isomerization of cyclopropane		Dehydration of 2-butanol			Surface area (m^2/g)	NH_3 adsorbed		SO_4^{2-} content (wt%)
T (°C)[a]	Rate[b]	c/t[c]	T (°C)[a]	Rate[b]	T (°C)[a]	Rate[b]	$1:t:c$[d]		mmol/g	mmol/m^2	
100	241	1.2	100	118	200	11	1:1:8	37.4	0.130	0.0036	2

[a–d] See footnotes *a–d*, Table 3.

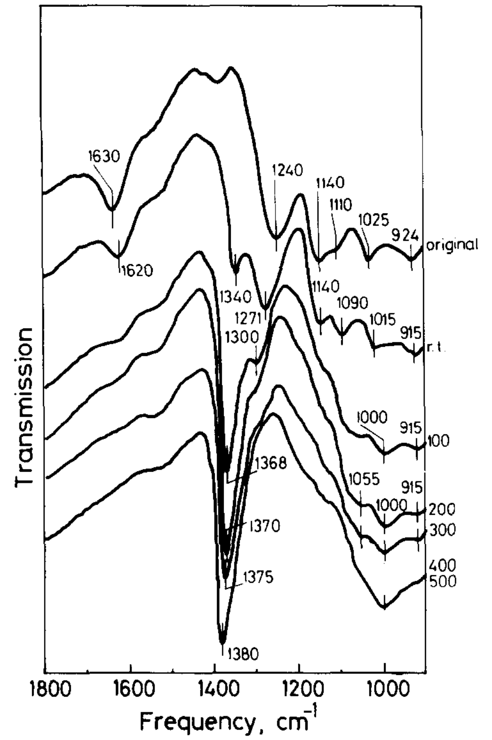


FIG. 4. Infrared spectra of Fe_2O_3(II). Original, original disc without evacuation; r.t., 100, 200, 300, 400, and 500; evacuation temperatures.

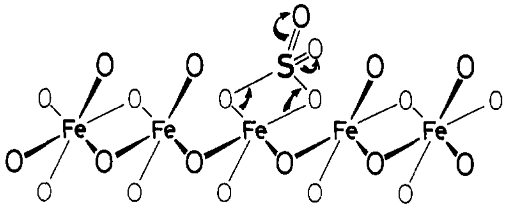
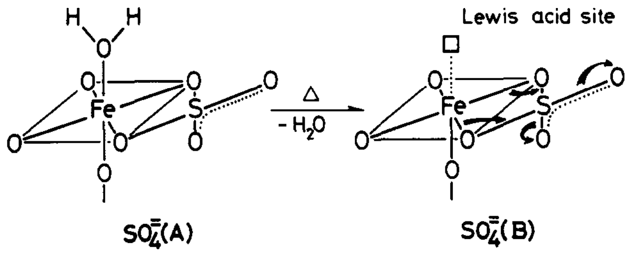


FIG. 5. A model of acid sites generated by the interaction with SO_4^{2-}.

cause of their positions and the lack of these bands in the other samples which do not contain sulfate ion. Considering the spectral changes after evacuation at various temperatures, the bands appeared after the evacuation at room temperature are classified into two sulfate groups; SO_4^{2-} (A) 1271, 1090, 1015, and 915 cm^{-1}, and SO_4^{2-} (B) 1340, 1140, 1015, and 915 cm^{-1}. These four bands are assigned to S=O asymmetric, S=O symmetric, S—O asymmetric, and S—O symmetric stretching frequencies, respectively. A bending vibration of adsorbed water was found at around 1620 ~ 1630 cm^{-1} on the samples evacuated at mild conditions. Behavior of this band is closely related to the spectral changes of sulfate species. When water molecules adsorbed were removed almost entirely by evacuation up to 100°C, and 1340 cm^{-1} band intensity increased markedly and shifted to 1368 cm^{-1}, and at the same time, the 1271 cm^{-1} band lost its intensity. Upon evacuation at higher temperatures, the S=O asymmetric band (both in groups A and B) shifted to higher frequencies and the relative intensity of these bands has changed. Namely, the S=O asymmetric band of group A decreased, while that of group B increased. Over 300°C, the bands corresponding to group A have almost disappeared and only the bands of group B remained. When the oxide sample was evacuated at 400°C, the SO_4^{2-} of group A species completely disappeared and a strong band was found at 1375–1380 cm^{-1}, which corresponds to asymmetric S=O stretching frequency of group B. Since the spectral changes were reversible during adsorption–desorption cycles in H_2O admission experiments, groups (A) and (B) are interconvertible. Without water molecule adsorbed, group (B) is preferential. Interconversion of those groups may be illustrated below.



The observed S=O frequency was higher than that of metal sulfate (usually 1235–1100 cm^{-1}) (*12*) and very close to that of covalent sulfates in organic substances (1440–1350 cm^{-1}) (*13*). Thus, the double bond nature of S=O of the complex formed by the interaction of Fe_2O_3 with SO_4^{2-} is much stronger compared to that of simple iron sulfate (14) which has only moderate acid strength. Therefore, the Lewis acid strength of Fe^{3+} becomes stronger by the inductive effect of S=O in the complex as illustrated in Fig. 5. Group (B) is responsible to the strong acid site, but once it adsorbs electron donating molecules such as water or pyridine, its conformation converts to that of group (A) which does not have strongly acidic properties. Enhancement of electron deficiency on Fe^{3+} by the introduction of sulfate ion is the origin of strongly acidic properties.

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