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Acid Structure of MgO-SiO₂ Binary Oxide Catalyst and Activity for Acid Catalysis

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A series of MgO-SiO₂ catalysts were prepared by coprecipitation from the mixed solution of magnesium chloride and sodium silicate. Some of the sample were modified with 1 N H₂SO₄ and used as modified catalysts. The addition of MgO to SiO₂ caused the increase of acidity and the shift of O-H and Si-O stretching bands of the silanol group to a lower frequency in proportion to the MgO content. The acid structure of MgO-SiO₂ agreed with that proposed by Tanabe *et al.*. Catalytic activity for 2-propanol dehydration increased in relation to the increase of acidity and band shift to a lower frequency.

Introduction

In many cases, the components are inactive while their mixtures have a high catalytic activity. Thus, recently many kinds of mixed oxides were reported to show catalytic activity for particular reactions.¹⁻⁶ TiO₂ alone is impractical as a catalyst because of its low catalytic activity. However, mixed oxide systems combining TiO₂ with such oxides as V₂O₅, MoO₃, P₂O₅, SiO₂ and ZnO are known to be effective for various reactions.⁷⁻¹¹ Pure silica gel, which has no catalytic activity with respect to dehydration of isopropyl alcohol, exhibits considerable acidity and catalytic activity on addition of only 0.1% ZrO₂.¹² These combinations seem to induce an unexpectedly great change in the catalytic behavior.

Acid catalyzed reaction is correlated with acid amount and acid strength. In cumene dealkylation the more acidic the catalysts, the higher catalytic activity they show.^{13,14} On the other hand, tert-butanol dehydration takes place on relatively weaker acid sites, while skeletal isomerization of isobutylene requires exceedingly strong acid sites.¹⁵ Thus to incorporate acidity and stronger acid strength, single or binary oxide catalysts are modified with sulfuric acid in many cases.¹⁶⁻²² High catalytic activity of catalyst modified with sulfuric acid is attributed to the enhanced acidic property by the inductive effect of S=O bonds of the complex formed

by the interaction of oxides with sulfate ion.^{21,23}

Pure silica gel shows no acidic property and is used mainly as the support of catalysts, while magnesium oxide is typical solid base catalyst. So far, however, only a small amount of work was done for the MgO-SiO₂ catalyst.^{24,25} In this work, the catalytic activities of MgO-SiO₂ series catalysts prepared by coprecipitation method and their correlations to the acidic properties have been studied. Also the catalytic activities of MgO-SiO₂ modified with H₂SO₄ are compared with those of unmodified catalysts. For this purpose the 2-propanol dehydration was used as test reaction.

Experimental

Catalysts. The coprecipitate of MgO-SiO₂ was obtained by adding aqueous ammonia slowly into the mixed aqueous solution of magnesium chloride and sodium silicate solution at 70 °C with stirring until the pH of the mother liquor reached 8. The ratio of magnesium chloride to sodium silicate was varied. The coprecipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected and dried at room temperature. The dried coprecipitate was again washed with successive portions of a 5% ammonium nitrate solution and then with hot distilled water to remove sodium ion in the coprecipitate. The dried precipitate was powdered below 100 mesh and was used as catalyst after calcination at 400 °C for 1.5 hr. Some samples were modified by pouring 30 mL of 1 N H₂SO₄ into each 2

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g of the powdered sample on a filter paper and then dried in air, followed by calcining at 400 °C for 1.5 hr, much as in previous work.²⁰⁻²² All the catalysts prepared are tabulated in Table 1 together with their surface area. The catalysts are denoted by following a mole percentage of MgO. For example, 10-MgO-SiO₂ means the catalysts having 10 mole% of MgO and 10-MgO-SiO₂/SO₄²⁻ means 10-MgO-SiO₂ catalyst modified with 1 N H₂SO₄.

Procedure. 2-Propanol dehydration was carried out at 180 °C in a pulse micro-reactor connected to a gaschromatography. Fresh catalyst in the reactor made of 1/4 inch stainless steel was pretreated at 400 °C for 1hr in the nitrogen atmosphere. Diethyleneglycol succinate on Simalite was used as packing material of gaschromatography and the column temperature was 180 °C for analyzing the product. Catalytic activity for 2-propanol dehydration was represented as mole of propylene converted from 2-propanol per catalyst gram.

The acid strength of catalyst was measured qualitatively using a series of the Hammett indicators. The catalyst in a glass tube was pretreated at 400 °C for 1hr and filled with dry nitrogen. For the determination of acid strength of the catalyst the color changes of indicators were observed by spot test. Chemisorption of ammonia was employed as a measure of acidity of catalysts. The amount of chemisorption was obtained as the irreversible adsorption of ammonia.^{23,26}

The specific surface area was determined by applying the BET method to the adsorption of nitrogen at -196 °C. IR spectra were recorded using a Bruker FTIR spectrometer. X-ray diffractogram of catalysts were by Rigaku model 2125D2 using copper target and nickel filter at 30 kV and 1000 cps.

Results and Discussion

Infrared spectra of catalysts. During the preparation of binary oxide catalysts such as SiO₂-NiO and SiO₂-Al₂O₃ by the precipitation method, a chemical reaction occurs between the two components.²⁷ It is possible to identify the silicate compound formed during the preparation by IR spectroscopy.^{28,29} A series of MgO-SiO₂ catalysts calcined at 400 °C was examined by IR absorption. The IR spectra of the catalysts are given in Figure 1, together with those of MgO and SiO₂ alone. The bands at 1200, 1103 and 800 cm⁻¹ are characteristic bands of SiO₂ assigned to

Si-O stretching vibrations, while the band at 470 cm⁻¹ is assigned to the Si-O bending vibration.³⁰ The band of SiO₂ at 974 cm⁻¹ is assigned to the Si-O stretching vibration of the silanol group.^{31,32} Comparing these IR spectra with those of MgO and SiO₂, it is clear that there are no new bands due to the chemical compound formed between MgO and SiO₂, indicating no formation of a new phase between them. The X-ray diffraction analysis of the calcined MgO-SiO₂ sample showed no detectable reflections of crystalline MgO or magnesium silicate phases. The binary oxides consisted mostly of amorphous regions. However, the band around 1200-1100 cm⁻¹ due to the Si-O skeletal vibrations and the Si-O stretching vibration band of the silanol group at 974 cm⁻¹ were shifted to lower wavenumber with increasing MgO content, suggesting the presence of some interaction between SiO₂ and MgO.³³

It is expected that the O-H bond of the silanol group is weakened by adding the MgO component to SiO₂, and by withdrawing electrons in the O-H bond due to the interaction between SiO₂ and MgO. This is supported by the shift of OH stretching band of silanol group in the MgO-SiO₂ samples. As illustrated in Figure 2, the IR spectra of some samples evacuated at 500 °C for 2 hr show some bands in the region 3800-3500 cm⁻¹ which could be assigned to O-H stretching vibration of surface hydroxyl groups. The spectrum(a) is the usual one for pure silica.³⁴ The high-frequency band at 3745 cm⁻¹ had been assigned to the ν(OH) of free silanol groups, while the lower-frequency absorption at 3640 cm⁻¹ is due to that of hydrogen-bonded hydroxyl groups. The addition of MgO seems not only to decrease the intensity of free silanol groups but also

Table 1. Specific surface areas of catalysts calcined at 400 °C

Catalyst	Surface area (m ² /g)	Catalyst	Surface area (m ² /g)
SiO ₂	416	MgO	107
5-MgO-SiO ₂	453	5-MgO-SiO ₂ /SO ₄ ²⁻	432
10-MgO-SiO ₂	447	10-MgO-SiO ₂ /SO ₄ ²⁻	418
20-MgO-SiO ₂	440	20-MgO-SiO ₂ /SO ₄ ²⁻	410
33-MgO-SiO ₂	435	33-MgO-SiO ₂ /SO ₄ ²⁻	402
50-MgO-SiO ₂	428	50-MgO-SiO ₂ /SO ₄ ²⁻	398
60-MgO-SiO ₂	420	60-MgO-SiO ₂ /SO ₄ ²⁻	490
75-MgO-SiO ₂	347	75-MgO-SiO ₂ /SO ₄ ²⁻	320
90-MgO-SiO ₂	232	90-MgO-SiO ₂ /SO ₄ ²⁻	202

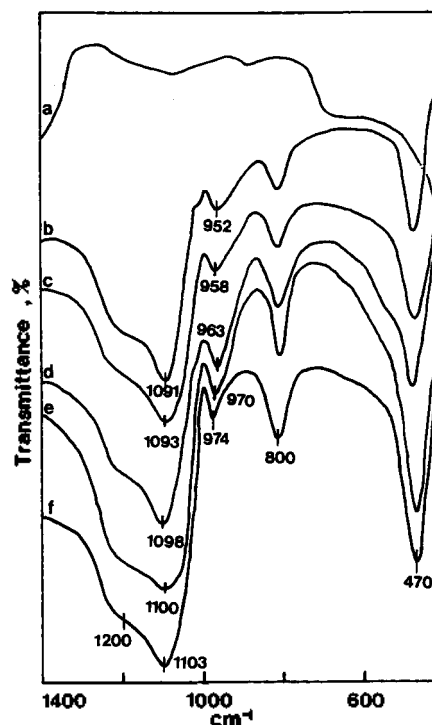


Figure 1. Infrared spectra of MgO-SiO₂ series of catalysts calcined at 400 °C; (a) MgO, (b) 75-MgO-SiO₂, (c) 60-MgO-SiO₂, (d) 33-MgO-SiO₂, (e) 5-MgO-SiO₂, (f) SiO₂.

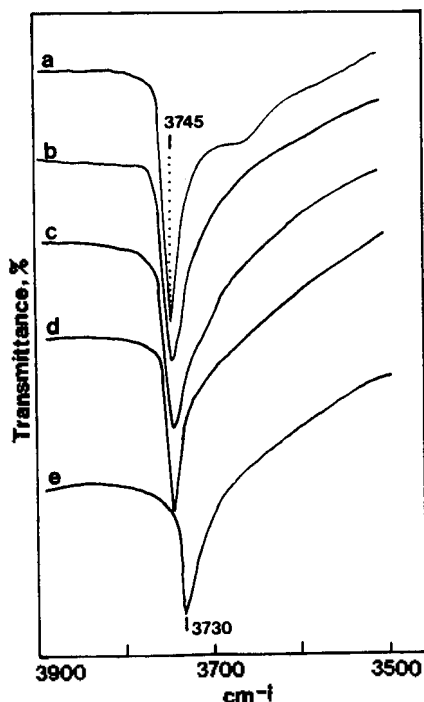


Figure 2. Infrared spectra in the O-H stretching region of (a) SiO₂, (b) 5-MgO-SiO₂, (c) 10-MgO-SiO₂, (d) 33-MgO-SiO₂, (e) MgO.

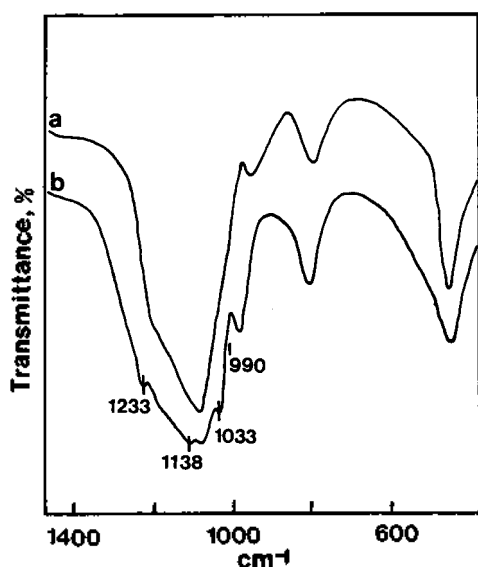


Figure 3. Infrared spectra of (a) 20-MgO-SiO₂ and (b) 20-MgO-SiO₂/SO₄²⁻.

to shift the position of free silanol groups toward a lower frequency. As shown in Figure 2, the positions are 3745 cm⁻¹ for pure SiO₂, 3743 cm⁻¹ for 5-MgO-SiO₂, 3740 cm⁻¹ for 10-MgO-SiO₂, 3738 cm⁻¹ for 33-MgO-SiO₂, and 3730 cm⁻¹ for pure MgO. It is also expected that the weakness of the O-H bond does influence both acidity and acid strength, and acid catalytic activity of the catalyst as will be described below.

The IR spectra of 20-MgO-SiO₂ modified with 1 N H₂SO₄ are given in Figure 3. In the case of SiO₂ or catalysts hav-

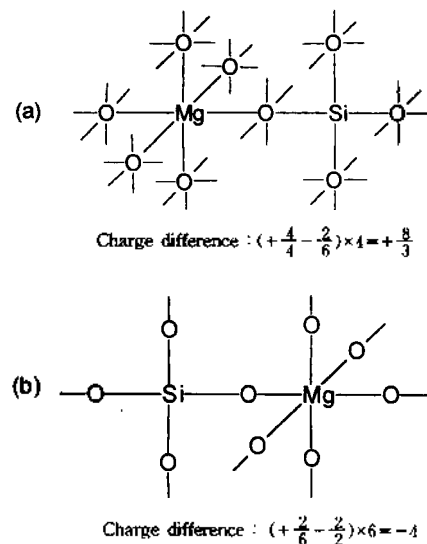
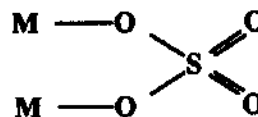


Figure 4. Model structure of MgO-SiO₂ pictured according to Tanabe's postulates (a) when MgO is major oxide, (b) when SiO₂ is major oxide.

ing high silica content, however, it was difficult to distinguish between the absorption bands of SiO₂ and those of sulfate ion, due to the IR overlap. The catalysts showed IR absorption bands at 1233, 1138, 1033 and 990 cm⁻¹ which are assigned to the bidentate sulfate ion coordinated to Mg²⁺ or Si⁴⁺ as follows.³⁵:



The $\nu(\text{SO})$ spectra from the adsorbed sulfate ion in the ν_1 and ν_3 frequency region (1400-900 cm⁻¹) support a species of reduced C_{2v} symmetry, with four bands arising from ν_1 and splitting of the triply degenerate ν_3 vibration.^{36,37}

Metal oxide which is inactive or slightly active by itself induced a high catalytic activity by the addition of other metal oxides in many cases.^{38,39} A hypothesis regarding the acidity generation of binary oxides has been proposed by Tanabe *et al.*⁴⁰ According to his hypothesis, acid sites are generated by an excess negative or positive charge in the model structure of binary oxide. The model structure can be pictured according to the following two postulates: i) The coordination numbers of positive elements in a binary oxide system are maintained even when mixed; ii) The coordination number of negative element (oxygen) in a major component oxide is retained for all the oxygen in a binary oxide. Model structures of MgO-SiO₂ pictured according to Tanabe's hypothesis are illustrated in Figure 4. The coordination numbers of the positive elements in these binary oxides remain 6 for Mg and 4 for Si when they are mixed. As shown in Figure 4, however, the coordination number of negative element (oxygen) should be 6 when major component is MgO and that should be 2 when major component is SiO₂. In the case of Figure 4a, where MgO is the major component oxide, the four positive charges of the silicon atom are distributed to four bonds, while the two ne-

Table 2. Acid strength of catalysts

Hammitt indicator	pK_a of indicator	SiO ₂	20-MgO-SiO ₂	20-MgO-SiO ₂ /SO ₄ ²⁻
Dimethylacetone	+3.3	+	+	+
Dicinnamalacetone	-3.0	-	+	+
Benzolacetophenone	-5.6	-	+	+
Antraquinone	-8.2	-	-	+
m-Nitrotoluene	-11.99	-	-	+

gative charges of the oxygen atom are distributed to six bonds. The difference in charge for one bond is $+4/4-2/6=+2/3$, and for all the bonds the valence unit of $+2/3 \times 4=+8/3$ is excess. In this case, the Lewis acidity is assumed to appear upon the presence of an excess of positive charge. On the other hand, when SiO₂ is major component as shown in Figure 4b, the two positive charges of the magnesium atom are distributed to six bonds, while the two negative charges of the oxygen atom are distributed to two bonds. The difference in charge for one bond is $+2/6-2/2=-2/3$, and for all the bonds the valence unit of $-2/3 \times 6=-4$ is excess. In this case, Brønsted acidity is assumed to appear, because four protons are considered to associate with six oxygens to keep electric neutrality. In both case, MgO-SiO₂ is expected to show acidic property because of the excess of a positive or negative charge.

Surface properties of catalysts. The surface areas of MgO-SiO₂ catalysts were checked by the BET method using nitrogen at -196°C . The results are listed in Table 1. The surface area increases gradually upon the addition of SiO₂ to MgO. That is, the more silica content the catalysts have, the larger surface area they show. This suggests that SiO₂ has more effect on the surface area than MgO. However, the surface areas of catalysts modified with H₂SO₄ were smaller than those of unmodified catalysts.

Acid strength of the catalysts was examined by color change method using Hammitt indicator,⁴¹ when a powder sample was added to an indicator dissolved in dried benzene. In Table 2, + indicates that the color of base form of an indicator was changed to that of the conjugated acid form. MgO prepared by calcining magnesium hydroxide at 400°C has been known to be a typical basic oxide, while SiO₂ had very weak acid strength of $H_0 \leq +3.3$.⁴² However, as shown in Table 2, 20-MgO-SiO₂ prepared by coprecipitation was estimated to be $H_0 \leq -5.6$, indicating the formation of new acid sites stronger than those of single oxide components. The other binary oxides with various molar ratio of MgO-SiO₂ also had the same acid strength of $H_0 \leq -5.6$ as 20-MgO-SiO₂. The acid strength of 20-MgO-SiO₂/SO₄²⁻ was estimated to be $H_0 \leq -11.99$ which corresponds to the stronger acid strength than 100% H₂SO₄. The increase of acid strength in the modified catalysts is attributed to the double bond nature of S=O which strengthen the acid sites by the inductive effect.^{20,31}

Infrared spectroscopic studies of pyridine adsorbed on solid surfaces have made it possible to distinguish between Brønsted and Lewis acid sites.⁴⁰ Figure 5 shows the infrared spectra of pyridine adsorbed on 20-MgO-SiO₂ and 75-MgO-SiO₂ evacuated at 400°C for 1.5 hr. The coordinated pyridine band at 1445 cm^{-1} and the pyridinium ion band at

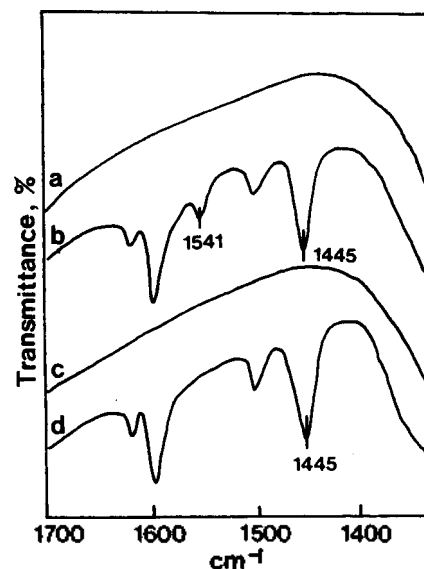


Figure 5. Infrared spectra of pyridine adsorbed on 20-MgO-SiO₂ and 75-MgO-SiO₂. (a) background of 20-MgO-SiO₂. (b) pyridine adsorbed on 20-MgO-SiO₂. (c) background of 75-MgO-SiO₂. (d) pyridine adsorbed on 75-MgO-SiO₂, gas phase was evacuated at 250°C for 1 hr after adsorption in (b) and (d).

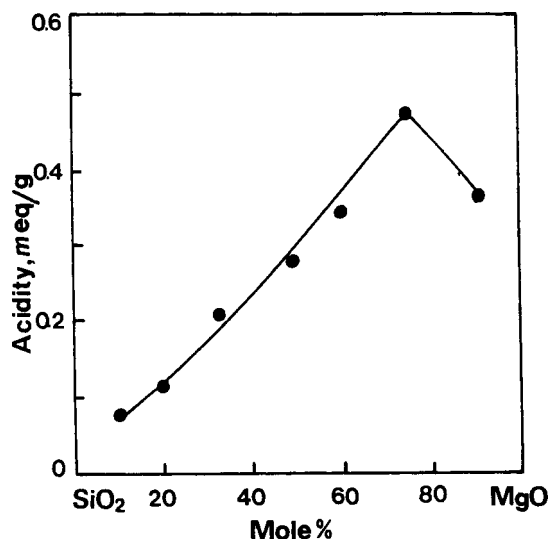


Figure 6. Acidity of catalysts as a function of MgO content.

1541 cm^{-1} are found with 20-MgO-SiO₂, where major component is SiO₂. It is clear that the new Lewis and Brønsted acid sites which are not present on single MgO and SiO₂ are formed by mixing MgO with SiO₂. However, the coordinated pyridine band at 1445 cm^{-1} is found with 75-MgO-SiO₂, where MgO is major component oxide, indicating the presence of only Lewis acid site. These results are in good agreement with those of acid model structures (Figure 4) suggested by Tanabe *et al.*

The acidity of catalysts, as determined by the amount of NH₃ irreversibly adsorbed at 230°C , is plotted as a function of the magnesium oxide content in Figure 6. Although single component, SiO₂ showed little acidity, mixing of the two component, MgO and SiO₂ resulted in remarkable increase in acidity. As shown in Figure 6, the acidity in-

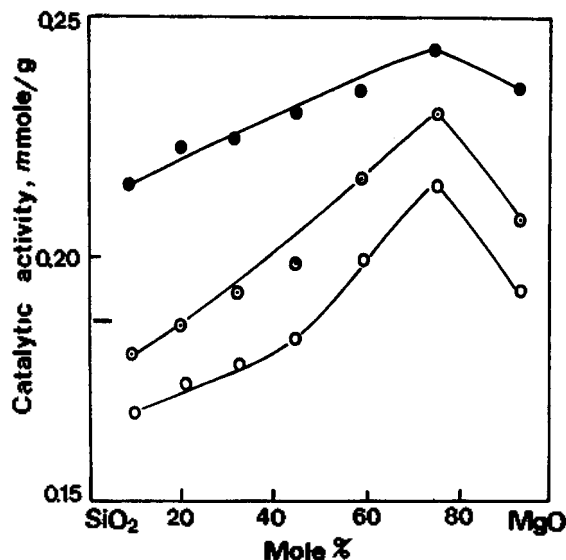


Figure 7. Variations of catalytic activity for 2-propanol dehydration with MgO content: (●) Catalyst modified with H₂SO₄ (200 °C); (◐) MgO-SiO₂ catalyst (200 °C); (○) MgO-SiO₂ catalyst (180 °C), where figure in parenthesis is reaction temperature.

creases gradually upon the addition of MgO to SiO₂ reaching a maximum at 75-MgO-SiO₂. This is not due to the increase of specific surface area, because in the view of Table 2 and Figure 6 there is no correlation between specific surface area and acidity. These results are correlated with those of IR OH and Si—O band shifts of silanol group to lower frequencies upon the addition of MgO to SiO₂ described above. That is, the more the band shift, the more acidity has the catalyst. Many kinds of combinations of two oxides were reported to generate acid sites on the surface.⁴⁰ The combination of MgO and SiO₂ generated the stronger acid sites and the more acidity as compared with the single components.

Acid catalysis. It is interesting to examine how the catalytic activity of acid catalyst depends on the acidic property. The catalytic activities for the 2-propanol dehydration are measured and the results are illustrated as a function of MgO content in Figure 7. In view of Figure 6 and 7, the variations in catalytic activities of MgO-SiO₂ catalysts are well correlated with the changes of their acidity. In many cases good correlations have been found between the total amount of acid and the catalytic activities of solid acid catalysts. For example the rates of both the catalytic dealkylation of cumene and the polymerization of propylene over SiO₂-Al₂O₃ catalysts were found to increase with increasing acid amounts.^{43,44}

As shown in Figure 7, 75-MgO-SiO₂ and 90-MgO-SiO₂ having high content of MgO which is known as a typical base oxide exhibit higher catalytic activities than those of the catalysts having low MgO content. From the above results, it is suggested that the catalysts containing high MgO content act not only as acid-catalyst but acid-base bifunctional catalyst. It is reported that the dehydration of various type of alcohols proceeds by a concerted mechanism of the acid-base bifunctional catalysis.^{45,46} However, from the

fact that the catalytic activity of 75-MgO-SiO₂ showing maximum acidity is higher than that of 90-MgO-SiO₂ having high MgO content, it seems likely that acid-catalysis for 2-propanol dehydration occurs more predominantly than acid-base bifunctional catalysis.

As shown in Figure 7, the catalysts modified with H₂SO₄ exhibit higher catalytic activity than unmodified catalysts. The high catalytic activity of modified catalyst seems to be due to the enhanced acidic property by the inductive effect of S=O bonds of the complex found by the interaction of oxides with sulfate ion.^{21,23}

In view of Figure 1, 2 and 6, it is clear that for MgO-SiO₂ catalysts the addition of MgO to SiO₂ causes the increase of acidity and the shift of O-H stretching and Si-O stretching band of the silanol groups to a lower frequency. Consequently, catalytic activities for 2-propanol dehydration increased in relation to the increase of acidity and the band shift to a lower frequency. It seems likely that the addition of MgO to SiO₂ produces new acid sites by weakening the O-H bond of the silanol group as described in the results of IR.

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Theoretical Studies on the Base-Catalyzed Deprotonation of Sulfonyl-Activated Carbon Acids

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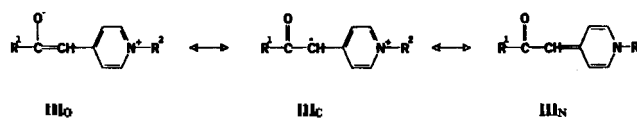
Theoretical AM1 MO studies are reported on the gas-phase deprotonations of N-methyl 4-((Y-phenylsulfonyl)pyridinium cations (IV) and N-(Y-benzyl) 4-((phenylsulfonyl)methyl pyridinium cations (V) using NH₃ as a base. Brønsted α values for deprotonation of IV and V are 0.18 and 0.17, respectively. Brønsted β value of 0.53 is found for the deprotonation of IV and V by substituted aniline bases. The negative transition state (TS) imbalances, $I (= \alpha - \beta) < 0$, are rationalized by the negative distance factor, $\Delta d (= d_p - d_{TS}) < 0$, where d_p and d_{TS} are the distance between anionic charge center and substituents in the product and in the TS, respectively. The inability of d - π -conjugation in IV, where instead n - σ^* type sigma delocalization occurs, causes very little lag in the structural reorganization in the TS.

Introduction

Transition state (TS) imbalances are a common phenomenon in many chemical reactions including proton transfers involving activated carbon acids.¹ Such imbalances have been formulated as a rule by Bernasconi, called the principle of nonperfect synchronization (PNS).² The PNS asserts that whenever resonance (and/or solvation) is involved as product (or reactant) stabilizing factor in a reaction, this factor will develop late (or be lost early) in the transition state.² In the proton transfers the TS imbalance (I) is expressed as $I = \alpha_{CH} - \beta_B$, where α_{CH} is the Brønsted coefficient obtained by varying the pK_a of the carbon acid and β_B is obtained by varying the pK_a of the base (amine or oxyanion).

The I value is in most cases positive, but in some cases the sign of I becomes negative.^{1,6,7}

In a previous work,³ we have shown theoretically that the negative I values for the base catalyzed deprotonations of 1-methyl-4-(Y-phenacyl)pyridinium, I ($R^1 = Y-C_6H_4-$ and $R^2 = CH_3$ in Scheme 1), and 1-benzyl-4-(Y-phenacyl)pyridinium, II ($R^1 = C_6H_5-$ and $R^2 = Y-C_6H_4-CH_2-$ in Scheme 1), cations



Scheme 1.