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ACIDIC PROPERTIES OF $CaO-SiO_2$ BINARY OXIDE CATALYST AND ACTIVITY FOR ACID CATALYSIS

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Abstract – A series of $CaO-SiO_2$ catalysts were prepared by coprecipitation from the mixed solution of calcium chloride and sodium silicate. The addition of CaO to SiO_2 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 CaO content. The acid structure of $CaO-SiO_2$ agreed with that proposed by Tanabe et al.. Catalytic activity for 2-propanol dehydration and cumene dealkylation increased in relation to the increase of acidity and band shift to a lower frequency.

Key words: *$CaO-SiO_2$ Catalyst, Acid Structure, 2-Propanol Dehydration, Cumene Dealkylation, Acidity*

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 [Riva et al., 1988; Baiker et al., 1988; Wang et al., 1983; Ai, 1975]. TiO_2 alone is impractical as a catalyst because of its low catalytic activity. However, mixed oxide systems combining TiO_2 with such oxides as V_2O_5, MoO_3, P_2O_5, SiO_2 and ZnO are known to be effective for various reactions [Hucknall, 1974; Itoh et al., 1974; Vogt et al., 1988]. 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 % ZrO_2 [Dzisko, 1964]. 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 [Tanabe, 1970]. On the other hand, tert-butanol dehydration takes place on relatively weaker acid sites, while skeletal isomerization of isobutylene requires exceedingly strong acid sites [Tanabe, 1978]. Thus to incorporate acidity and stronger acid strength, single or binary oxide catalysts are modified with sulfuric acid in many cases [Hino et al., 1979; Sohn and Kim; 1986]. 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 [Sohn et al., 1987].

Pure silica gel shows no acidic property and is used mainly as the support of catalysts, while calcium oxide is typical solid base catalyst. So far, however, only a small amount of work was done for the $CaO-SiO_2$ catalyst [Niiyama and Echigoya, 1971]. In this work, the catalytic activities of $CaO-SiO_2$ series catalysts prepared by coprecipitation method and their correlations to the acidic properties have been studied. For this purpose the 2-propanol dehydration and cumene dealkylation were used as test reactions.

EXPERIMENTAL

1. Catalysts

The coprecipitate of $CaO-SiO_2$ was obtained by adding aqueous ammonia slowly into the mixed aqueous solution of calcium chloride and sodium silicate solution at 70 °C with stirring until the pH of the mother liquor reached 8. The ratio of calcium 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 washed again 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. All the catalysts prepared are tabulated in Table 1 together with their surface area. The catalysts are denoted by following a mole percentage of CaO. For example, $10-CaO-SiO_2$ means the catalysts having 10 mole % of CaO.

2. Procedure

2-Propanol dehydration was carried out at 180°C in a pulse micro-reactor connected to a gas chromatograph. Fresh catalyst in the reactor made of 1/4 inch stainless steel was pretreated at 400 °C for 1 hr in the nitrogen atmosphere. Diethyleneglycol succinate on Simalite was used as packing material of gas chromatograph 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 gram of catalyst. Cumene dealkylation was carried out at 400 °C in the same reactor as above. Packing material for the gas chromatograph was Bentone 34 on Chromosorb W and column temperature was 130 °C. Catalytic activity for cumene dealkylation was represented as mole of benzene converted per gram of catalyst. Conversions for both reactions were taken as the average of the first to sixth pulse values.

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The acid strength of catalyst was measured qualitatively using a series of the Hammett indicators [Hammett and Deyrup, 1932]. The catalyst in a glass tube was pretreated at 400 °C for 1 hr 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 [Sohn and Ozaki, 1980; Sohn and Ryu, 1993]. Thus the first adsorption of ammonia at 20 °C and 300 torr was followed by evacuation at 230 °C for 1 hr and readsorption at 20 °C, the difference between two adsorptions at 20 °C giving the amount of chemisorption.

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 Brucker 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

1. Infrared Spectra of Catalysts

During the preparation of binary oxide catalysts such as SiO$_2$-NiO and SiO$_2$-Al$_2$O$_3$ by the precipitation method, a chemical reaction occurs between the two components [Schuit and Reijen, 1958]. It is possible to identify the silicate compound formed during the preparation by IR spectroscopy [Sohn and Ozaki, 1979]. A series of CaO-SiO$_2$ catalysts calcined at 400 °C were examined by IR absorption. The IR spectra of the catalysts are given in Fig. 1, together with those of CaO and SiO$_2$ alone. The bands at 1200, 1103 and 800 cm^{-1} are characteristic bands of SiO$_2$ assigned to Si-O stretching vibrations, while the band at 470 cm^{-1} is assigned to the Si-O bending vibration [Farmer and Russell, 1964]. The band of SiO$_2$ at 974 cm^{-1} is assigned to the Si-O stretching vibration of the silanol group [Sohn et al., 1994; Boccuzzi et al., 1978]. Comparing these IR spectra with those of CaO and SiO$_2$, it is clear that there are no new bands due to the chemical compound formed between CaO and SiO$_2$, indicating no formation of a new phase between them. The X-ray diffraction analysis of the calcined CaO-SiO$_2$ sample showed no detectable reflections of crystalline CaO or calcium 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 CaO content up to 50 mol%, suggesting the presence of some interaction between SiO$_2$ and CaO [Sohn and Jang, 1991].

It is expected that the O-H bond of the silanol group is weakened by adding the CaO component to SiO$_2$ and by withdrawing electrons in the O-H bond due to the interaction between SiO$_2$ and CaO. This is supported by the shift of OH stretching band of silanol group in the CaO-SiO$_2$ samples. As illustrated in Fig. 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 [Peri, 1966]. 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 CaO seems not only to decrease the intensity of free silanol groups but also to shift

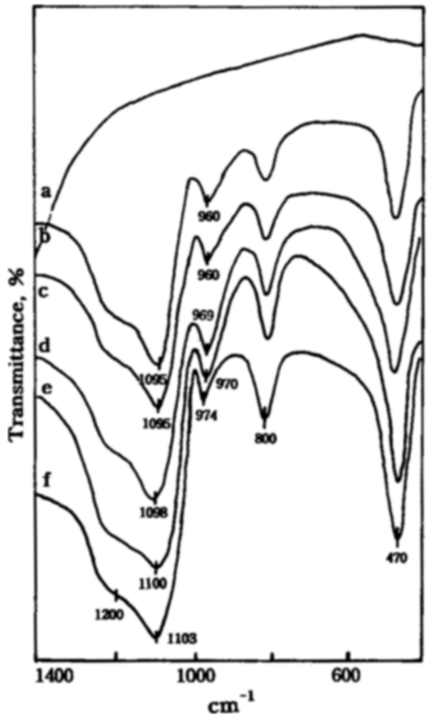

Fig. 1. Infrared spectra of CaO-SiO$_2$ series of catalysts calcined at 400 °C; (a) CaO, (b) 60-CaO-SiO$_2$, (c) 50-CaO-SiO$_2$, (d) 33-CaO-SiO$_2$, (e) 10-CaO-SiO$_2$, (f) SiO$_2$.

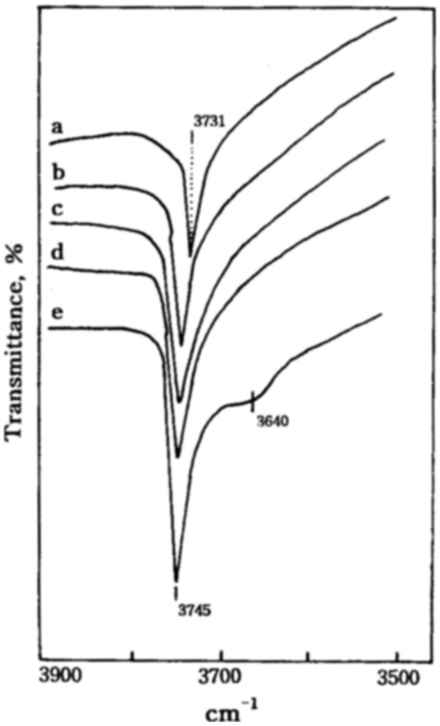

Fig. 2. Infrared spectra in the O-H stretching region of (a) CaO, (b) 50-CaO-SiO$_2$, (c) 33-CaO-SiO$_2$, (d) 10-CaO-SiO$_2$, (e) SiO$_2$.

the position of free silanol groups toward a lower frequency. As shown in Fig. 2, the positions are 3745 cm^{-1} for pure SiO_2, 3742 cm^{-1} for 10-CaO-SiO_2, 3739 cm^{-1} for 33-CaO-SiO_2, 3736 cm^{-1} for 50-CaO-SiO_2, and 3731 cm^{-1} for pure CaO. It is also expected that the weakness of the O-H bond does influences both acidity and acid strength, and acid catalytic activity of the catalyst as will be described below.

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 [Riva et al., 1988; Baiker et al., 1988]. A hypothesis regarding the acidity generation of binary oxides has been proposed by Tanabe et al. [Tanabe et al., 1974]. 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 CaO-SiO_2 pictured according to Tanabe's hypothesis are illustrated in Fig. 3. The coordination numbers of the positive elements in these binary oxides remain 6 for Ca and 4 for Si when they are mixed. As shown in Fig. 3, however, the coordination number of negative element (oxygen) should be 6 when major component is CaO and that should be 2 when major component is SiO_2. In the case of Fig. 3a, where CaO is the major component oxide, the four positive charges of the silicon atom are distributed to four bonds, while the two negative 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 × 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 SiO_2 is major component as shown in Fig. 3b, the two positive charges of the calcium 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 × 6= − 4 is excess. In this case, Brönsted acidity is assumed to appear, because four protons are considered to associate with six oxygens to keep electric neutrality. In both case, CaO-SiO_2 is expected to show acidic property because of the excess of a positive or negative charge.

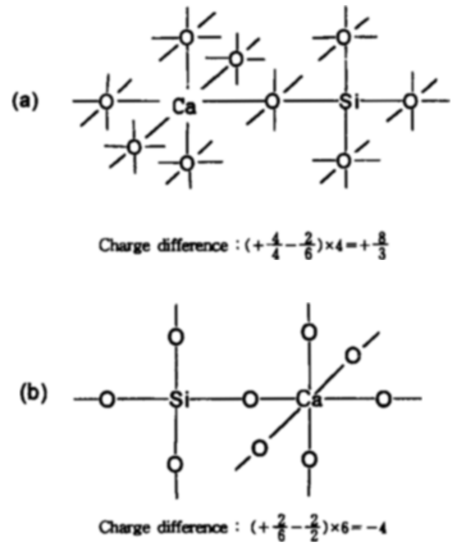

Fig. 3. Model structure of CaO-SiO_2 pictured according to Tanabe's postulates (a) when CaO is major oxide, (b) when SiO_2 is major oxide.

2. Surface Properties of Catalysts

The surface areas of CaO-SiO_2 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 SiO_2 to CaO. That is, the more silica content the catalysts have, the larger surface area they show. This suggests that SiO_2 has more effect on the surface area than CaO.

Acid strength of the catalysts was examined by color change method using Hammett indicator [Hammett and Deyrup, 1932], 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. CaO prepared by calcining calcium hydroxide at 400 °C has been known to be a typical basic oxide, while SiO_2 had very weak acid strength of $H_0 \leq +3.3$ [Miura et al., 1969]. However, as shown in Table 2, 20-CaO-SiO_2 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 CaO-SiO_2 also had the same acid strength of $H_0 \leq -5.6$ as 20-CaO-SiO_2.

Infrared spectroscopic studies of pyridine adsorbed on solid surfaces have made it possible to distinguish between Brönsted and Lewis acid sites [Parry, 1963]. Fig. 4 shows the infrared spectra of pyridine adsorbed on 10-CaO-SiO_2 and 60-CaO-SiO_2 evacuated at 400 °C for 1.5 hr. The coordinated pyridine band at 1447 cm^{-1} and the pyridinium ion band at 1542 cm^{-1} are found with 10-CaO-SiO_2, where major component is SiO_2. It is clear that the new Lewis and Brönsted acid sites which are not present on single CaO and SiO_2 are formed by mixing CaO with SiO_2. However, the coordinated pyridine band at 1447 cm^{-1} is found with 60-CaO-SiO_2, where CaO is major component oxide, indicating the presence of only Lewis acid site. These results are in good agreement with those of acid model structures (Fig. 3) suggested by Tanabe et al. [Tanabe et al., 1974].

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	50-CaO-SiO_2	287
5-CaO-SiO_2	367	60-CaO-SiO_2	279
10-CaO-SiO_2	342	75-CaO-SiO_2	261
20-CaO-SiO_2	322	90-CaO-SiO_2	219
33-CaO-SiO_2	314	CaO	102

Table 2. Acid strength of catalysts

Hammett indicator	pKa of indicator	SiO_2	20-CaO-SiO_2
Dimethylacetone	+3.3	+	+
Dicinnamalacetone	− 3.0	-	+
Benzolacetophenone	− 5.6	-	+
Antraquinone	− 8.2	-	-
m-Nitrotoluene	− 11.99	-	-

The acidity of catalysts, as determined by the amount of NH$_3$ irreversibly adsorbed at 230 °C to remove the physically adsorbed NH$_3$, is plotted as a function of the calcium oxide content in Fig. 5. Although single component, SiO$_2$ showed little acidity, mixing of the two component, CaO and SiO$_2$ resulted in remarkable increase in acidity. As shown in Fig. 5, the acidity increases gradually upon the addition of CaO to SiO$_2$ reaching a maximum at 50-CaO-SiO$_2$. This is not due to the increase of specific surface area, because in the view of Table 1 and Fig. 5 there is no correlation between specific surface area and acidity. These results are correlated with those of IR O-H and Si-O band shifts of silanol group to lower frequencies upon the addition of CaO to SiO$_2$ 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 [Tanabe et al., 1974]. The combination of CaO and SiO$_2$ generated the stronger acid sites and the more acidity as compared with the single components.

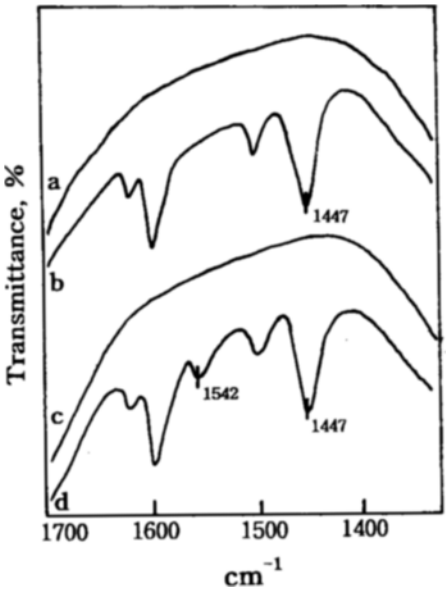

Fig. 4. Infrared spectra of pyridine adsorbed on 60-CaO-SiO$_2$ and 10-CaO-SiO$_2$; (a) background of 60-CaO-SiO$_2$; (b) pyridine adsorbed on 60-CaO-SiO$_2$; (c) background of 10-CaO-SiO$_2$; (d) pyridine adsorbed on 10-CaO-SiO$_2$, gas phase was evacuated at 250 °C for 1 hr after adsorption in (b) and (d).

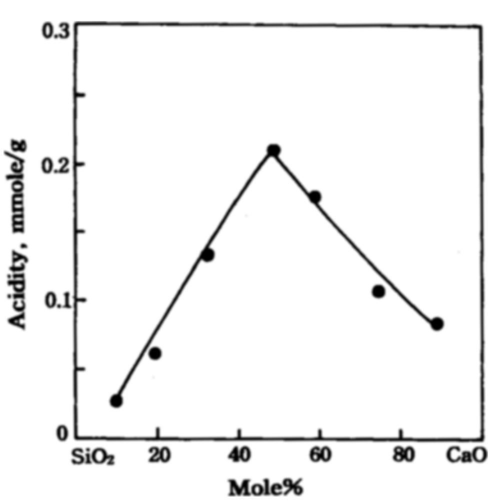

Fig. 5. Acidity of catalysts as a function of CaO content.

3. 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 CaO content in Fig. 6, where the reaction temperatures were 180 °C and 200 °C. In view of Figs. 5 and 6, the variations in catalytic activities of CaO-SiO$_2$ 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 SiO$_2$-Al$_2$O$_3$ catalysts were found to increase with increasing acidity [Tanabe, 1970].

Catalytic activities for cumene dealkylation against CaO content are represented in Fig. 7, where the reaction temperatures were 400 °C and 450 °C. In view of Figs. 5 and 7, the catalytic activities are also correlated with the acidity of catalysts. However, comparing Figs. 6 and 7, the catalytic activity for cumene

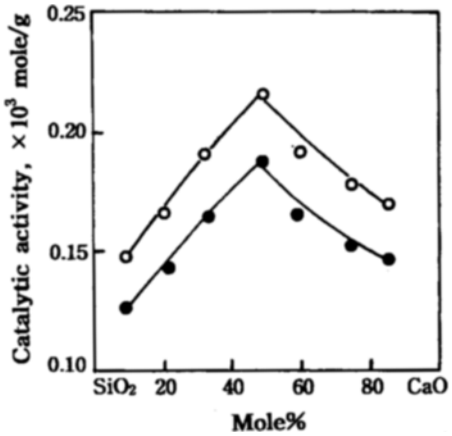

Fig. 6. Variations of catalytic activity for 2-propanol dehydration with CaO content at the reaction temperature of 180 °C (●) and 200 °C (○).

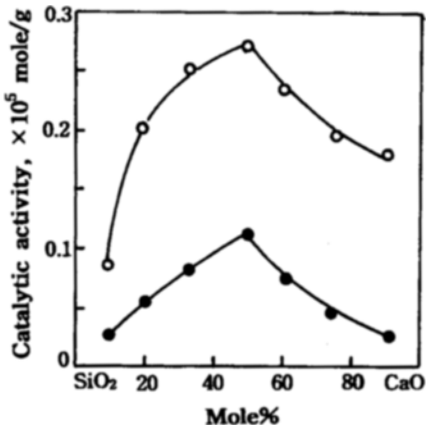

Fig. 7. Variations of catalytic activity for cumene dealkylation with CaO content at the reaction temperature of 400 °C (●) and 450 °C (○).

Table 3. Si-O stretching frequency, acidity, and catalytic activity of $CaO-SiO_2$ series catalysts

Catalyst	Si-O stretching frequency (cm^{-1})	Acidity (mmol/g)	Catalytic activity	
			2-propanol dehydration at 200 °C $\times 10^3$ mol/g	Cumene dealkylation at 450 °C $\times 10^5$ mol/g
60-$CaO-SiO_2$	960	0.17	0.19	0.23
50-$CaO-SiO_2$	960	0.22	0.22	0.27
33-$CaO-SiO_2$	969	0.13	0.19	0.25
10-$CaO-SiO_2$	970	0.03	0.14	0.08
SiO_2	974	0	0	0

dealkylation is much lower than that for 2-propanol dehydration. This result may be attributed to the fact that $CaO-SiO_2$ catalysts have a small number of relatively strong acid sites necessary for cumene dealkylation, while the number of weak acid sites necessary for 2-propanol dehydration is relatively abundant.

In view of Figs. 1, 2, 5, 6 and 7, it is clear that for $CaO-SiO_2$ catalysts the addition of CaO to SiO_2 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, as listed in Table 3. Consequently, catalytic activities for both reactions increased in relation to the increase of acidity and the band shift to a lower frequency. It seems likely that the addition of CaO to SiO_2 produces new acid sites by weakening the O-H bond of the silanol group as described in the results of IR. The acid strength required to catalyze acid reaction is different depending on the type of reactions. In fact, it has been known that 2-propanol dehydration takes place very readily on weak acids, while cumene dealkylation does so on relatively moderate acid sites [Decanio et al., 1986]. As seen in Figs. 6 and 7, the catalytic activity for cumene dealkylation, in spite of higher reaction temperature, is much lower than that for 2-propanol dehydration.

CONCLUSIONS

A series of catalysts, $CaO-SiO_2$ with different compositions were prepared by a coprecipitation method, and the following facts are demonstrated in this work. The addition of CaO to SiO_2 gave rise to the formation of new acid sites stronger than those of single oxide components and caused shifts in the O-H and Si-O streching bands of silanol group to lower frequencies in proportion to the CaO content up to 50 mole%. These band shifts were correlated with both acidity and catalytic activities for 2-propanol dehydration and cumene dealkylation reactions. The acid structure of $CaO-SiO_2$ agreed with that proposed by Tanabe et al.

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