Acidic and Catalytic Properties of Modified Silica Catalyst with Benzenesulfo Groups

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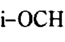
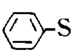
Two types of new silica catalysts modified with benzenesulfonic acid derivatives were prepared by esterification or phenylation followed by sulfonation. Both catalysts thus prepared were tested as acid catalysts for 2-propanol dehydration and cumene dealkylation reactions. B catalyst (> Si--SO_3H) were more active than A catalyst (> Si-OCH_2--SO_3H). Higher catalytic activity for B catalyst may be accounted for by higher resistance to water, higher acid strength, more acidity, and better thermal stability as compared with A catalyst.

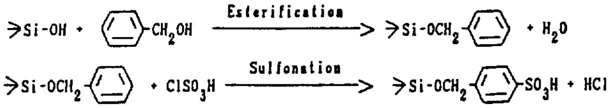
Introduction

Amorphous silica and surface reactions are of interest for a variety of reasons. Silica is empolyed as a filler for plastics and rubbers[1-3], and it serves as a catalyst suppor[4-6]. Silica surfaces are usually covered with a layer of OH groups and adsorbed H_2O. Heating at elevated temperatures removes most of this layer, but some OH groups are retained very tenaciously[7-10]. Substitution of other groups for the OH groups is often sought to modify adsorptive and catalytic properties of silica.

A heterogeneous catalyst can be readily separated from the reaction mixture by simple means. This ease of separation gives heterogeneous catalysts a great advantages over homogeneous catalysts. So, many attempts to immobilize catalytically active species on inorganic supports have been made, as some examples are listed in references[11-17]. Acid-catalyzed reactions are the most important reactions involved in the rearrangement and conversion of hydrocarbons. Ionexchanged resin catalysts having benzenesulfo group are known to exhibit relatively high catalytic activity and selectivity for acid-catalyzed reactions at lower reaction temperature[18, 19]. However, with resin catalysts there are some disadvantages of weak thermal stability and weak mechanical strength except a swelling property[20]. The present work is concerned with the preparation of new silica catalysts modified with benzenesulfonic acid derivatives and their acidic and catalytic properties.

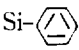
Experimental

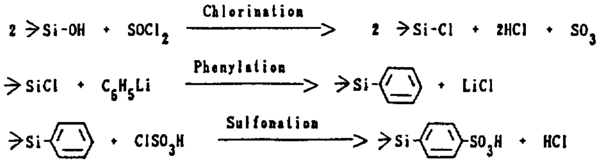
Preparation of Catalysts. Two types of modified silica catalysts with benzenesulfo groups were prepared. A catalyst (>Si-OCH_2--SO_3H): 10g of silica gel (Davision 952 grade) was added to the mixture of 20g of phenylmethanol and 40g of tetradecane, and was refluxed under stirring for 5 hr. Then the sample was filtered and washed benzene and acetone. The esterified sample was added to the mixture of 16 m*l* of chlorosufonic acid and 60 m*l* of chloroform, and was refluxed under stirring for 3 hr[21]. The final catalyst thus prepared was filtered, washed with chloroform, and dried at 50 °C. The reactions are as follows.



(1)

(2)

B catalyst (>Si--SO_3H): 10g of silica gel was added to the mixture of 250g of benzene and 80 m*l* of thionyl chloride, and was chlorinated by refluxing under stirring of 3 hr. The silica thus chlorinated was phenylated by adding 350 m*l* of 0.5 M phenyllithium solution (in the mixture of cyclohexane and diethyl ether) drop by drop to the sample followed by heating at 40 °C under stirring for 1 hr[22]. Then the sample was filtered, washed with methanol and acetone, and dried at 50 °C. The phenylated sample was sulfonated by the same procedure as A catalyst. The reactions are as follows.



(3)

(4)

(5)

Procedure. Catalytic activities were measured in a pulse-type microreactor constructed of 1/4 in. stainless steel. The reactor was packed with quartz chips which both positioned the catalyst sample near an external thermocouple and served as a preheating stage for the reactant gas. The catalyst were activated by heating them under flowing N_2 gas for 1 hr at 100 °C followed by 1 hr at 200 °C. Pluses of 1 μ*l* reactant were injected into a N_2 gas stream which passed over 0.01~0.1g catalyst at 15 m*l*/min. The amount of catalyst was chosen so as to obtain conversions less than 10%. During the 2-propanol dehydration reaction a Diethyleneglycol Succinate on Shimalite column at 150 °C was employed, while for the cumene dealkylation reaction a Bentone 34 on Chromosorb W column at 130 °C was used. Conversion were taken as the average of the first to the sixth pulse value. Catalystic activity was represented as micromoles or millimoles of reactant converted per gram of

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Table 1. Specific Surface Area and Acidity

Catalyst	Surface area (m^2/g)	Acidity	
		Before water treatment	After water treatment
A	190	0.26	0.16
B	184	0.50	0.49

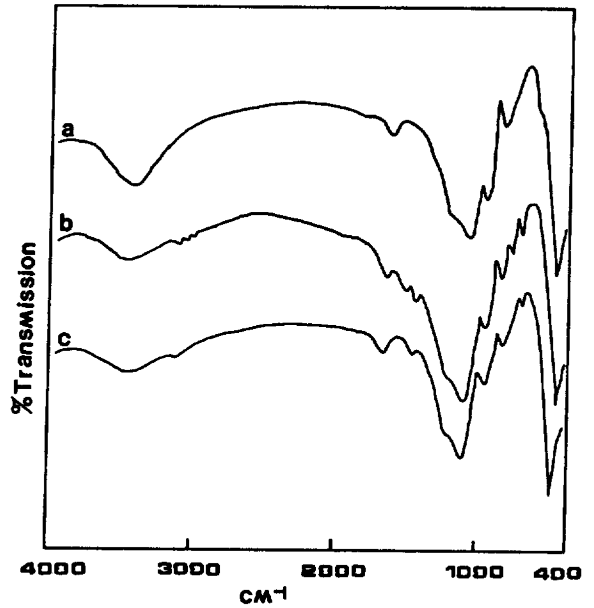

Figure 1. Infrared spectra of silica gel and modified silica catalysts: (a) original silica gel (b) >Si-OCH$_2$-⌬-SO$_3$H catalyst (c) >Si-⌬-SO$_3$H catalyst.

catalyst.

The infrared spectra were recorded on a Bruker FTIR spectrometer in the range of 4000~400 cm^{-1} at room temperature. Catalyst was mixed with KBr and pressed into a disk (600 kg/cm^2). The thermal analysis was carried out in argon atmosphere with Dupont 2100 thermal analyzer, where heating rate was 10 °C/min. The specific surface area was determined by applying BET method to the adsortion of nitrogen at -196 °C. Chemisorption of ammonia was empolyed as a measure of acidity of catalysts. The amount of chemisorption was obtained as an irreversible adsorption of ammonia[23]. 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 areas are listed in Table 1 together with acidity.

Results and Discussion

Infrared spectroscopy was employed to identify the modified silica catalyst with benezensulfo group. Infrared spectra of silica and two prepared catalysts are shown in Figure 1. The bands at 1200, 1100, and 800 cm^{-1} are characteristic bands of SiO$_2$ assigned to Si-O stretching vibrations, while the bands at 950 and 470 cm^{-1} are assigned to the bending vibrations of surface silanol and Si-O, respectively[24]. A catalyst exhibits the 3030, 2960~2850, 1495~1420, 750 and 700 cm^{-1} bands which are attributed to the aromatic ring and methylene group.[25] Absorptions at 1495 and 700 cm^{-1} are caused by the C-H bending vibrations of methylene group and benzene ring, respectively, whil that at 1420 cm^{-1} is caused by C=C skeletal in-plane vibration of benzene ring. B catalyst exhibits 1420 and 700 cm^{-1} bands which are attributed to >Si-⌬. Absorptions at 1420 and 700 cm^{-1} are caused by C=C skeletal in-plane and C-H bending vibrations of benzene ring, respectively. For both catalysts, the intensity of a 950 cm^{-1} band corresponding to the surface silanol of silica decreased slightly as compared with that of original silica. So we presume that the surface silanols were phenylated or esterified, and for B catalyst the surface phenyl group was bonded directly to silicon atom on silica. It is reported that S-O stretching vibrations of sulfo group appear in the region of 1400~1300 and 1200~1100 cm^{-1},[26]. However, it was difficult to observe these bands due to the overlaps with those of skeletal vibrations of silica as shown in Figure 1.

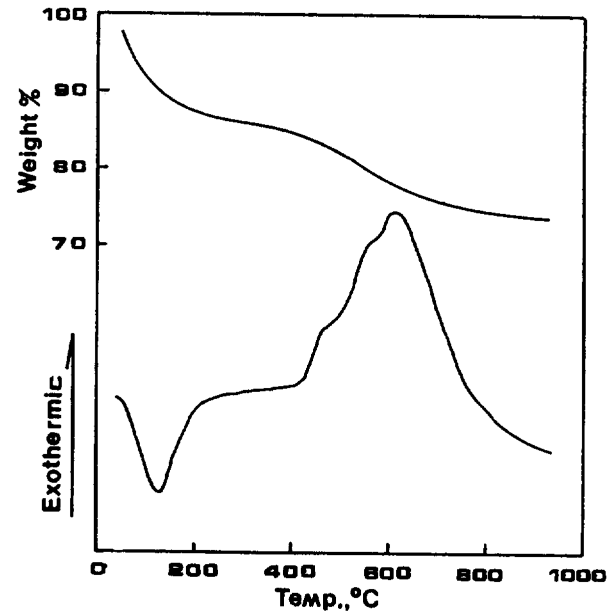

Figure 2. DTA and TGA curves of A catalyst

To examine the thermal properties of modified silica catalysts, their thermal analysis was carried out and illustrated in Figure 2 and 3. For both A and B catalysts, a maximum of endothermic peak appeared at about 120 °C. It seems that the peak in the range of 60~200 °C is attributed to the removal of physically adsorbed water. Based on the TGA curves shown in Figure 2 and 3, the amount of water adsorbed on the surface of catalysts was estimated to be 15~20 wt%. For A catalyst, the exothermic peak began to appear at 430 °C, showing the overlaps of three peaks as illustrated in Figure 2. These exothermic peaks are responsible for the decomposition of benzyl sulfonic acid bonded to silica surface and the concomitant formation of several new chemical species.

For B catalyst, on the other hand, the exothermic peak began to appear at 530 °C indicating that the thermal stability of B catalyst is better than that of A catalyst. That is, the

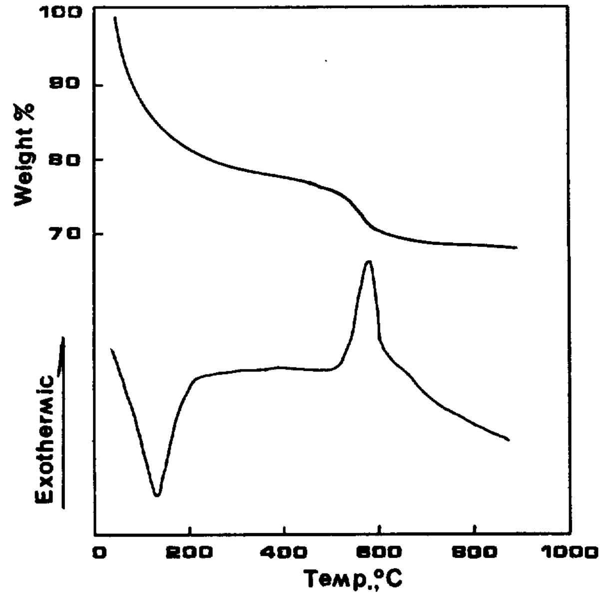

Figure 3. DTA and TGA curves of B catalyst

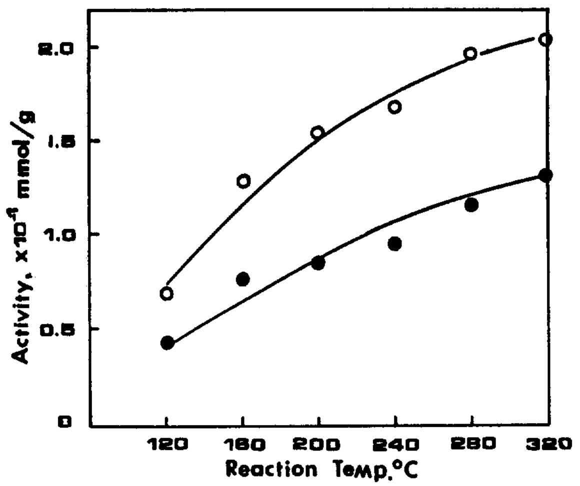

Figure 4. Catalytic activity of A catalyst for 2-propanol dehydration against reaction temperature: ○ ; before water treatment ● ; after water treatment.

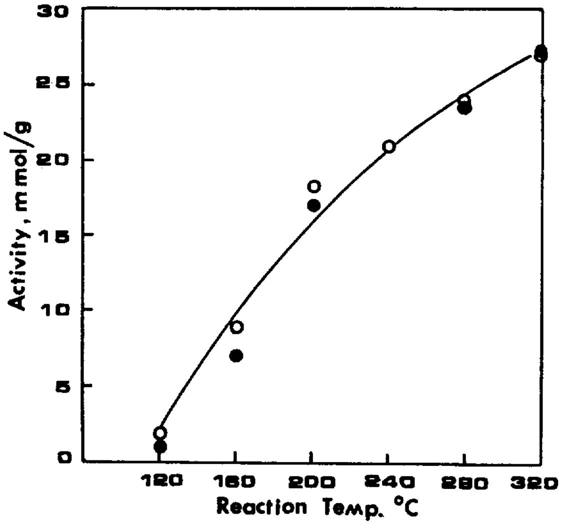

Figure 5. Catalytic activity of B catalyst for 2-propanol dehydration agains reaction temperature: ○ ; before water treatment ● ; after water treatment.

thermal stability of B catalyst is as high as 100 °C than A catalyst. As mentioned above, for B catalyst the surface phenyl group was bonded directly to silicon atom on silica, while for A catalyst benzyl group was bonded to oxygen atom of silanol on silica surface.

At this point, it is necessary to relate the decomposition temperatures of catalysts to bond energies. For A catalyst, the bond energies of Si-O and O-C were estimated to be 128 and 91 Kcal/mol, respectively[27]. Therefore, it is considred that the decomposition of A catalyst occurs through the fission of O-C bond. On the other hand, the bond energy of Si-C (alkyl group was estimated to be 89 Kcal/mol[27]. However, the bond energy of Si-C (benzene ring) in B catalyst seems to be greater than that of Si-C (alkyl group) because the bond of Si-C (benzene ring) has some character of double bond. Although we don't know the value of Si-C (benzene ring) bond energy exactly, it is guessed that on the basis of DTA results, the bond energy of Si-C (benzene ring) is greater than that of Si-C (91 Kcal/mol).

The two catalysts prepared were tested as acid catalysts for 2-propanol dehydration and cumene dealkylation reactions. Catalytic activity for 2-propanol dehydration was plotted as a function of reaction temperature in Figure 4 and 5. Both catalysts were effective for 2-propanol dehydration and the catalytic activities increased with the reaction temperature. However, it is known that the silica sample such as A catalyst prepared by the esterification with alcohol is weakiy resistant to water due to hydrolysis, whille B catalyst whose surface silicon atoms are bonded directly with the benzene ring is very resistant to water[25]. So we examined the effect of water treatment on the catalytic activity. In Figure 4 and 5, open circles and indicate the catalytic activities of original catalysts before water treatment, while black circules represent those of catalysts treated with water at 25 °C for 24 hr followed by drying at 100 °C for 12 hr. As expected, in the case of A catalyst, te catalytic activity afer water treatment decreased because the number of acid site decreased due to hydrolysis. In fact, the acidity of A catalyst after water treatment decreased to the extent of 38% as listed in Table 1. However, we could not observe the effect of water vapor produced during 2-propanol dehydration reaction on the catalytic activity, although the catalytic activities of A and B catalysts decreased slightly with the number of injection pulse due to carbon formation.

On the other hand, B catalyst was very resistant to water and consequently both catalytic activity and acidity was nearly retained as original even after water treatment (Figure 5 and Table 1). Moreover, in view of Figure 4 and 5, B catalyst is about 100 times as active as A catalyst. Higher catalytic activity for B catalyst may be accounted for by higher resistance to water, higher acid strength, and more acidity as compared with A catalyst. Acidity of B catalyst is twice that of A catalyst as shown in Table 1. It is considered that there are two factors for the explanation of less acidity of A catalyst than B catalyst. The first factor is that A catalyst has less acidity originally because of hydrolysis during catalyst preparation. The second one is that the acid strength of A

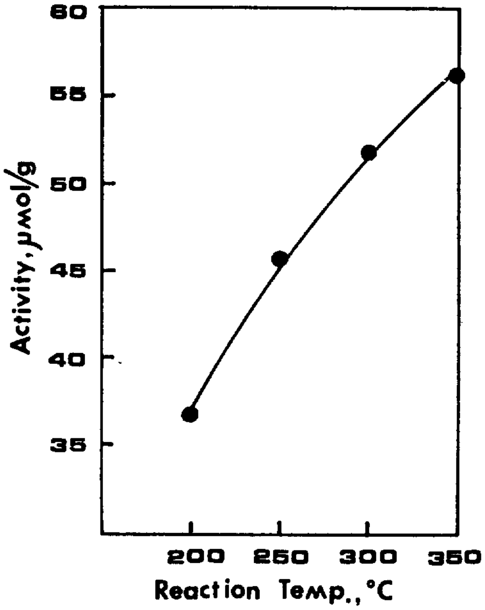

Figure 6. Catalytic activity of B catalyst for cumene dealkylation against reaction temperature.

catalyst is weaker than that of B catalyst as seen later. Namely, since acidity is the amount of ammonia chemisorbed on the ctalyst after evacuation at 230 °C, there is a possibility that A catalyst with weak acid strength has less acidity as compared with B catalyst with strong acid strength. Alcohol dehydration takes place very readily even on the weak acid sites, while cumene dealkylation requires acid sites of moderate strength[28]. Actually, A catalyst exhibited very low activity for cumene dealkylation, while B catalyst was active for the same reaction as shown in Figure 6. Therefore, it is clear that the acid strength of B catalyst is considerably stronger than that of A catalyst.

Conclusions

Two types of modified catalysts with benzenesulfo groups were effective for 2-propanol dehydration and cumene dealkylation reactions. However, for B catalyst of which phenyl group was bonded to silicon atom on silica, thermal stability, resistance to water, catalytic activity, and acid strength were superior to A catalyst prepared by esterification with phenylmethanol.

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