

Catalytic and Acidic Properties of TiO_2 - SiO_2 Unmodified and Modified with H_2SO_4

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TiO_2 - SiO_2 및 H_2SO_4 으로 개질된 TiO_2 - SiO_2 의 촉매특성과 산 성질

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Abstract : A series of TiO_2 - SiO_2 catalysts were prepared by coprecipitation from the mixed solution of titanium tetrachloride and sodium silicate. Some of the samples were treated with 1N H_2SO_4 and used as modified catalysts. The catalytic activities of modified catalysts were higher than those of unmodified catalysts, and the effect of modification on the catalytic activity was higher for 2 - propanol dehydration than for cumene dealkylation. The catalytic activity of unmodified catalysts was correlated with their acid amount for the above two reactions. As TiO_2 - SiO_2 catalysts had relatively large amount of weak acid sites and small amount of strong acid sites, the catalytic activity for 2 - propanol dehydration was higher than that for cumene dealkylation. The effect of modification on catalytic activity increased with increasing TiO_2 content of the catalysts. Actually, 92 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$ had the highest increment in catalytic activity and 10 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$ had the lowest increment for the 2 - propanol dehydration.

요 약

일련의 TiO_2 - SiO_2 촉매를 TiCl_4 와 Na_2SiO_3 혼합용액을 공침전시켜 제조하였으며 이중 일부의 촉매는 1N H_2SO_4 로 처리하여 촉매표면을 개질하였다. 개질된 촉매의 촉매활성은 개질 안된 촉매보다 높은 촉매활성을 나타내었으며 cumene dealkylation 반응에서 보다 2 - propanol dehydration 반응에서 더욱 효과가 크게 나타났다. 개질 안된 촉매의 상기 두 반응에 대한 촉매활성은 산의 양과 관계가 있었다. TiO_2 - SiO_2 촉매는 비교적 많은 양의 약한 산자리와 작은 양의 강한 산자리를 가졌기 때문에 cumene dealkylation 반응에서 보다 2 - propanol dealkylation 반응에 더 높은 촉매활성을 나타내었다. 촉매활성에 미치는 H_2SO_4 의 개질효과는 TiO_2 함량에 비례하였으며 92 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$ 가 2 - propanol dealkylation 반응에 가장 큰 촉매활성의 증가를 나타내었다.

1. INTRODUCTION

Recently, many kinds of mixed oxides were reported to show acidic property on the surfaces. Metal oxide which is inactive or slightly active by itself induces a high catalytic activity by the addition of other oxide. Silica - alumina and silica - zirconia catalysts may be cited as an example of this phenomenon[1,7]. The activity of $ZrO_2 - SiO_2$ catalyst was directly proportional to the number of acid centers on the surface [8]. The combination of TiO_2 and SiO_2 generated very strong acid sites and showed high catalytic activity and selectivity for the amination of phenol with ammonia to produce aniline[9]. The properties of these coprecipitated $TiO_2 - SiO_2$ gels have also been reported[10,11].

Acid catalyzed reaction is correlated with acid amount and acid strength. In cumene dealkylation the more acidity the catalysts have the higher catalytic activity they show[12,13]. On the other hand, tert-butanol dehydration takes place on relatively weaker acid sites, while skeletal isomerization of isobutylene requires exceedingly strong acid sites[14]. Thus to have more acidity and stronger acid strength, single or binary oxide catalysts are modified with sulfuric acid in many cases[15,26]. 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[22,24,27].

In this work, the catalytic activities of $TiO_2 - SiO_2$ series catalysts prepared by coprecipitation method and their correlations to the acidic properties have been studied. Also the catalytic activities of $TiO_2 - SiO_2$ modified with H_2SO_4 are compared in detail with those of unmodified catalysts.

2. EXPERIMENTAL

2. 1. Catalysts

The coprecipitate of $Ti(OH)_4 - Si(OH)_4$ was obtained by adding aqueous ammonia slowly into the mixed

aqueous solution of titanium tetrachloride and sodium silicate solution at room temperature with stirring until the pH of the mother liquor reached 8. The ratio of titanium tetrachloride 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 precipitate was powdered below 100 mesh and was used as catalyst after calcination at $350^\circ C$ for 1.5hr. To obtain the modified catalysts 2g of each dried precipitate was treated with each 30ml of 1N sulfuric acid followed by drying the sample in air as described elsewhere[24,27]. The dried solid powders were used as modified catalysts after calcination at $400^\circ C$ for 1.5hr. All the catalysts prepared are tabulated in table 1 together with their surface area. The catalysts are denoted by following a mole percentage of TiO_2 . For example, 92 - $TiO_2 - SiO_2$ means the catalysts having 92 mol% of TiO_2 and 92 - $TiO_2 - SiO_2/SO_4^{2-}$ means 92 - $TiO_2 - SiO_2$ catalyst modified with 1N H_2SO_4 .

2. 2. Procedure

2-Propanol dehydration was carried out at $180^\circ C$ in a pulse micro-reactor connected with gaschromatography. Fresh catalyst in the reactor made of 1/4 in. stainless steel was pretreated at $400^\circ C$ for 1hr in the nitrogen atmosphere. Diethyleneglycol succinate on Simalite was used as packing material of gaschromatography and the column temperature was $180^\circ C$ for analyzing the product. Catalytic activity for 2-propanol dehydration was represented as μ moles of propylene converted from 2-propanol per surface area. Cumene dealkylation was carried out at $400^\circ C$ in the same reactor as above. Packing material of gaschromatography was Bentone 34 on Chromosorb W and column temperature was $150^\circ C$. Catalytic activity for cumene dealkylation was represented as μ moles of converted benzene per surface area.

The acid amount and acid strength of catalyst were measured quantitatively and qualitatively, respectively, 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. Acid amount was determined by the amount of n - butylamine which was dropped into the catalyst steeped in dry benzene until the color of indicator adsorbed on catalyst disappeared.

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 taken by Rigaku model 2125D2 using copper target and nikel filter at 30kV and 1000 cps. X - ray photoelectron spectroscopy was performed on Hitachi 507 photoelectron spectrometer equipped with cylindrical mirror analyzer using Al anode (9kV, 50mA). Binding energies were calculated in reference to the C_{1s} level at 285.0 eV.

3. RESULTS AND DISCUSSION

3. 1. Physical properties of catalysts

To examine the effect of sulfate ion on the surface and catalytic properties of modified catalysts, various physical properties, specific surface area, infrared spectra, crystalline structure, and oxidation state of sulfur were investigated. The specific surface areas of prepared catalysts are listed in Table 1. The more silica content the catalysts had, the larger surface area they showed. Modified catalysts had smaller specific surface area than unmodified catalysts except for the catalyst having low content of SiO₂ such as 92 - TiO₂ - SiO₂ and TiO₂. This suggests that SiO₂ has more effect on the surface area than TiO₂. Fig. 1 gives the infrared spectra of 92 - TiO₂ - SiO₂ and 92 - TiO₂ - SiO₂/SO₄²⁻ showed infrared absorption bands at 1200, 1130, 1060 and 990 cm⁻¹ which were assigned to bidentate sulfate ion coordinated to the metal such as Ti⁴⁺ and Si⁴⁺ [28]. Strong absorption bands of sulfate ion still remained even after evacuation at 400°C, indicating a very strong interaction between the sulfate ion

Table 1. Specific Surface Areas of Catalysts Calcined at 400 °C

Catalyst	Surface area(m ² /g)
SiO ₂	361.9
10 - TiO ₂ - SiO ₂	550.7
17 - TiO ₂ - SiO ₂	518.6
23 - TiO ₂ - SiO ₂	487.0
37 - TiO ₂ - SiO ₂	485.9
53 - TiO ₂ - SiO ₂	372.7
73 - TiO ₂ - SiO ₂	338.5
87 - TiO ₂ - SiO ₂	156.1
92 - TiO ₂ - SiO ₂	134.5
TiO ₂	96.6
TiO /SO ₄ ²⁻	174.0
10 - TiO ₂ - SiO ₂ /SO ₄ ²⁻	474.8
23 - TiO ₂ - SiO ₂ /SO ₄ ²⁻	425.1
53 - TiO ₂ - SiO ₂ /SO ₄ ²⁻	320.1
73 - TiO ₂ - SiO ₂ /SO ₄ ²⁻	267.7
92 - TiO ₂ - SiO ₂ /SO ₄ ²⁻	194.4
SiO ₂ /SO ₄ ²⁻	269.0

and metal.

For the samples modified with H₂SO₄ followed by calcination at 400°C, based on infrared spectra results, the sulfur is considered to reach the highest oxidation state, S⁺⁶ of SO₄²⁻. However, the oxidation state of sulfur varies with the reduction - oxidation process [27]. To obtain further information on the oxidation state of sulfur, X - ray photoelectron spectroscopic investigation was performed. Fig. 2 shows the X - ray photoelectron spectra for the TiO₂/SO₄²⁻ and 92 - TiO₂ - SiO₂/SO₄²⁻. As expected, both samples give the signal attributed to S⁺⁶ [27], suggesting that the oxidation state of sulfur as SO₄²⁻ is the main species. The S_{2p} binding energy of S⁺⁶ was 168.8eV [27,29], calculated in reference to the C_{1s} binding energy of 285.0eV.

The crystalline structures of catalysts were checked by X - ray diffraction. Fig. 3 represents the X - ray diffraction patterns of 92 - TiO₂ - SiO₂ catalyst calcined in air at different temperature for 1.5 hr. At 400°C

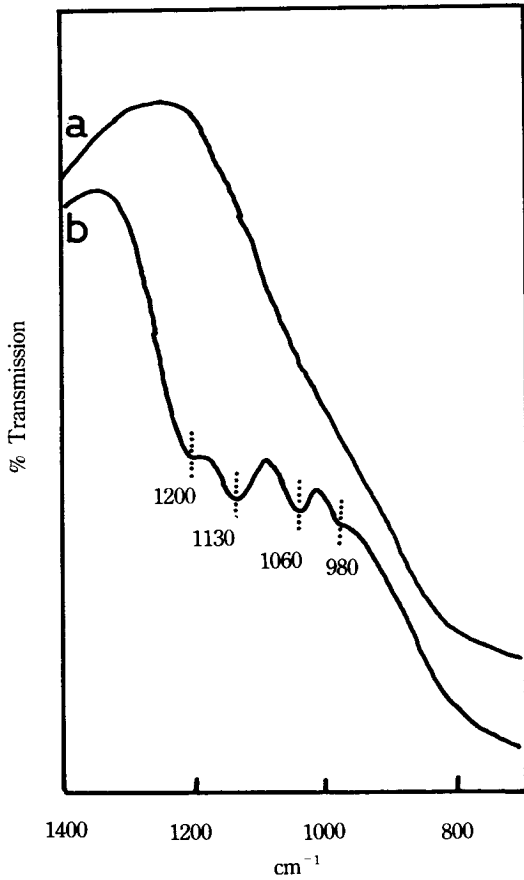


Fig. 1. Infrared spectra of (a) 92 - TiO_2 - SiO_2 and (b) 92 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$.

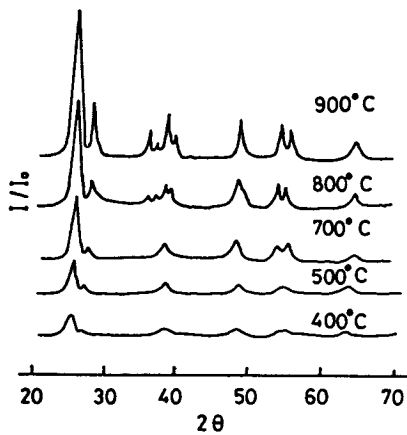


Fig. 3. X - ray diffraction patterns of 92 - TiO_2 - SiO_2 calcined at different temperatures for 1.5hr.

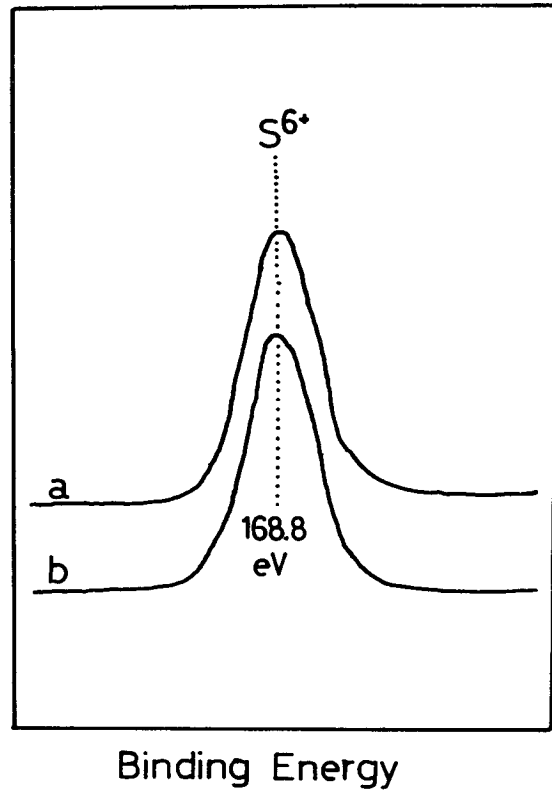


Fig. 2. Sulfur XPS spectra of (a) $\text{TiO}_2/\text{SO}_4^{2-}$ and (b) 73 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$.

of calcination temperature, anatase form of TiO_2 was observed with tiny amount of rutile form of TiO_2 . However, the amount of both anatase and rutile increased with increase of calcination temperature up to 900°C , and the relative amount of anatase to rutile was quite high at 900°C . On the other hand, in the case of 92 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$, there was only anatase at 400°C , but small amount of rutile was observable at 500°C , as shown in Fig. 4. However, the increase of amount of anatase and rutile with the calcination temperature was similar to that of 92 - TiO_2 - SiO_2 . For TiO_2 and $\text{TiO}_2/\text{SO}_4^{2-}$, catalysts changed completely from anatase to rutile at 900°C unlike binary oxide catalysts of 92 - TiO_2 - SiO_2 . It seems that the presence of amorphous silica or the modification with

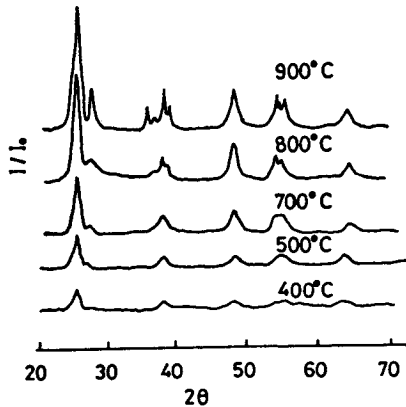


Fig. 4. X - ray diffraction patterns of 92 - TiO₂ - SiO₂ /SO₄²⁻ calcined at different temperatures for 1.5hr.

H₂SO₄ retards the transition from anatase to rutile.

3. 2. Amount of acid

The acid amount(acidity) of TiO₂ - SiO₂ and TiO₂ - SiO₂/SO₄²⁻ series catalysts after evacuation at 400 °C for 1hr was determined by the amine titration method at H₀ = -3.0, where H₀ is hammett acidity function[30]. Fig. 5 shows the acid amount of both series catalysts. The used indicator was dicinnamalacetone of H₀ = -3.0 and acid amount was expressed as μeq/m² of used catalyst. Although single component, SiO₂ showed little acidity, mixing of the two component, TiO₂ and SiO₂ resulted in remarkable increase in acidity. This increase was not caused only by increase in surface area. As shown in Fig. 5, the acidity increases gradually upon the addition of TiO₂ to SiO₂ reaching a maximum at 73 - TiO₂ - SiO₂. Many kinds of combinations of two oxides were reported to generate acid sites on the surface[8,9]. The combination of TiO₂ and SiO₂ generated the stronger acid sites and the more acid amount than in the case of single component. The mechanism of the generation of acid sites by mixing of two oxides has been proposed by Tanabe et al[9]. They explained that the acidity generation is caused by an excess of a negative or positive

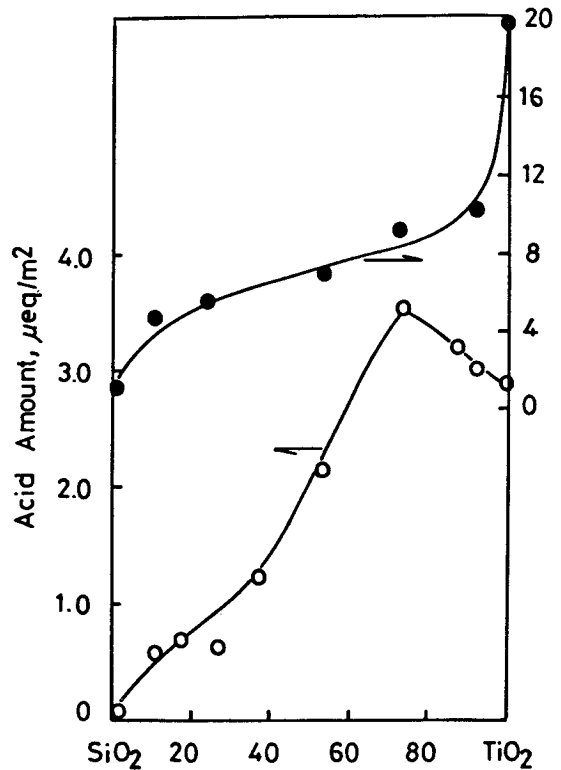


Fig. 5. Acid amount of catalysts as a function of TiO₂ content : ○, unmodified catalyst ; ●, modified catalyst.

charge in a model structure of a binary oxide related to the coordination number of a positive element. Moreover, the modified catalysts had much more acid amount than the unmodified catalysts. These results mean that the weak acid sites of unmodified catalysts are converted into strong acid sites by means of modifying the sample with H₂SO₄. On the other hand, it is necessary to examine the acid amount with pK_a value, which tells which site of particular acid strength is more effective for acid catalyzed reactions. Fig. 6 shows the acid amount of 73 - TiO₂ - SiO₂ with pK_a value. This catalyst had small amount of strong acid sites and relatively large amount of weak acid sites.

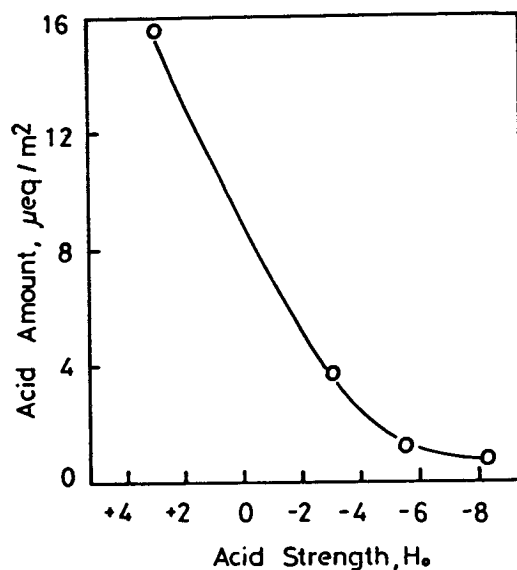


Fig. 6. Acid amount against acid strength for 73 - TiO_2 - SiO_2 catalyst.

3. 3. Acid strength

Acid strength of the catalyst was examined by color change method using Hammett indicator[30], when an indicator was added to the powdered sample 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. TiO_2 prepared by evacuating titanium hydroxide at 400°C had acid

strength of $H_0 \leq -3.0$, while SiO_2 had very weak acid strength of $H_0 \leq +3.3$ [31]. However, as shown in Table 2, 73 - TiO_2 - SiO_2 prepared by coprecipitation was estimated to be $H_0 \leq -8.2$, indicating the formation of new acid sites stronger than those of single oxide components. The other binary oxides with different molar ratio of $\text{TiO}_2/\text{SiO}_2$ also had the same acid strength of $H_0 \leq -8.2$ as 73 - TiO_2 - SiO_2 . The acid strength of $\text{SiO}_2/\text{SO}_4^{2-}$ was estimated to be $H_0 \leq -5.6$, and that of $\text{TiO}_2/\text{SO}_4^{2-}$ and 73 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$ was $H_0 \leq -14.5$. The increase of acid strength in the modified catalysts is attributed to the double bond nature of $\text{S}=\text{O}$ which strengthen the acid sites by the inductive effect[24].

3. 4. Infrared spectra of adsorbed pyridine

Infrared spectroscopic studies of pyridine adsorbed on solid surfaces have made it possible to distinguish between Brønstead and Lewis acid sites[32]. Fig. 7 shows the infrared spectra of pyridine adsorbed on 92 - TiO_2 - SiO_2 and 92 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$. Both the pyridinium ion band at 1543cm^{-1} and the coordinated pyridine band at 1445cm^{-1} are found with the catalysts evacuated at 400°C for 1hr, indicating the presence of both Brønstead and Lewis acid sites. Spectrum c shows the changes which occur upon the modification of catalyst with H_2SO_4 . The increases in both 1543 and 1445cm^{-1} bands indicate that a considerable

Table 2. Acid strength of catalysts

Hammett indicator	pKa value of indicator	SiO_2	$\text{SiO}_2/\text{SO}_4^{2-}$	TiO_2	$\text{TiO}_2/\text{SO}_4^{2-}$	73 - TiO_2 - SiO_2	73 - TiO_2 - $\text{SiO}_2/\text{SO}_4^{2-}$
dimethyl yellow	+ 3.3	+	+	+	+	+	+
dicinnamal-acetone	- 3.0	-	+	+	+	+	+
benzalaceto-phenone	- 5.6	-	+	-	+	+	+
antraquinone	- 8.2	-	-	-	+	+	+
nitrobenzene	- 12.4	-	-	-	+	-	+
2,4-dinitro-fluorobenzene	- 14.5	-	-	-	+	-	+

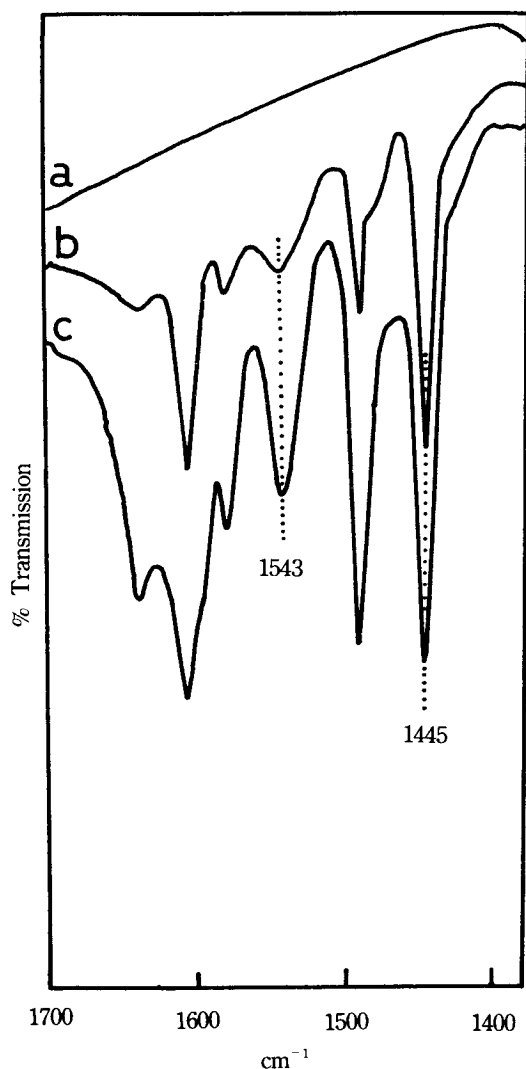


Fig. 7. Infrared spectra of pyridine adsorbed on 92 - TiO₂ - SiO₂ : (a) background of 92 - TiO₂ - SiO₂ after evacuation at 400° for 1.5hr ; (b) pyridine adsorbed on 92 - TiO₂ - SiO₂ ; (c) pyridine adsorbed on 92 - TiO₂ - SiO₂/SO₄²⁻, gas phase was evacuated at 250°C for 1hr after adsorption in (b) and (c).

amount of Brönstead and Lewis acid sites have been formed newly by treating with H₂SO₄. With other catalysts similar results were obtained.

3. 5. Catalytic activity and acidic property

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 TiO₂ content in Fig. 8. In view of Fig. 5 and Fig. 8, the variations in catalytic activities of unmodi-

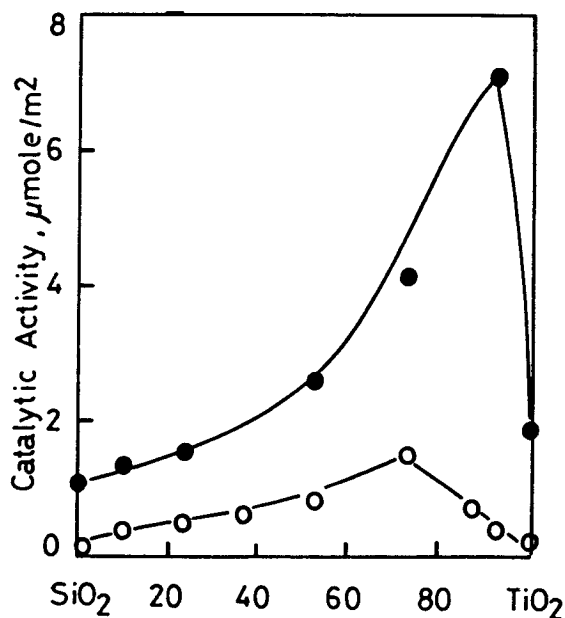


Fig. 8. Variations of catalytic activity for 2 - propanol dehydration with TiO₂ content : ○, unmodified catalyst ; ●, modified catalyst.

fied TiO₂ - SiO₂ catalysts are roughly correlated with the changes of their acid amount. As shown in Fig. 8, the catalysts modified with H₂SO₄ exhibit higher catalytic activity than unmodified catalysts. The modification effect on the catalytic activity was much greater in the catalysts having high TiO₂ content. Actually, the catalytic activity of 92 - TiO₂ - SiO₂/SO₄²⁻ were 20 times as high as 92 - TiO₂ - SiO₂, while 10 - TiO₂ - SiO₂/SO₄²⁻ exhibited only 1.5 times activity. These results suggest that TiO₂ has an effect on the modification more than SiO₂. However, in the case of modified catalysts, the correlation between catalytic activity

and acid amount does not hold good. Although the acidity of $\text{TiO}_2/\text{SO}_4^{2-}$ is the highest, its catalytic activity is relatively low. It has been known that 2-propanol dehydration takes place very readily on weak acid sites[33]. Therefore, it seems that in the case of $\text{TiO}_2/\text{SO}_4^{2-}$ the number of weak acid sites have decreased due to the conversion of weak acid sites into strong acid sites by the modification with H_2SO_4 .

Cumene dealkylation takes place on relatively strong acid sites of the catalysts[33]. Catalytic activities for cumene dealkylation at 400°C against TiO_2 content are represented in Fig. 9. Comparing Fig. 8 and Fig. 9, the catalytic activity for cumene dealkylation is much lower than that for 2-propanol dehydration. This result may be attributed to the fact that TiO_2 - SiO_2 catalysts have small amount of relatively strong acid sites necessary for cumene dealkylation, while the number of weak acid sites necessary for 2-propanol dehydration is relatively abundant. Ho-

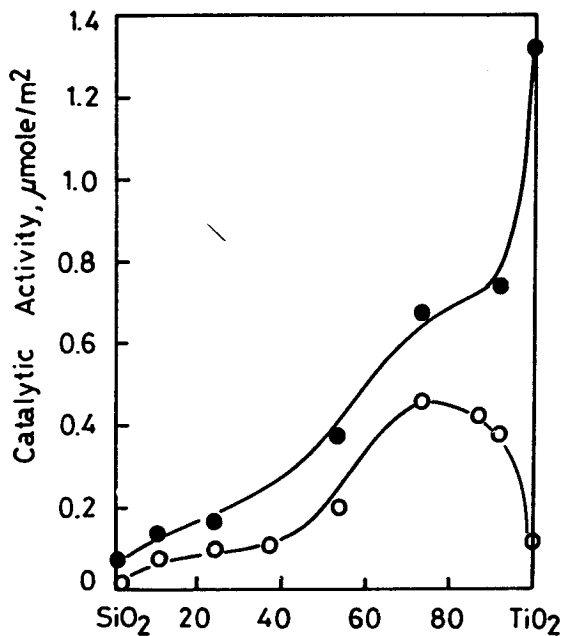


Fig. 9 Variations of catalytic activity for cumene dealkylation with TiO_2 content : ○, unmodified catalyst ; ●, modified catalyst.

wever, regardless of the modification, the catalytic activities are correlated with acid amount of two series catalysts as shown in Fig. 9. The modification effect on catalytic activity also increased with increasing the TiO_2 content of catalysts, showing a maximum effect in single oxide of TiO_2 .

4. CONCLUSION

TiO_2 - SiO_2 series catalysts unmodified and modified with H_2SO_4 have been prepared, and their acid properties and catalysis for 2-propanol dehydration and cumene dealkylation have been observed. The following results are obtained in this work.

- (1) TiO_2 - SiO_2 series catalysts have relatively large amount of weak acid sites and small amount of strong acid sites.
- (2) The catalytic activities of TiO_2 - SiO_2 catalysts for the above two reactions are correlated with the acid amount of the catalysts.
- (3) The modification effect on catalytic activity is higher in 2-propanol dehydration than in cumene dealkylation.
- (4) Modification of the catalyst by treating with H_2SO_4 has increased its catalytic activity in proportion to TiO_2 content.
- (5) $\text{TiO}_2/\text{SO}_4^{2-}$ had much increment in acid strength by modification and its catalytic activity is the highest in cumene dealkylation.

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