

Catalytic Activity and Acidic Property of Silicon Pyrophosphate*

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Abstract

Catalytic activity test was carried out by a pulse reactor over a silicon pyrophosphate catalyst, which was prepared by the reaction of triethyl phosphate and silicon tetrachloride. Acidic property, X-ray pattern and infrared spectrum of catalyst sample were measured to characterize the catalyst structure. In the cracking of cumene 80.8% of conversion to benzene was obtained over the silicon pyrophosphate catalyst, while a commercial solid phosphoric acid catalyst gave a 57.5% conversion under the same reaction conditions.

Introduction

Silicon phosphate has been used as a catalyst for polymerization of olefins,¹ oligomerization of propylene,² hydrocarbon conversion to gasoline,³ dehydration of alcohols,^{4,5} etc. Almost all the silicon phosphates have been prepared from SiO₂ and phosphoric acid, although Gerrard and Jeacocke⁶ reported a novel production of silicon phosphate by using the reaction of triethyl phosphate and silicon tetrachloride in 1959. Little work has been done on the catalytic property of silicon phosphates prepared by the latter method, while some works⁷⁻⁹ have been reported on the catalytic property of those prepared by the former method. It is well known that the catalytic activity of a catalyst is closely related to its preparation method. The present paper reports the acidic property and catalytic activity of silicon pyrophosphate formed from triethyl phosphate and silicon tetrachloride.

Experimental

Catalysts: Silicon pyrophosphate was prepared by a modification of the Gerrard and Jeacocke⁶ method. A mixture of triethyl phosphate (73 g-0.4 mol) and silicon tetrachloride (34 g-0.2 mol) was kept at 20°C for about 5 hr. Ethyl chloride evolved during the reaction was condensed in a trap at -80°C. The obtained gel was heated at about 90°C for 2 days and then pressed at 1600 kg/cm² into a tablet. Prior to use the catalyst sample was crushed, sieved (16-30 mesh), and calcined at temperatures ranging 400°C to 700°C in air for 3 hr.

Several solid acid catalysts were also used for comparison. The silica-alumina

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and solid phosphoric acid used were N631 (L) and N501, respectively, from Nikki Chemical Co. BPO_4^{10} and AlPO_4 (N-7-W)¹¹ were prepared as reported previously.

Measurements.

Acid Strength and Surface Area: The acid strengths of the catalysts were measured by the conventional indicator method using dicinnamalacetone ($\text{pK}_a = -3.0$), benzalacetophenone ($\text{pK}_a = -5.6$), and anthraquinone ($\text{pK}_a = -8.2$). Surface areas were determined by applying the BET method to the adsorption isotherm of nitrogen at -196°C .

X-Ray Diffraction: The powder pattern of each specimen was obtained with a Rigaku X-ray diffractometer, using $\text{CuK}\alpha$ radiation.

Infrared: A Shimadzu IR27G infrared spectrophotometer was used. Samples were measured in a 200 mg KBr disk containing 0.5% of the sample.

Catalytic Activity: The cracking of cumene, which was selected as a model reaction, was carried out at 400°C using a microcatalytic pulse reactor. In every run 0.10 g of catalyst was used. The amount of each pulse was $2\mu\text{l}$, hydrogen being used as a carrier gas (flow rate: 46 ml/min). Effluent products were directly introduced into a gas chromatographic column for analysis.

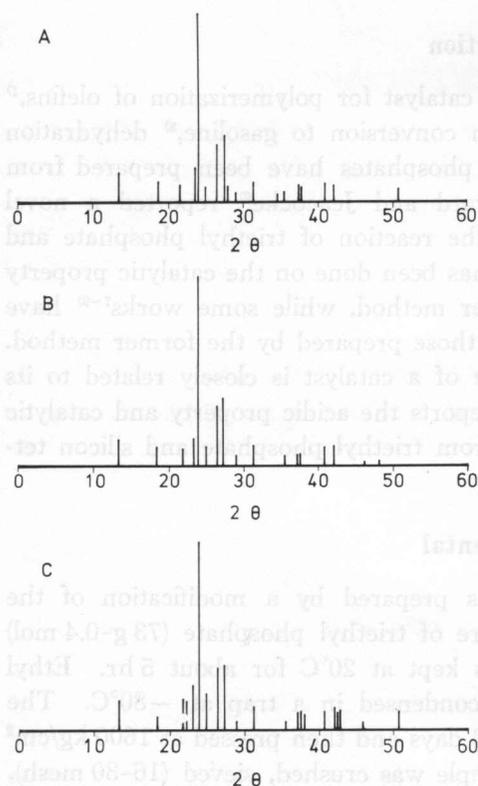


Fig. 1. Powder X-ray diffraction patterns of silicon pyrophosphate sample calcined at various temperatures.

Calcined at

A: 750°C , B: 600°C , C: 400°C .

Results and Discussion

X-Ray Diffraction Patterns: Figure 1 shows the results of the X-ray diffraction analysis of the silicon pyrophosphate

Table 1. Comparison of X-ray diffraction pattern of silicon pyrophosphate sample calcined at 400°C with that of $\text{SiP}_2\text{O}_7^{\text{a}}$

Sample			SiP_2O_7	
2θ	I	I/I_1	2θ	I/I_1
13.4	4.0	18	13.6	60
22.1	3.5	16	18.7	30
22.4	3.5	16		
23.3	5.0	22		
23.9	22.3	100	23.9	100
25.1	4.0	18		
26.6	7.4	33	26.7	80
27.4	8.0	36	27.5	80

a) Ref. 12.

catalysts calcined at various temperatures. The diffraction lines at $2\theta=23.9^\circ$, 26.5° , and 27.3° agree almost entirely with those of powder diffraction file No. 17-577¹²⁾ and indicate that each specimen is essentially a single phase of SiP_2O_7 . In Table 1 the diffraction data of the catalyst calcined at 400°C are compared with those of SiP_2O_7 .

Infrared Spectrum: According to Corbridge and Lowe¹³⁾ four absorption bands at $1170\text{--}1060\text{ cm}^{-1}$, $1045\text{--}970\text{ cm}^{-1}$, $940\text{--}870\text{ cm}^{-1}$, and $735\text{--}690\text{ cm}^{-1}$ are usually found in the spectra of pyrophosphates, and similar absorptions in roughly the same regions with the additional bands at $1400\text{--}1200\text{ cm}^{-1}$ are produced by acid pyrophosphates. Figure 2 shows infrared spectrum of the silicon pyrophosphate calcined at 620°C . The spectrum seems to have almost all the characteristic of a pyrophosphate. The absorption at 1280 cm^{-1} might imply that the sample contain small amount of acid pyrophosphate.

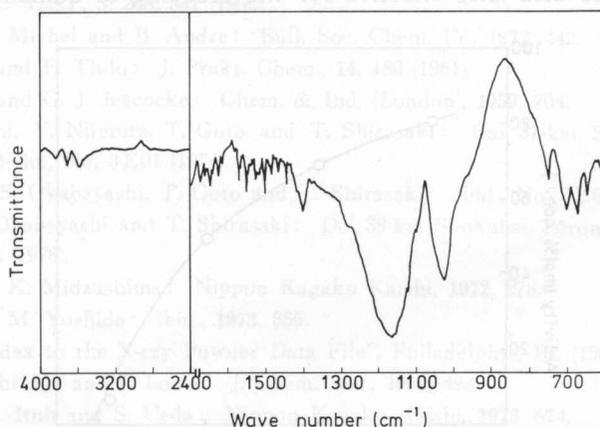


Fig. 2. Infrared spectrum of silicon pyrophosphate sample calcined at 620°C .

Acid Strength and Surface Area: The calcined silicon pyrophosphate samples were generally colored, and it was difficult to measure their acid amounts by the usual amine titration method. Therefore, only their acid strengths were measured. These results are shown in Table 2 with those of surface area measurements. The samples calcined at $400\text{--}600^\circ\text{C}$ showed an acid strength of $\text{p}K_a \leq -5.6$, which was never observed in ZrP_2O_7 ¹⁴⁾.

Table 2. Surface area and acid strength of silicon pyrophosphate sample calcined at various temperatures

Calcination temperature ($^\circ\text{C}$)	Surface area (m^2/g)	Acid Strength ($\text{p}K_a$)
400	20.2	≤ -5.6
500	23.4	≤ -5.6
600	22.5	≤ -5.6
700	15.4	≤ -3.0

Catalytic Activity: Since the silicon pyrophosphate samples were found to show strong acidity, their catalytic activity was tested for the cracking of cumene. The main products arising from the reaction on the silicon pyrophosphate catalysts were benzene and propylene. The effect of calcination temperature on the conversion percent of cumene is shown in Figure 3. Comparing Fig. 3 with Table 2, no correlation is found between the activity and the surface area. Thus the change of the activity with calcination is not attributed to that of the surface area. It is reported that ZrP_2O_7 having no acid sites at $pK_a \leq -5.6$ does not exhibit any activity in the cracking of cumene.¹⁴⁾ A similar phenomenon was observed in the case of the silicon pyrophosphate calcined at 700°C. These facts suggest that the active sites for the cracking of cumene are the acid sites which have the acid strength of $pK_a \leq -5.6$ under the reaction conditions given above. The activity change shown in Fig. 3 would be caused by the change of the acid sites effective for the cracking of cumene.

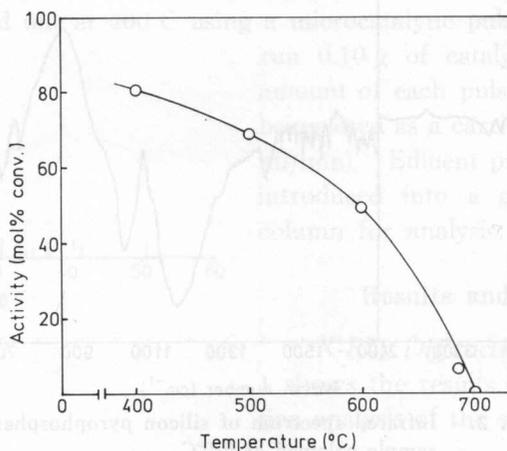


Fig. 3. Dependence of cumene cracking activity on calcination temperature.

The catalytic properties of the silicon pyrophosphate catalyst calcined at 400°C are compared with those of several solid acid catalysts in Table 3. The catalytic activity of the former catalyst was inferior to that of silica-alumina which has acid strength of $pK_a \leq -8.2$. However, it is worthy to note that

Table 3. Catalytic properties of several solid acid catalysts

Catalyst	Calcination temperature (°C)	Surface area (m ² /g)	Acid strength (pK _a)	Conversion (%)
SiP ₂ O ₇	400	20.2	≤ -5.6	80.8
BPO ₄	400	20.6	≤ -5.6	12.1
AlPO ₄	400	217	≤ -5.6	0
Silica-Alumina	500	510	≤ -8.2	100
Solid phosphoric acid	400	0.8	≤ -5.6	57.5

the former exhibits not only higher activity than BPO_4 or AlPO_4 which is the well known phosphate catalyst, but higher activity than a commercial solid phosphoric acid catalyst. AlPO_4 calcined at 400°C did not show any catalytic activity, although it has a similar acid strength to BPO_4 or solid phosphoric acid. In view of the fact that Brönsted (B) sites are responsible for cumene cracking activity,¹⁵⁾ the AlPO_4 is presumed to have predominantly Lewis (L) sites. On the other hand, the high activity of the silicon pyrophosphate suggests that its acid sites consist of only B sites or both L and B sites, with the former probably in predominance.

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