

Si-substituted $\text{AlPO}_4\text{-5}$ by Silanation with SiCl_4

V. R. Choudhary,* M. Y. Pandit, and S. D. Sansare

Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India

Reaction of gaseous SiCl_4 with crystalline molecular sieve $\text{AlPO}_4\text{-5}$ at 300–600 °C has given Si-substituted $\text{AlPO}_4\text{-5}$ without significantly affecting its crystal structure.

$\text{AlPO}_4\text{-5}$ belongs to a novel class of crystalline microporous aluminium phosphate phases introduced by Wilson *et al.*¹ More recently Lok *et al.*² have reported the synthesis of SAPO-5, which is a crystalline microporous (channel or pore diameter 0.8 nm) silicon aluminium phosphate of similar structure to $\text{AlPO}_4\text{-5}$ and shows interesting, unique properties of potential use in catalytic, adsorptive, and ion-exchange applications. We report here our initial results on the reaction of gaseous SiCl_4 with $\text{AlPO}_4\text{-5}$ at 300–600 °C, to form $\text{SiAlPO}_4\text{-5}$.

The preparation and characterization of $\text{AlPO}_4\text{-5}$, the evaluation of its acidity and of its adsorptive and catalytic properties, have been described in our earlier papers.^{3,4} The reaction of SiCl_4 with $\text{AlPO}_4\text{-5}$ was carried out in a conventional flow tubular quartz reactor (internal diameter 1 cm) by passing SiCl_4 vapour and nitrogen (moisture-free) over particles (0.15 mm) of $\text{AlPO}_4\text{-5}$ packed between quartz wool plugs, at different temperatures and concentrations of SiCl_4 under atmospheric pressure. The chlorides of Al and P formed in the reaction were absorbed from the reactor effluents in water and quantitatively determined by chemical means. After the reaction, the resulting silicon aluminium phosphate was heated in a flow of pure nitrogen ($50 \text{ cm}^3 \text{ min}^{-1}$) at 500 °C for 2 h to remove traces of adsorbed chlorides of Al and P. The acidity of the silicon aluminium phosphate samples was determined by measuring the chemisorption of pyridine at 400 °C using a g.c. pulse technique.⁵ The catalytic activities/selectivities of the silicon aluminium phosphate in iso-octane cracking, *o*-xylene isomerization, and ethanol-to-aromatics conversion reactions have been determined in a pulse micro-reactor³ (internal diameter 4 mm) connected to a gas chromatograph using the following conditions: catalyst, 0.1 g; N_2 flow rate, $60 \text{ cm}^3 \text{ min}^{-1}$; temperature, 400 °C; pressure, 180 kPa; and pulse size, 2.0 μl . Figure 1 shows how the replacement of Al by Si depends on temperature and pressure. Both Al and P are replaced, in the ratio Al : P $\sim 2.6 \pm 0.5 : 1$.

The surface and catalytic properties of the $\text{SiAlPO}_4\text{-5}$ obtained under various conditions are shown in Table 1. The powder X-ray diffraction patterns and surface areas of these

$\text{SiAlPO}_4\text{-5}$ samples are very similar to those of the parent $\text{AlPO}_4\text{-5}$. These facts indicate that the crystal structure of $\text{AlPO}_4\text{-5}$ remained intact during its reaction with SiCl_4 , even at 600 °C. The increase in the catalytic activity of the $\text{SiAlPO}_4\text{-5}$ in the cracking of iso-octane, *o*-xylene isomerization, and the formation of aromatics in the ethanol conversion reaction, is consistent with the increase in strong acid sites created by the SiCl_4 treatment of the $\text{AlPO}_4\text{-5}$. Figure 2 shows

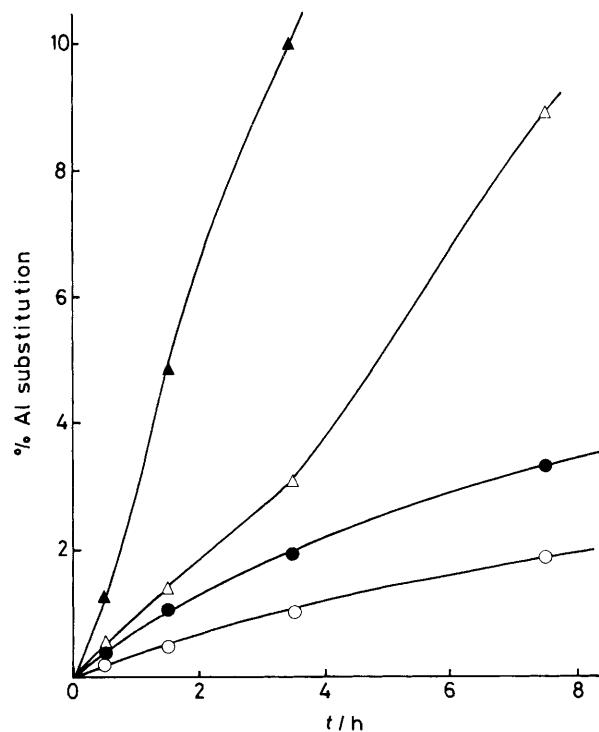


Figure 1. Substitution of Al by Si in $\text{AlPO}_4\text{-5}$ by reaction with SiCl_4 . \circ 300 °C; \bullet 400 °C; \triangle 500 °C [$P(\text{SiCl}_4)$ 65 torr; GHSV, 5590 h^{-1}]; \blacktriangle 500 °C [$P(\text{SiCl}_4)$ 160 torr; GHSV 2270 h^{-1}]. 1 Torr = 133.322 Pa.

Table 1. Surface and catalytic properties of $\text{SiAlPO}_4\text{-5}$ obtained by treating $\text{AlPO}_4\text{-5}$ with SiCl_4 at different conditions

Reaction conditions				<i>o</i> -Xylene isomerization					
<i>T</i> / °C	Partial pressure <i>P</i> (SiCl_4)/torr	GHSV ^a / h^{-1}	Reaction time/ h	Surface area/ $\text{m}^2 \text{ g}^{-1}$	Strong acid sites/ mmol g^{-1}	Conversion of iso-octane/ %	Conversion of <i>o</i> -xylene/ %	Selectivity for <i>p</i> - and <i>m</i> -xylene/%	Concn. of aromatics ^b / (wt%)
				312	<0.01	<1.0	12.6	79.7	3.7
300	65	5590	8	299	0.04	4.2	29.3	58.3	11.2
400	65	5590	8	293	0.07	4.8	43.7	49.6	20.0
500	65	5590	8	303	0.19	5.0	42.1	52.7	22.1
600	65	5590	8	292	0.25	5.8	44.1	46.4	23.8
500	160	2270	4	294	0.23	5.2	43.3	50.1	25.2
500	290	1120	4	297	0.70	16.4	47.4	53.5	26.6

^a GHSV = gas hourly space velocity at standard temperature and pressure (S.T.P.), *i.e.*, volume of gaseous mixture of SiCl_4 and N_2 per volume of $\text{AlPO}_4\text{-5}$ per h. ^b Concentration of aromatics, formed during ethanol conversion, wt% of total hydrocarbons formed.

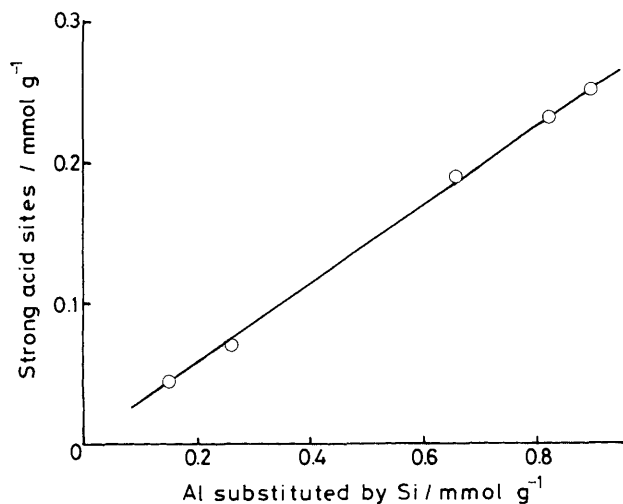


Figure 2. Dependence of strong acid sites created on amount of Al substituted by Si in $\text{AlPO}_4\text{-5}$.

that the strong acid sites (measured in terms of pyridine chemisorbed at 400°C) of the $\text{SiAlPO}_4\text{-5}$ increase almost linearly with the amount of Al substituted by Si in the $\text{AlPO}_4\text{-5}$.

The results thus show that $\text{SiAlPO}_4\text{-5}$ having high acidity and catalytic activity can be obtained from $\text{AlPO}_4\text{-5}$ by reaction with SiCl_4 at $300\text{--}600^\circ\text{C}$, without collapse of the crystal structure. During the silanation, both Al and P in $\text{AlPO}_4\text{-5}$ are partly substituted by Si.

Received, 28th November 1988; Com. 8/04702B

References

- 1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146; *ACS Symp. Ser.*, 1983, **218**, 79.
- 2 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.*, 1984, **106**, 6092.
- 3 V. R. Choudhary and D. B. Akolekar, *J. Catal.*, 1987, **103**, 115.
- 4 V. R. Choudhary, D. B. Akolekar, A. P. Singh, and S. D. Sansare, *J. Catal.*, 1988, **111**, 23.
- 5 V. R. Choudhary and V. S. Nayak, *Appl. Catal.*, 1982, **4**, 31.