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Generation of acid catalytic activity in Si-VPI-5 by partial Si for P substitution during hydrothermal synthesis

J.A. Martens, H. Geerts, L. Leplat, G. Vanbutsele, P.J. Grobet and P.A. Jacobs

Centrum voor Oppervlaktechemie en Katalyse, KU Leuven, Kard. Mercierlaan 92, B-3001 Heverlee, Belgium

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Si-VPI-5 crystals containing Si atoms in Si(4Al) environments are synthesized. The crystals contain occluded amine. It is protonated and neutralizes the residual negative lattice charges associated with the Si(4Al) sites. Calcined Si-VPI-5 is active in the isomerisation of decane and exhibits extra-large pore characteristics.

Keywords: VPI-5; isomorphic substitution; decane test

1. Introduction

VPI-5 is a family of crystalline aluminophosphate based molecular sieves possessing micropores with 18-membered ring windows [1] and crystallizes from an aluminophosphate gel under hydrothermal conditions [2]. The synthesis can be performed with [2–6] or without [7] addition of organic amines to the gel. Generally, only trace amounts of the organic amines or quaternary ammonium ions used in the synthesis are occluded in the VPI-5 crystals [2–5,8]. In this respect, the behaviour of VPI-5 is different from that of the other microporous crystalline aluminophosphates ($AlPO_4$-n) patented by Lok et al. [9], the micropores of which are filled with organic material after synthesis [10]. In their protonated forms, occluded amines compensate for residual lattice charges, arising e.g. from isomorphic substitution of lattice P atoms by Si [11]. After calcination of a microporous crystalline silicoaluminophosphate (SAPO-n) sample, protons are left in the pores, which render the materials catalytically active [12].

Silicon containing VPI-5 samples have been prepared by Davis et al. using synthesis recipes which do not lead to a substantial incorporation of organic amine [3]. Such Si-VPI-5 crystals were enriched with silicon at their external surface. XPS and ^{29}Si MAS NMR spectra of these samples suggested substitution of Al + P pairs for Si + Si mainly, not generating residual negative framework charges [3]. The catalytic activity of such Si-VPI-5 samples is much lower than that of SAPO-5 and SAPO-11 samples with comparable Si contents [13]. The selectivities observed in the decane test suggest that the activity arises from traces of dense phases and SAPO-11 impurities, present in the samples [13].

An alternative crystallization method used to introduce silicon in the aluminophosphate framework of VPI-5 involves the use of two immiscible liquid phases [14]. In this method, an organosilicon compound is dissolved in the organic solvent and hydrolysed slowly into the aqueous phase, containing aluminium and phosphorus. The MCM-9 materials prepared according to this bisolvent method present a mixture of phases [15], the major one possessing the same framework topology as VPI-5 [15,16]. Di-n-propylamine and silicon are incorporated in the MCM-9 crystallization product [16], but, due to the presence of more than one phase, it is not possible to assign the organic and the silicon to the individual phases present.

A synthesis of VPI-5 crystals with occluded tributylamine was recently realized by Perez et al. [6]. In the present work we successfully adapted this recipe for the synthesis of a Si-VPI-5 sample exhibiting acid catalytic activity and the typical selectivity of very large pore materials.

2. Experimental procedures

For the synthesis of Si-VPI-5, an amount of 13.8 g of pseudoboehmite was slurried in 41 ml water. 23 g of concentrated orthophosphoric acid (85%), diluted in 27.4 ml of water was added dropwise under stirring. This addition was spread over 50 minutes. Subsequently, the mixture was aged first at 95°C during 25 minutes, and subsequently at 20°C during 165 minutes under gentle stirring. Further, 21 g of tributylamine and 3.2 g of dipentylamine were added dropwise under stirring. Finally, 2.9 g of Ludox AS-40 was added at once. The hydrothermal treatment was performed in a stainless steel autoclave at 150°C during 20 h. The solid product was filtered, washed and dried at 20°C. The XRD pattern of the product revealed that a pure VPI-5 phase was obtained.

^{29}Si MAS NMR and ^{13}C CP MAS NMR were performed on a Bruker 400 MSL instrument. ^{29}Si MAS NMR was performed using a pulse length of 4 μs, a pulse angle of 45°, a recycle delay of 5 s, a spinning rate of 3.5 kHz and a number of scans of 17,500. In the ^{13}C CP MAS NMR experiments, the contact time 2.5 ms, the recycle delay 3 s, the spinning rate 4 kHz and the number of scans 44,400.

Thermoanalysis of 50 mg of Si-VPI-5 was done on a SETARAM TG-DTA92 thermobalance in helium atmosphere, using a flow rate of 50 ml per minute and

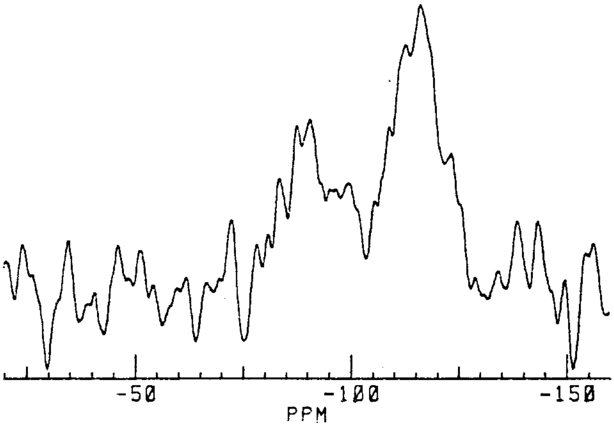

Fig. 1. ^{29}Si MAS NMR spectrum of as-synthesized Si-VPI-5.

a heating rate of 5°C per minute. The infrared spectrum was recorded on a Perkin Elmer 580 B instrument equipped with data station.

Si-VPI-5 was transformed into a bifunctional catalyst by impregnation with a minimum amount of aqueous $Pt(NH_3)_4Cl_2$ solution to obtain a Pt loading of 0.5% by weight and dried in ambient air at 20°C. The sample was further dehydrated during 12 h under high vacuum at a temperature of 20°C, in order to avoid phase transition into $AlPO_4$-8 [17], calcined subsequently in flowing oxygen at 350°C, and reduced in flowing hydrogen at the same temperature. The conversion of decane was performed in a fixed bed tubular microreactor. The H2/decane ratio in the feed was 100, the pressure in the reactor 0.35 MPa and the space time of decane 1.3 kg s $mmol^{-1}$.

3. Results and discussion

The most intense resonances in the ^{29}Si MAS NMR spectrum of Si-VPI-5 have chemical shifts of ca. −90 and −115 ppm, respectively (fig. 1). By analogy to the ^{29}Si MAS NMR spectra of SAPO-5 [11], these signals are assigned to Si(4Al) and Si(4Si) environments, respectively. The presence of Si(4Al) sites confirms that part of the Si atoms occupy P atoms positions of the VPI-5 structure. The low signal to noise ratio remaining at the high number of scans used, indicates that the silicon content of the sample is low.

The ^{13}C CP MAS NMR spectrum of Si-VPI-5 reveals the presence of tributylamine in the sample (fig. 2). The resonances at the chemical shifts of ca. 52, 25, 20 and 12 ppm are ascribed to C_1, C_2, C_3 and C_4 carbon atoms of the tributylamine molecule, but the presence of dipentylamine in the crystallization product is also possible. The resolution in ^{13}C CP MAS NMR is probably too low to distinguish between the protonated and non-protonated form of the

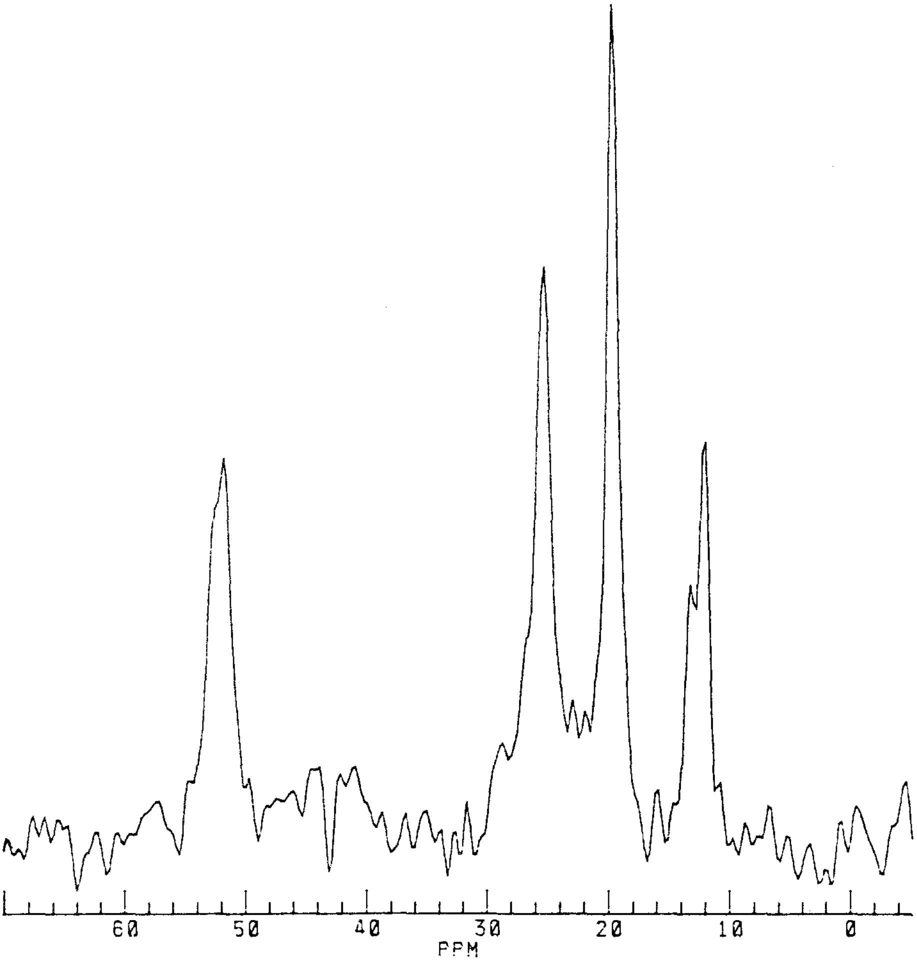

Fig. 2. ^{13}C CP MAS NMR spectrum of as-synthesized Si-VPI-5.

trialkylamine, as was previously found for tripropylamine in ZSM-5 [18,19]. The weight loss (TGA) curve showed a loss of ca. 5% between 150 and 450°C, whereas other VPI-5 samples without occluded amine do not lose weight in this temperature range. The infrared spectrum of the sample outgassed at 200°C is shown in fig. 3. The absorption band at 1430 cm^{-1} is assigned to δNH^+ and consequently to protonated tributylamine. These protonated species probably neutralize the residual lattice charges associated with the generation of Si(4Al) environments.

In the catalytic experiment, products from decane isomerisation, cracking and aromatisation were obtained, depending on the reaction temperature. The yield of isomers from decane on Pt/Si-VPI-5 is plotted in fig. 4 against the reaction temperature and compared with data on Si-VPI-5 samples for which no substan-

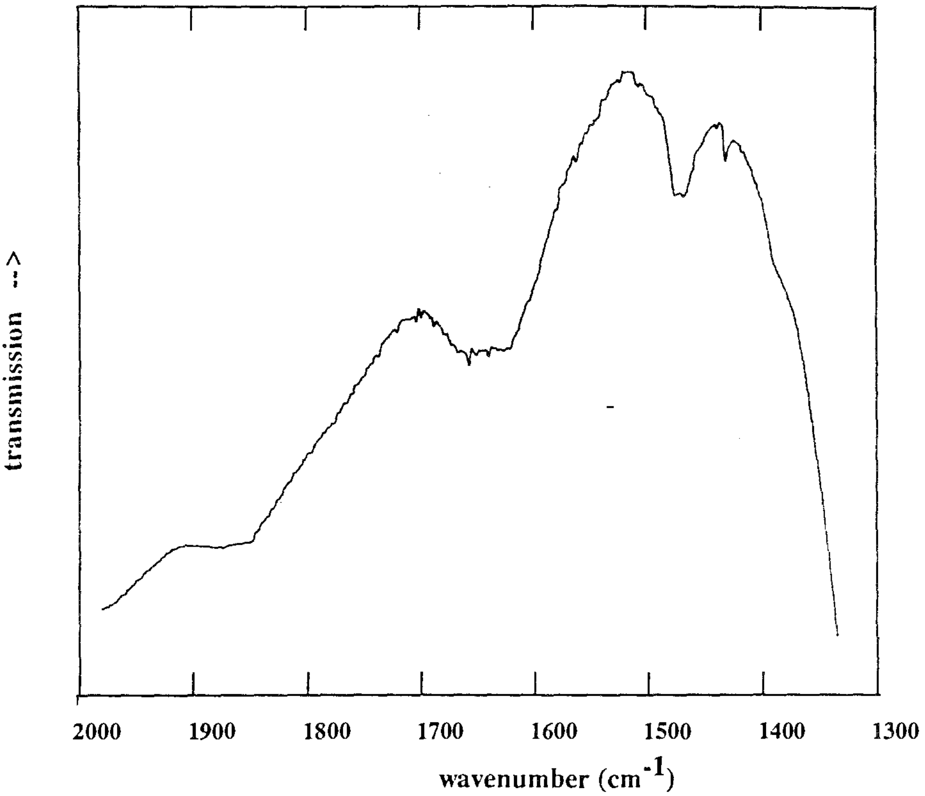

Fig. 3. Infrared spectrum of a self-supporting wafer of Si-VPI-5, outgassed in vacuum (10 mPa) for 30 minutes at 200 °C.

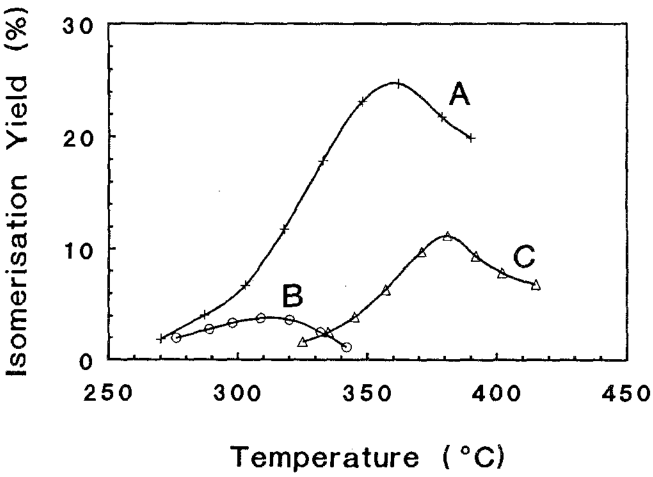

Fig. 4. Yield of isodecanes on Pt/Si-VPI-5 samples. A, Si-VPI-5 sample synthesized with occluded tributylamine; B and C, Si-VPI-5 samples containing only traces of occluded organic after synthesis (B, sample Si-VPI-5(1) and C, sample Si-VPI-5(2) from ref. [13]).

tial amine occlusion occurred during synthesis. The significant improvement of the yield of isodecanes results from a higher concentration of Brønsted acid sites in the sample, since decane isomerisation is catalysed by Brønsted acid sites in the catalyst [20].

The refined constraint index, CI°, is the 2-methylnonane/5-methylnonane product ratio at 5% isomerisation conversion of decane [21]. The CI° value of Si-VPI-5 is 1.3, which classifies the material among the zeolites with pore apertures larger than 0.7 nm [21]. The CI° criterion is not sensitive enough to allow discrimination among pore sizes larger than 0.7 nm.

A second criterion of the decane test is the ethyloctane (EC8) yield in the monobranched isomers at 5% isomerisation yield [22]. This criterion has proven to be very sensitive to the shape and size of 12-membered ring zeolites [22]. The bulky EC8 isomers are formed via voluminous substituted corner-protonated cyclobutane intermediates [23]. On Si-VPI-5, the EC8 content in the monobranched isodecanes is 13.7%. This is among the highest values ever obtained for zeolites. The corresponding EC8 yield on H-Y zeolites is 11.0% [22], increasing to 13.5% when mesopores are generated by dealumination with steam [24]. The EC8 criterion confirms the presence of extra-large pores in Si-VPI-5 under reaction conditions.

4. Conclusions

The synthesis of Si-VPI-5 in the presence of tributylamine and dipentylamine offers new opportunities for isomorphic substitution of P and Al atoms in the framework by low valency elements. In this work we have demonstrated partial Si for P substitution which generates framework acidity. In as-synthesized Si-VPI-5, the negative framework charge associated with Si(4Al) framework environments is neutralised with protonated amine. After calcination, the sample contains Brønsted acid sites which are responsible for its catalytic activity in decane isomerisation. The decane test reveals that under reaction conditions Si-VPI-5 possesses pores which are wider than the pores of faujasites.

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