

Improvement of the hydrothermal stability of SAPO-34†

F. D. P. Mees,^{*a} L. R. M. Martens,^b M. J. G. Janssen,^b A. A. Verberckmoes^b and E. F. Vansant^a^a University of Antwerp (U.I.A.), Department of Chemistry, Universiteitsplein 1, B-2610, Wilrijk, Belgium.

E-mail: Filip.Mees@ua.ac.be

^b ExxonMobil Chemical Europe Inc., Hermeslaan 2, B-1831 Machelen, Belgium

Received (in Cambridge, UK) 23rd October 2002, Accepted 12th November 2002

First published as an Advance Article on the web 22nd November 2002

Hydrothermal stability of SAPO-34 is greatly improved by the treatment of the acidic form of the SAPO-34 with NH_3 .

In 1982 the family of aluminosilicate zeolites was extended by the discovery of the aluminophosphate zeolites.^{1,2} In these crystalline microporous aluminophosphates (AlPO_4 's), the tetrahedral (T) sites are occupied alternately by Al^{3+} and P^{5+} ions. By substituting a Si for a P a negatively charged framework is obtained so that Brønsted acidity can be introduced. Silicon substituted AlPO_4 's are designated SAPO-n where n represents a structure type.³ SAPO-34, which is structurally analogous to the zeolitic mineral chabazite,⁴ is known to be a very powerful catalyst for the MTO-process (methanol-to-olefins), exhibiting high light olefin selectivities.⁵

SAPO-34 can be synthesised with either TEOAH (tetraethylammonium hydroxide) or morpholine as a template. It has been found for the morpholine templated SAPO-34 that, after activation, the catalyst's structure and its acidity deteriorate rapidly and irreversibly during exposure to moisture.⁶ This rapid loss of acidity and structural integrity is a major drawback for their applicability. Since the rational design of superior catalysts is often based on post-synthesis modification techniques, there is a need for template-free, stabilised catalysts.

We report a new method for the stabilisation of hydrothermally unstable SAPO-34, based on the reversible reaction of NH_3 with the acid sites.⁷ It will be shown that the deterioration of the framework and consequently the Brønsted acidity is caused by hydrolysis reactions starting at the acid sites. These hydrolysis reactions are essentially irreversible.⁶ After transforming the acidic form of the SAPO-34 into an NH_4^+ -form, the reaction of H_2O with acid sites is prevented. The interaction of H_2O with other framework atoms appears to be much weaker and is reversible.

SAPO-34 was crystallised in the presence of morpholine as a templating agent, following a procedure described elsewhere.[†] The as-synthesised SAPO-34 was activated in a muffle furnace at 625 °C for 4 h (heating rate: 5 °C min⁻¹) to form an H^+ -SAPO-34. Part of the activated material was transferred in a dynamic gas volumetric adsorption apparatus and reacted with NH_3 at 220 °C leading to an NH_4^+ -SAPO-34. The NH_4^+ -SAPO-34 and the H^+ -SAPO-34 were transferred in stainless steel, Teflon lined autoclaves and steamed at 110 °C under autogenous pressure for 5 to 25 h. The steamed samples were dehydrated in a muffle furnace at 625 °C (heating rate: 5 °C min⁻¹) for 4 h and characterized together with the activated parent sample. During dehydration, NH_3 is simultaneously desorbed from the NH_4^+ -SAPO-34.

The steamed samples were thermogravimetrically analysed. The H^+ -SAPO-34 shows a strong weight loss at 140 °C due to desorption of water. The NH_4^+ -SAPO-34 shows weight losses at 80 °C and at 400 °C attributed to desorption of physisorbed H_2O and chemisorbed NH_3 , respectively. This shift from 140 °C

to 80 °C in the DTG curve already indicates a strongly weakened interaction of the NH_4^+ -SAPO-34 with water. The

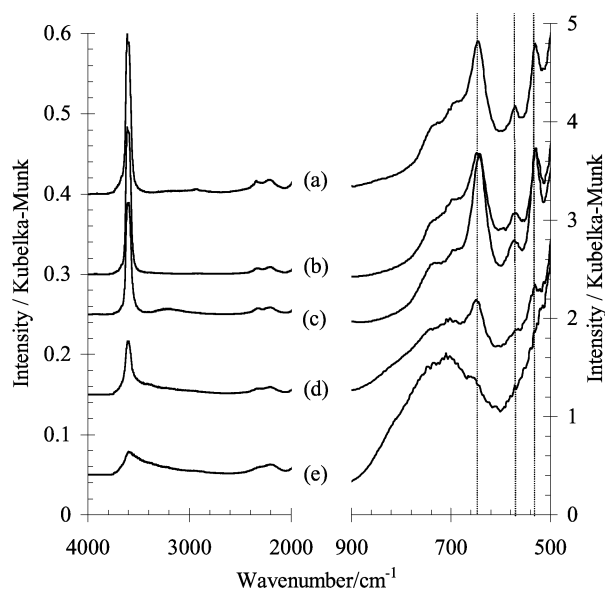


Fig. 1 In situ diffuse reflectance IR spectra of samples (a) fresh H^+ -SAPO-34, (b) and (c) NH_4^+ -SAPO-34 after 5 h and 25 h steaming respectively, (d) and (e) H^+ -SAPO-34 after 5 h and 25 h steaming respectively. The spectra were recorded at 400 °C under vacuum. Prior to recording the spectra, the samples were dehydrated and deammoniated at 625 °C.

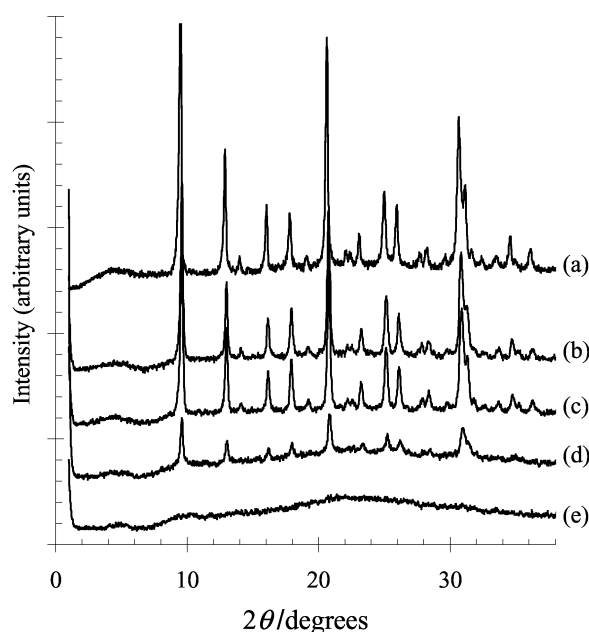


Fig. 2 XRD diffractograms of samples (a) fresh H^+ -SAPO-34, (b) and (c) NH_4^+ -SAPO-34 after 5 h and 25 h steaming respectively, (d) and (e) H^+ -SAPO-34 after 5 h and 25 h steaming respectively.

† Electronic supplementary information (ESI) available: detailed description of the synthesis procedure of SAPO-34. See <http://www.rsc.org/suppdata/cc/b2/b210337k>

desorption of NH_3 at 400 °C indicates that it is possible to regenerate strong acid sites (Brønsted acidity) after the steaming. This is confirmed by infrared spectroscopy (Fig. 1). After dehydration and removal of the NH_3 , the characteristic Brønsted bands at 3600 and 3625 cm^{-1} reappear for the NH_4^+ -SAPO-34. The H^+ -SAPO-34 however lost a large part of the original acidity after only 5 hours of steaming and all of its acidity after 25 h of steaming. In the area of the framework vibrations between 500 and 900 cm^{-1} , strong absorption bands are observed at 535, 573 and 645 cm^{-1} for the fresh H^+ -SAPO-34 and the steamed, dehydrated NH_4^+ -SAPO-34. These bands, however are absent in the spectra of the steamed, dehydrated H^+ -SAPO-34.

Not only the acidity of the fresh H^+ -SAPO-34 is protected by the transformation into an NH_4^+ -SAPO-34, also the crystallinity is preserved during steaming as can be seen in Fig. 2. The X-ray diffractograms show that an unprotected H^+ -SAPO-34 rapidly loses its structure during steaming. The intensity of the

diffraction peaks has diminished severely after only 5 h of steaming and a very broad band appears around $2\theta = 22^\circ$. The NH_4^+ -SAPO-34 however maintains its structural integrity, even after an extended period of steaming. The results from the infrared measurements together with the X-ray diffractograms strongly indicate that the deterioration of the SAPO-34 framework during steaming starts at the acid sites and is essentially irreversible.

These findings are further supported by N_2 -adsorption and desorption measurements (Fig. 3). For the SAPO-34, typical Langmuir type I isotherms are observed. The isotherms of the fresh H^+ -SAPO-34 and of the steamed (25 h), dehydrated NH_4^+ -SAPO-34 are essentially the same, while the steamed, dehydrated H^+ -SAPO-34 has a much lower N_2 -uptake. The micropore volume of the steamed, dehydrated NH_4^+ -SAPO-34, as calculated from De Boer's t-method, is the same as that of the parent sample (0.26 cc g^{-1}). The unprotected H^+ -SAPO-34, however, lost almost all of its micropore volume after 25 h of steaming.

In summary, the results presented here strongly indicate that structural deterioration of H^+ -SAPO-34 during steaming starts on the Brønsted acid sites and is irreversible. Our method transforms the H^+ -SAPO-34 into an NH_4^+ -SAPO-34 in a reversible way. It has been proven that the NH_4^+ -SAPO-34 can withstand severe steaming for an extended period without loss of its structural integrity and acidity. This simple procedure to stabilise SAPO-34 is an important step forward to the commercial applicability of these materials.

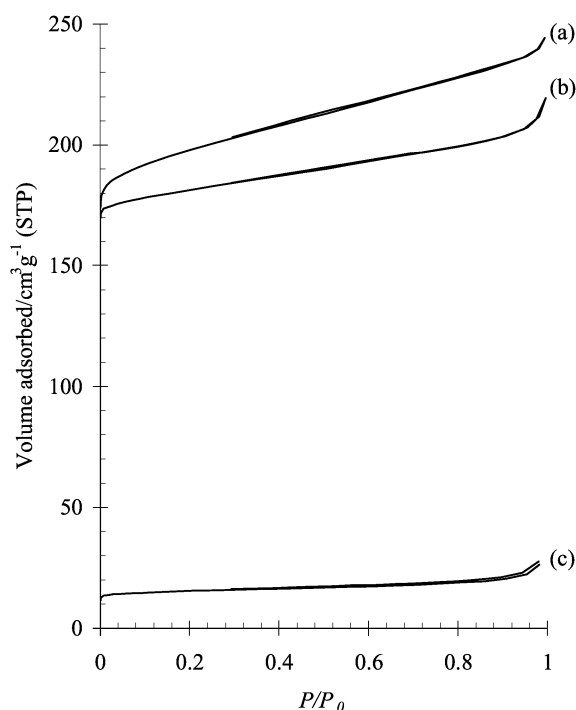


Fig. 3 N_2 sorption isotherms of (a) fresh H^+ -SAPO-34, (b) NH_4^+ -SAPO-34 after 25 h steaming and (c) H^+ -SAPO-34 after 25 h of steaming.

Notes and 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.
- 2 S. T. Wilson, B. M. Lok and E. M. Flanigen, US Patent 4310440, 1982.
- 3 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannon and E. M. Flanigen, US Patent 4440871, 1984.
- 4 M. Ito, Y. Shimoyama and Y. Saito, *Acta Crystallogr.*, 1985, **C41**, 1698.
- 5 S. W. Kaiser, US Patent 4499327, 1983; S. W. Kaiser, US Patent 4677242, 1987; L. Juan, S. Q. Zhao, H. Y. Li, W. G. Guo and M. L. Ying, *Stud. Surf. Sci. Catal.*, 1989, **46**, 59; M. W. Anderson, B. Sulikowski, P. J. Barrie and J. Klinowski, *J. Phys. Chem.*, 1990, **94**, 2730; T. Inui, S. Phatanasri and H. J. Matsuda, *J. Chem. Soc., Chem. Commun.*, 1990, 205.
- 6 M. J. G. Janssen, C. W. M. Van Oorschot, S. C. Fung, L. R. Martens, W. J. Mortier, R. G. Searle, M. M. Mertens and S. N. Vaughn, US Patent 6316683, 2001.
- 7 Patent pending.