ChemComm
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Improvement of the hydrothermal stability of SAPO-34†

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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 TEAOH (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.†[7] 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 autogeneous 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

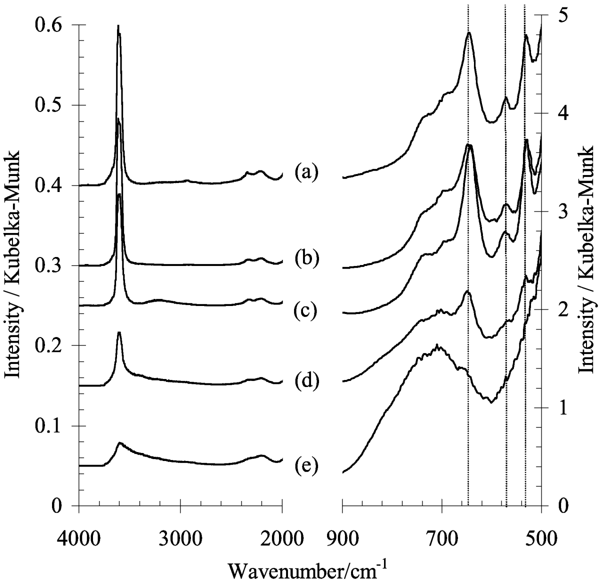

Fig. 1 In situ diffuse reflectance IR spectra of samples (a) fresh H^+-SAPO-34, (b) and (c) NH_4^+-SAPO-34 after 5 h and 25 h steaming respectively, (d) and (e) H^+-SAPO-34 after 5 h and 25 h steaming respectively. The spectra were recorded at 400 °C under vacuum. Prior to recording the spectra, the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

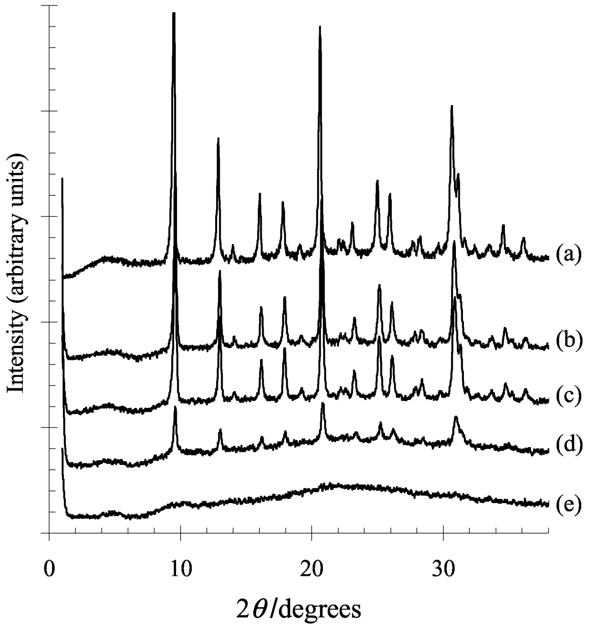

Fig. 2 XR diffractograms of samples (a) fresh H^+-SAPO-34, (b) and (c) NH_4^+-SAPO-34 after 5 h and 25 h steaming respectively, (d) and (e) H^+-SAPO-34 after 5 h and 25 h steaming respectively.

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

DOI: 10.1039/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 645cm^{-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 $2\theta = 22°$. 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.

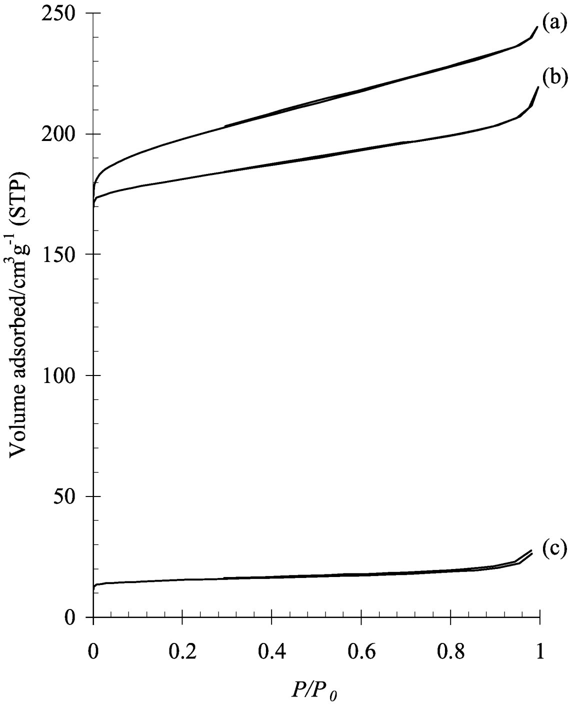

Fig. 3 N_2 sorption isotherms of (a) fresh H^+-SAPO-34, (b) NH_4^+-SAPO-34 after 25 h steaming and (c) H^+-SAPO-34 after 25 h of steaming.

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