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Correspondence and requests for materials should be addressed to C.D. (dekker@qt.tn.tudelft.nl).

## Organic-functionalized molecular sieves as shape-selective catalysts

Christopher W. Jones, Katsuyuki Tsuji & Mark E. Davis

Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

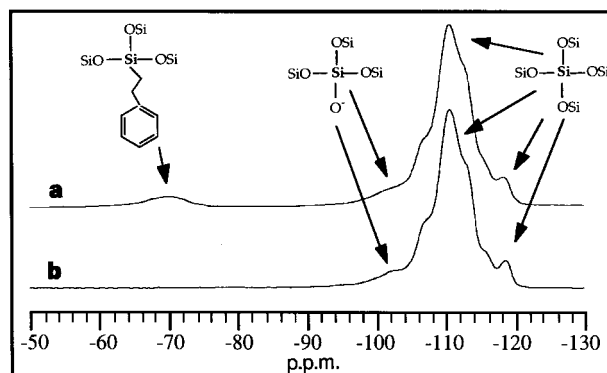
Zeolites and related crystalline molecular sieves can possess catalytically active acid sites, as well as uniformly sized and shaped pores and voids, that allow for their industrial use as shape-selective catalysts<sup>1</sup>. Some catalytic reactions that are not mediated by acids (such as oxidation) have also been shown to occur in zeolites in a shape-selective manner<sup>2</sup>, but the diversity in active sites in these materials remains restricted. For mesoporous materials<sup>3</sup>, the diversity in catalytic activity has been broadened by grafting organosilanes that contain organic functional groups onto the internal pore surfaces<sup>4–6</sup> or by incorporating them into the structure during the synthesis process<sup>7–12</sup>. The former approach has not proven straightforward for microporous zeolites because a large fraction of the grafted functional groups become attached instead to the exterior surfaces of the crystal, where there is no shape selectivity<sup>13</sup>. The synthesis of zeolites and molecular sieves using organosilanes as structure-directing agents has been accomplished<sup>14,15</sup>, but the subsequent creation of porosity requires the complete loss of the organic functional groups. Here we report a new methodology that overcomes these problems and allows the production of microporous molecular sieves containing organic functionalities within their pores. During the initial synthesis phase, phenethyl groups covalently tethered to silicon atoms are incorporated into the framework. The external surface-bound functionalities and the structure-directing agents residing within the intracrystalline spaces are then removed to create a microporous material. Subsequent sulphonation of the phenyl rings produces intrapore sulphonic acid sites that perform shape-selective catalysis. Different active-site types can be created by attaching other functional groups to the framework silicon, and we therefore expect that our method will lead to the formation of a wide range of shape-selective catalysts.

A major key to success in synthesizing organic-functionalized molecular sieves (OFMSs) is the identification of a molecular sieve that can be prepared in the absence of an organic structure-directing agent (SDA) such as NaY, or where the SDA can be removed by extraction. We have synthesized OFMs by both routes, for example NaY (no organic SDA) or pure-silica zeolite beta using tetraethylammonium fluoride (TEAF) as the SDA. We prefer the use of high-silica materials because they provide a hydrophobic void space in which to conduct chemical reactions. An example of the synthetic methodology is illustrated by the synthesis of pure-silica zeolite beta using TEAF as the SDA in the presence of phenethyltrimethoxy silane (PETMS). Following the procedure of Cambior *et al.*<sup>16</sup> for the

synthesis of pure-silica zeolite beta using TEAF as the SDA, we crystallized the hybrid material with 5 atom% or less (2.8 atom% for the sample described here) of the silicon substituted by PETMS. The X-ray diffraction pattern of the hybrid material clearly identifies it as crystalline zeolite beta (diffraction pattern available: see Supplementary information). Figure 1 shows the <sup>29</sup>Si cross-polarization magic angle spinning (CPMAS) NMR spectra for the as-synthesized, pure-silica zeolite beta and the organic-functionalized beta. It is clear from the spectrum of the hybrid material that the phenethyl group (the presence of the aromatic ring was verified by Raman spectroscopy, spectra available, see Supplementary information) is covalently linked to the framework silicon atom (peak at –68 p.p.m.: C–Si–(OSi)<sub>3</sub>; refs 14, 17). This resonance indicates that the linking silicon atom is fully condensed in the framework<sup>18</sup>.

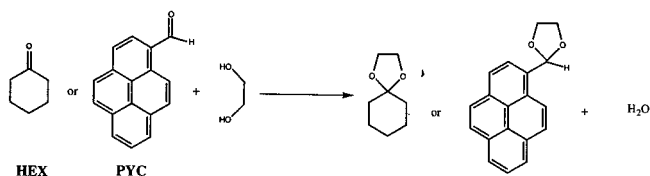
Organic functionalities on the exterior surface of the beta crystals can be removed by reacting the as-synthesized material with concentrated sodium hydroxide solutions (~8 M NaOH, 5% methanol, 25 °C, 1 h). Subsequently, extraction of TEAF from the hybrid material is possible by repeated exposures to acetic acid/water mixtures at 140 °C. Essentially complete removal of TEAF is accomplished for the sample described here (>99% removed as determined by thermogravimetric analysis). The extracted OFMS is sulphonated by contact with vapour from 30% SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> at room temperature after heating at ~100 °C under a vacuum of less than 10<sup>–6</sup> torr overnight. Following sulphonation, the sample is washed with water and then dioxane to remove residual sulphuric acid resulting from the sulphonation procedure. Scanning electron microscopy (SEM) images of this fully modified material do not appear different from the images of the as-made material. Before use as a catalyst, the solid is dehydrated at ~100 °C for at least 6 h under a vacuum of less than 10<sup>–6</sup> torr. Verification of sulphonic acid formation is obtained by Raman spectroscopy (spectrum available, see Supplementary information). Nitrogen adsorption isotherms indicated that the extraction procedure creates significant microporosity (isotherm available, see Supplementary information). Figure 2 illustrates this synthetic procedure.

The reaction of a cyclic ketone with ethylene glycol is used to illustrate the catalytic activity and shape-selectivity of the sulphonated, extracted phenyl-functionalized beta (beta/PETMS/SO<sub>3</sub>H). The beta/PETMS/SO<sub>3</sub>H is an active catalyst for the formation of 2,2-pentamethylene-1,3-dioxolane (cyclic ketal) from ethylene glycol and cyclohexanone (HEX). This activity is due to the phenyl-sulphonic acid groups covalently linked to the zeolite framework. The data in Table 1 show that *para*-toluenesulphonic acid monohydrate, phenyl-sulphonic acid anchored to controlled-pore-glass (CPG-240, mean pore diameter 240 Å), and beta/PETMS/SO<sub>3</sub>H are active catalysts for this transformation. None of the OFMS synthesis intermediates and the non-functionalized, pure-silica materials are



**Figure 1** <sup>29</sup>Si CPMAS NMR spectra of **a**, organic-functionalized beta and **b**, pure-silica beta. Spectra are from as-synthesized materials and are referenced to tetramethylsilane.

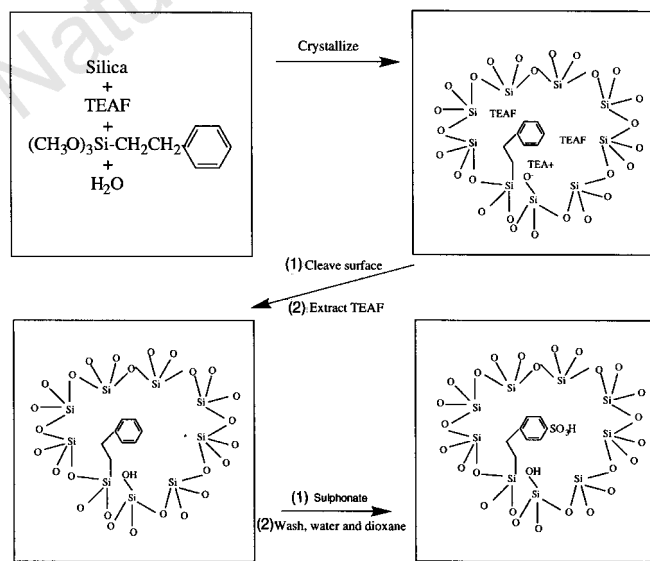
active catalysts. The results clearly indicate that on beta/PETMS/SO<sub>3</sub>H the phenyl-sulphonic acid site is the active centre.



To illustrate shape selectively, 1-pyrenecarboxaldehyde (PYC), which is too large to enter the pore system of beta, is reacted with ethylene glycol. Both HEX and PYC react with ethylene glycol over *para*-toluenesulphonic acid monohydrate to form a ketal or acetal (see Table 1). These two reactions are used to elucidate the location of the phenyl-sulphonic acid moieties in the beta/PETMS/SO<sub>3</sub>H material. Figure 3 illustrates the conversion of PYC or HEX as a function of time using beta/PETMS/SO<sub>3</sub>H as a catalyst. The acetal of PYC is undetectable over the initial 3.5 h of contact. This is due to the lack of sufficient surface catalytic sites that would be required to catalyse the reaction of the bulky PYC within this timeframe. In contrast, HEX is readily converted to its ketal. Upon the addition of di(2-naphthyl)-2-pyrrolidinemethanol (NPM: a bulky poison that cannot access the beta pore system) after 1.15 h of reaction, the conversion of HEX proceeds, thus indicating that the active sites are intrazeolitic. Addition of a small poison that can enter the molecular sieve pores, triethylamine (Et<sub>3</sub>N), stops all reaction at 0.5 h, as indicated by the data in Fig. 3.

As a further control, phenethyl sulphonic acid sites are prepared on the surface of CPG-240. This material has a uniform pore diameter of 240 Å and cannot be a shape-selective catalyst. Over this catalyst, both HEX and PYC are converted, as denoted in Table 1. However, if NPM is added at the outset neither HEX or PYC is reacted. Thus, the shape-selectivity of the OFMS catalyst is demonstrated by the fact that NPM poisons all active sites in CPG-240/PETMS/SO<sub>3</sub>H, but has little effect on beta/PETMS/SO<sub>3</sub>H.

A commercial zeolite beta (PQ, Si/Al = 25) is able to catalyse the



**Figure 2** Schematic illustration of the preparation procedures used to create a sulphonic acid-functionalized molecular sieve.

**Table 1** Ketal or acetal formation with cyclohexanone or 1-pyrenecarboxaldehyde and ethylene glycol

Catalyst	Conversion (%) of HEX
None	<2
CPG-240	<2
CPG-240/PETMS	<2
CPG-240/PETMS/SO <sub>3</sub> H†	71.0
Si-beta, as made	<2
Si-beta, extracted	<2
Si-beta, sulphonated	<2
Si-beta/PETMS, as-made	<2
Si-beta/PETMS, as-made sulphonated	<2
Si-beta/PETMS, extracted	<2
Si-beta/PETMS, extracted, SO <sub>3</sub> H‡	72.0
<i>Para</i> -toluenesulphonic acid†	70.0
<i>Para</i> -toluenesulphonic acid, NPM§	0
<i>Para</i> -toluenesulphonic acid†	40.0
CPG-240/PETMS/SO <sub>3</sub> H§	0
CPG-240/PETMS/SO <sub>3</sub> H	40.0

\* CPG-240/PETMS/SO<sub>3</sub>H: ~0.13 mmol H<sup>+</sup> g<sup>-1</sup> catalyst.

‡ Si-beta/PETMS, extracted, SO<sub>3</sub>H: ~0.14 mmol H<sup>+</sup> g<sup>-1</sup> catalyst.

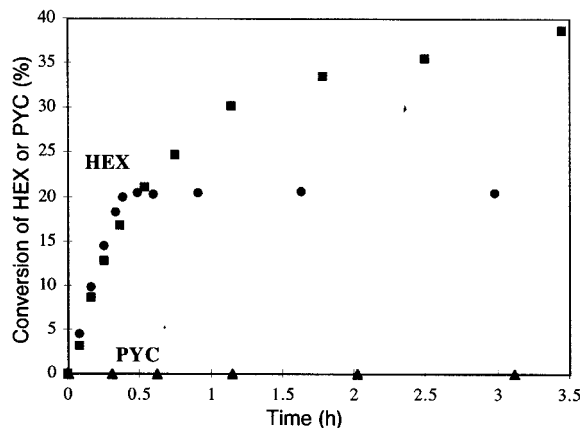
† Conversions are limited by equilibrium.

§ No conversion for both HEX and PYC. NPM poisons all active sites in CPG-240 and *para*-toluenesulphonic acid, unlike beta.

|| Conversion of PYC.

reaction demonstrated here. However, in the absence of the surface poison NPM, there is significant conversion of PYC by this catalyst (initial rates: HEX/PYC = 16, same conditions as those for experiments described in Fig. 3). Thus, the aluminosilicate is not as shape-selective because of the reactivity of the external crystal surface. Also, there are no proven examples of shape-selective catalysis with organic-functionalized mesoporous solids. The pores of the mesoporous MCM-41-type materials can be constricted into the micropore range by silanation treatments. However, these modifications will probably not result in a single, fixed-diameter pore opening as found in crystalline silicate molecular sieves. Instead, a distribution of pore sizes would be expected. In addition, the crystalline OFMSs are physically and chemically more robust than amorphous, mesoporous materials.

The organic-functionalized materials of the type described here provide new opportunities for shape-selective catalysis. In principle, any functional group that catalyses homogeneous reactions can be 'tailor-made' into an intrazeolitic organic moiety. Thus far, we have prepared OFMS using zeolite beta (TEAF as SDA), ZSM-5 (hexamethylenediamine as SDA) and NaY and have placed numerous



**Figure 3** Shape-selective catalysis over organic-functionalized beta. Reactions of PYC (▲) and HEX (■, ●); 27.5 mg NPM added at 1.15 h for the experiment denoted by ■ and 100 mg Et<sub>3</sub>N added at 0.5 h for the experiment denoted by ●. Acid content of catalyst: ~0.14 mmol H<sup>+</sup> g<sup>-1</sup> catalyst.

functional groups into their structures, for example phenethyl, cyclohexenyl, aminopropyl (information regarding zeolite NaY with tethered cyclohexenylethyl groups is included in Supplementary information). Additionally, we have demonstrated not only acid catalysis, but base-catalysed conversions. Finally, the organic moieties may perform functions other than catalysis, for example, synthesis of vicinal diols through oxidation of tethered cyclohexenyl groups could be used as a chelating site for adsorbing metal ions from solution. We believe that this synthetic method should be a general method for high-silica molecular sieve syntheses, and particularly syntheses mediated by  $F^-$ , so long as the SDA is extractable and there exists sufficient intracrystalline space for both the organic functional group and the SDA. Thus, organic-functionalized molecular sieves should provide for new applications of shape-selectivity. □

## Methods

**Catalytic reactions.** For Table 1. Reactions were conducted in magnetically stirred glass reactors at 70 °C for 24 h. The reactor was charged with 9 g toluene, 10 mmol of each reactant, and about 10 mg catalyst. Products were identified by gas chromatography using authentic samples.

For Figure 3. Reactions were conducted in magnetically stirred glass reactors at 70 °C. The reactor was charged with 10 g toluene, 10 mmol of reactants in the case of HEX or 3 mmol in the case of PYC, and 13 mg catalyst. Samples were taken periodically and analysed by GC/MS spectroscopy. Acid content of catalyst:  $\sim 0.14$  mmol  $H^+$   $g^{-1}$  catalyst.

**Active site density.** Beta/PETMS/SO<sub>3</sub>H (0.21 g) was washed with 15 ml saturated NaCl solution at room temperature. The OFMS was removed by filtration. Several drops of phenolphthalein solution were added to the filtrate and then this solution was titrated with 0.001 M NaOH to neutrality. The active-site density obtained from this method agreed well with the total mass of organic material as determined by TGA, and elemental analysis for sodium.

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Supplementary information is available on Nature's World-Wide Web site (<http://www.nature.com>) or as paper copy from the London editorial office of Nature.

Correspondence and requests for materials should be addressed to M.E.D. (e-mail: mdavis@chem.caltech.edu).

## Correlation between Arabian Sea and Greenland climate oscillations of the past 110,000 years

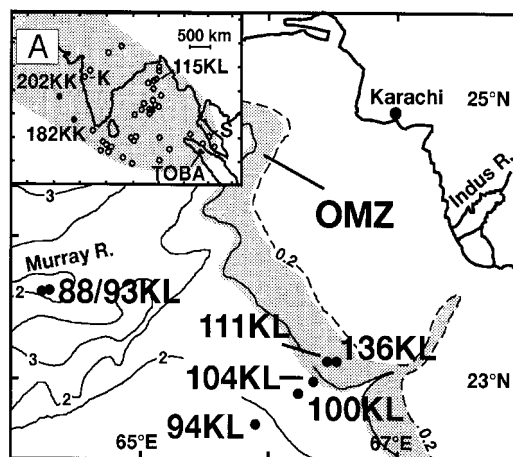
Hartmut Schulz\*, Ulrich von Rad\* & Helmut Erlenkeuser†

\* Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), PF 510153, D-30631 Hannover, Germany

† Leibniz-Labor für Altersbestimmung und Isotopenforschung, Universität Kiel, Max-Eyth-Strasse 11-13, D-24118 Kiel, Germany

Palaeoclimate studies have revealed the general high-frequency instability of Late Pleistocene climate—for example, the so-called Dansgaard-Oeschger and Heinrich events—on timescales of a few millennia, centuries or even decades<sup>1–11</sup>. Here we present evidence for a general relationship between low-latitude monsoonal climate variability and the rapid temperature fluctuations of high northern latitudes that are recorded in the Greenland ice records. Sediment cores from the northeastern Arabian Sea show laminated, organic-carbon-rich bands, reflecting strong monsoon-induced biological productivity, that correlate with the mild interstadial climate events in the northern North Atlantic region. In contrast, periods of lowered southwest monsoonal intensity, indicated by bioturbated, organic-carbon-poor bands, are associated with intervals of high-latitude atmospheric cooling and the injection of melt water into the North Atlantic basin. Our records suggest that Dansgaard-Oeschger and Heinrich events are strongly expressed in low-latitude (monsoonal) climate variability, suggesting the importance of common forcing agents such as atmospheric moisture and other greenhouse gases.

Today, the northern Arabian Sea is characterized by (1) warm and highly saline near-surface waters originating from the Persian Gulf,



**Figure 1** Location of sediment cores off Pakistan. OMZ, oxygen-minimum zone impinging on the continental slope between 200 and 1,200 m water depth (w.d.) with contours in km. Labelled sites and key cores SO90-88KL and SO90-93KL (23° 35' E, 64° 13' E, 1,783 m and 1,802 m w.d.), SO90-111KL (23° 06' N, 66° 29' E, 775 m w.d.), SO90-136KL (23° 07' N, 66° 30' E, 568 m w.d.) are discussed in the text. Inset map showing sites of youngest Toba ash occurrences between Toba (Sumatra) and the northeastern Arabian Sea. 'A' indicates position of main map. Open circles, localities from the Bay of Bengal, India (K indicates Kukdi) and southern Malaysia (S indicates Serdang)<sup>23–25</sup> (H. R. Kudrass, personal communication); filled circles: Arabian Sea IIOE cores<sup>12</sup>.