Heterogeneous Catalysis |Hot Paper|



Facile Synthesis, Characterization, and Catalytic Behavior of a Large-Pore Zeolite with the IWV Framework

Joel E. Schmidt,^[a] Cong-Yan Chen,^[b] Stephen K. Brand,^[a] Stacey I. Zones,^[b] and Mark E. Davis^{*[a]}

Abstract: Large-pore microporous materials are of great interest to process bulky hydrocarbon and biomass-derived molecules. ITQ-27 (IWV) has a two-dimensional pore system bounded by 12-membered rings (MRs) that lead to internal cross-sections containing 14 MRs. Investigations into the catalytic behavior of aluminosilicate (zeolite) materials with this framework structure have been limited until now due to barriers in synthesis. The facile synthesis of aluminosilicate IWV in both hydroxide and fluoride media is reported herein using simple, diquaternary organic structure-directing

Introduction

Microporous crystalline materials are solids with pores of less than 2 nm. They are formed from three dimensional networks of oxide tetrahedra, and offer shape- and size-selective environments for catalysis, absorption and ion exchange in materials that often exhibit robust hydrothermal stability. There are currently over 200 distinct microporous material frameworks that differ in pore shape, size and dimensionality, presence or absence of internal cages, and composition.^[1] One of the most important distinctions between frameworks is the size of the pores, which are defined by the number of tetrahedral (T-atoms) that border them. Pores defined by eight T-atoms (8 MR) are considered small-pore materials, 10 MR are medium pore materials, and 12 MR are termed large-pore materials. Materials with large pores are of great interest to process bulky hydrocarbon and biomass-derived molecules.^[2] The commercial market for zeolites is dominated by five frameworks, *BEA, FAU, FER, MFI, and MOR, and of these, three are large-pore materials (*BEA, FAU, and MOR), and a single large-pore material, FAU, dominates 95% of the synthetic zeolite market, as it is used for fluidized catalytic cracking.[3-5] Although such market dominance may seem to imply research stagnation in the field, the fact that only a single framework and composition (as well

[a]	Dr. J. E. Schmidt, S. K. Brand, Prof. M. E. Davis	
	Chemical Engineering, California Institute of Technology	
	Pasadena, CA 91125 (USA)	
	E-mail: mdavis@cheme.caltech.edu	

[b] Dr. C.-Y. Chen, Dr. S. I. Zones Chevron Energy Technology Company, Richmond, CA 94802 (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504717. agents (OSDAs) that are based on tetramethylimidazole. In hydroxide media, a zeolite product with Si/Al = 14.8–23.2 is obtained, while in fluoride media an aluminosilicate product with Si/Al up to 82 is synthesized. The material produced in hydroxide media is tested for the hydroisomerization of *n*hexane, and results from this test reaction suggest that the effective pore size of zeolites with the IWV framework structure is similar to but slightly larger than that of ZSM-12 (MTW), in fairly good agreement with crystallographic data.

as further modification by post-synthetic treatments) often delivers adequate performance in a given application means that the development of new microporous material frameworks and compositions is an area of considerable research efforts.^[4,6-10]

Some of the strategies employed in recent years in the quest for new materials include: new organic structure-directing agents (OSDAs), the use of fluoride as a mineralizing agent coupled with low-water syntheses and germanium as a framework element.^[11] Among these strategies, the use of new OSDAs has received a great amount of attention. Although computational guidance has been used in some limited cases to predict OSDAs for desired phases a priori, the majority of discoveries are made through serendipity.^[12-16] OSDAs are generally quaternary alkylammonium molecules, though OSDAs based on phosphonium^[7, 11, 17-20] and sulfonium^[21] chemistry are also known. Phosphonium OSDAs are especially advantageous as they do not undergo Hoffman degradation, making their use under severe crystallization conditions possible. However, a potential drawback of phosphonium OSDAs is that phosphorous remains in the materials after calcination. One of the first, new microporous materials discovered using phosphonium OSDAs is ITQ-27 (IWV), that consists of a 2D pore system limited by 12 MRs, but containing internal 14 MRs.^[17,22] ITQ-27 was discovered by using dimethyldiphenylphosphonium as the osda and a synthesis composition of SiO₂:0.014 Al₂O₃:0.50 Me₂Ph₂POH:0.50 HF:(3-4.2) H₂O. The preparation was reported to take 59 days to form the product (the addition of seeds only shortens this by one week). While a broad compositional range was claimed for ITQ-27 in the patent literature^[22], the product was only reported as having a Si/Al = 29.5.

Wiley Online Library



We have recently been examining the use of diquaternary OSDAs, and have reported products such as *BEA, CIT-7, CIT-8P, CIT-10, STF, and STW by using a wide-range of inorganic conditions.^[23-25] In these publications, we disclosed IWV as a product, but did not discuss the material further. Herein, we report the synthesis and characterization of aluminosilicate IWV across a broad compositional range in both fluoride and hydroxide media, as well as titanogermanosilicate IWV in fluoride media. These materials are made using easily prepared OSDAs. Additionally, we have characterized IWV and assessed its catalytic activity for the hydroisomerization of *n*-hexane.

Results and Discussion

Synthesis and characterization of IWV

Recently, we have demonstrated that tetramethylimidazolebased diquats of varying linker length are capable of synthesizing a diverse range of microporous material frameworks including 8, 10, and 12 MRs in a variety of pore dimensionalities and containing cages. We have found many competing phases, and have primarily used seeding as a method to reliably synthesize desired frameworks. In addition to *BEA and MTW, we have found IWV as a third large-pore product.

Herein, screening reactions were run with diquats of varying linker lengths in both hydroxide and fluoride-mediated syntheses across a wide range of inorganic conditions, and results are given in Tables S1 and S2, Supporting Information. In our previous work, we mentioned that IWV was found as a product under certain conditions, but did not expand on its synthesis.^[23,24] Interestingly, we have found that IWV can be prepared under both hydroxide- and fluoride-mediated aluminosilicate reactions, as well as a titanogermanosilicate composition in fluoride-mediated conditions. Based on the synthesis results in Table S1 and S2, Supporting Information, the five-carbon diquat is the most strongly directing towards IWV, but the framework can also be prepared with the four- and six-carbon diquats.

Hydroxide-mediated syntheses

In hydroxide-mediated syntheses IWV could be prepared using a variety of sources of inorganics, both amorphous and crystalline, at a gel composition of Si/Al = 10-30 (atomic ratio; see the Experimental Section for an explanation). The characterized products had Si/Al = 14.8–23.2. Although this composition range appears somewhat narrow, it is significant for several reasons: 1) It is the first demonstration of aluminosilicate IWV prepared under hydroxide-mediated conditions (most largescale zeolite preparations are conducted in hydroxide media; thus, this method makes IWV available for realistic production and testing) and 2) the product Si/Al range is favorable for producing materials with a sufficient number of acid sites to demonstrate catalytic activity, but also in a range that can allow for robust hydrothermal stability.

With the as-made material prepared in hydroxide media, ¹³C CPMAS NMR results demonstrate that the organic is occluded

intact (Figure 1). The TGA analysis shows a mass loss of 19 wt% (Figure 2), similar to values obtained for other largepore microporous materials. The ²⁹Si MAS NMR of the calcined material shows the presence of Si(OSi)₄ environments, as well as Si(OSi)₃(OAI) environments (Figure 3), which is consistent with an aluminosilicate material.



Figure 1. ¹³C liquid NMR of OSDA in D_2O (lower, methanol added as internal standard), ¹³C CPMAS NMR of IWV prepared in hydroxide media (middle, sample 1), and ¹³C CPMAS NMR of IWV prepared in fluoride media (upper).



Figure 2. TGA analysis of IWV prepared in hydroxide media (black, sample 1) and fluoride media (gray).

Two samples of IWV produced in hydroxide media were selected for further catalytic testing, and additionally characterized by PXRD, SEM, EDS, nitrogen adsorption, and ²⁷Al MAS NMR. The sample designations, inorganic sources, product Si/ Al ratios, and nitrogen micropore volumes are given in Table 1. The PXRDs of the materials in ammonium form are illustrated in Figure 4, and show that both samples are pure-phase IWV. The ²⁷Al MAS NMR spectra of the samples in ammonium form are given in Figure 5 and both show only tetrahedral (framework) aluminum. The SEM images of the samples are illustrated in Figure 6. Both samples show a plate-like morphology but the crystallites of sample 1 are larger than sample 2.





Figure 3. ²⁹Si NMR of calcined aluminosilicate IWV prepared in hydroxide media (lower, gel Si/Al = 15, product Si/Al = 14.8, sample 1) and fluoride media (upper, gel Si/Al = 200, product Si/Al = 82).

Table 1. H	-IWV samples use	ed for catalytic	testing.
Sample	Inorganic	Product	Nitrogen micropore volume
	source	Si/Al	[cc/g]
1	CBV 720	14.8	0.237
2	CBV 760	23.2	0.193



Figure 4. PXRD of sample 1 (lower) and 2 (upper) in ammonium form. Spectra have been normalized to the highest intensity peak.



Figure 5. ²⁷AI MAS NMR of 1 (lower) and 2 (upper) in ammonium form.

Chem. Eur. J. 2016, 22, 4022 – 4029

www.chemeurj.org

CHEMISTRY A European Journal Full Paper



Figure 6. SEM images of 1 (lower) and 2 (upper) in ammonium form.

Fluoride-mediated syntheses

Results of the screening reactions in fluoride media are given in Table S1. In fluoride media, the five carbon diquat was the most strongly directing to IWV. It was able to produce aluminosilicate IWV with a product Si/Al as high as 82 (gel Si/Al = 200). Additionally, it was also possible to prepare titanogermanosilicate IWV, which is a potential large-pore Lewis acid catalyst. Interestingly, it was necessary to have aluminum or germanium to form IWV, and even with seeds present it was not possible to prepare pure-silica IWV in fluoride media. The ability of germanium to help direct towards IWV agrees with the structure of IWV, as it contains double four rings (d4rs); however, if the germanium content is too high, STW forms instead. A representative SEM image of IWV prepared in fluoride media is shown in Figure 7. As is typical for samples prepared in fluoride media, the crystal size is larger than that observed in hydroxide media.

The ¹⁹F NMR spectrum of the as-made material prepared in fluoride media is shown in Figure 8 and contains a single resonance at $\delta = -35.5$ ppm, consistent with fluoride occluded in d4rs. ¹³C CPMAS NMR of the as-made material demonstrates that the organic is occluded intact (Figure 1) and that the material was not prepared from a decomposition product. The TGA analysis shows a mass loss of 19 wt%, similar to values obtained for other large-pore materials (Figure 2). The ²⁹Si MAS NMR of the calcined material shows the presence of Q⁴, Si(OSi)₄, environments as well as Q³, Si(OSi)₃(OAI), environments (Figure 3), which is consistent with an aluminosilicate zeolite.

The fluoride-mediated reactions show a novel method to prepare high-silica IWV as well as Lewis acidic IWV. However, as these samples are prepared in fluoride media, making them



Figure 7. SEM image of calcined IWV prepared in fluoride media from gel. $\mbox{Si/Al}\,{=}\,200.$



Figure 8. ¹⁹F NMR of as-made IWV prepared in fluoride media.

difficult to scale up, they were not selected for further characterization.

Hydroisomerization of n-hexane

The hydroisomerization of *n*-hexane was selected as a test reaction to probe the effective pore-size of the materials. As described in references [26, 27], n-hexane cracks only slowly under the conditions applied in this work by secondary carbenium ions due to its short carbon-carbon chain, leading to a high selectivity to hydroisomerization of n-hexane (kinetic diameter: 4.3 Å) to form only four paraffinic isomers of different molecular sizes, that is, 2-methylpentane (5.0 Å), 3-methylpentane (5.0 Å), 2,2-dimethylbutane (6.2 Å), and 2,3-dimethylbutane (5.8 Å). This provides a relatively simple case for studying the shape-selective properties of zeolites that have effective pore sizes close to the molecular kinetic dimensions of these C₆ isomers. The results from *n*-hexane hydroisomerization over two ITQ-27 samples (1 and 2) loaded with 0.27 wt.% Pd are shown in Figure 9 and compared to those of other zeolites in Table 2.

The conversion of *n*-hexane increases with the increasing reaction temperature. At low temperatures, hydroisomerization is the only reaction. When the reaction temperature increases, the hydrocracking reaction takes off and its yield and selectivity go up progressively. With the competing cracking reaction occurring, as the temperature increases, the yield and

selectivity to hydroisomerization products increase initially, proceed to a maximum, and then decrease. The distribution of the C_6 isomers reveals how the hydroisomerization proceeds versus temperature. *n*-Hexane is isomerized only to 2- and 3-methylpentane at low temperatures. As the temperature increases, 2- and 3-methylpentane are further isomerized to 2,2- and 2,3-dimethylbutane toward the thermodynamic equilibrium. The cracking products, although the yield and selectivity are fairly low, consist predominantly of propane because the formation of methane and pentanes, as well as ethane and butanes, involves primary carbenium ions and are energetically less favorable than the formation of propane.

When comparing the shape selectivities of these zeolites in a catalytic test reaction, it is always important to refer the catalytic properties to a certain reaction parameter at the same or similar value level. We found that the distributions of the branched isomers of *n*-hexane at the maximum isomer yields (in contrast to e.g., 10 or 20 mol% conversion of *n*-hexane) provide a very useful platform for correlating the shape selective properties of *n*-hexane hydroisomerization with the effective pore/channel structures of zeolites.^[26,27] Therefore, such results from ITQ-27 and some selected zeolites are summarized in Table 2, together with the thermodynamic equilibrium distributions of isomers calculated according to reference [28].

Zeolite Y, beta, and mordenite are the representatives of 12 MR zeolites with wide pore/channel openings and behave similarly in *n*-hexane hydroisomerization. The effective pore/ channel sizes do not appear to have spatial restrictions to the formation of the two relatively bulky dibranched isomers, 2,2- and 2,3-dimethylbutane, leading to a yield ratio of 2,2- to 2,3-dimethylbutane of roughly 2:1 at their maximum isomer yields, while the yield ratio of dibranched isomers (2,2- and 2,3-dimethylbutane) to the monobranched isomers (2- and 3-methylpentane) is approximately 0.5:1.

ZSM-12 (MTW) is a one-dimensional, 12 MR zeolite with a fairly narrow ring opening. Its yield ratio of 2,2- to 2,3-dimethylbutane is 1.7:1 and the yield ratio of dibranched isomers (2,2- and 2,3-dimethylbutane) to the monobranched isomers (2- and 3-methylpentane) is ~0.35:1 at the maximum isomer yield, in good correlation with its effective pore size, which lies between those of the 10 MR zeolite ZSM-5 and 12 MR zeolites Y, beta and mordenite. In contrast to these large-pore zeolites, the formation of the bulky 2,2- and 2,3-dimethylbutane is essentially hindered by the narrow pores in the 10 MR zeolite ZSM-5.

The two ITQ-27 catalysts show very similar results in spite of the difference in reaction temperature. The curves depicted in Figure 9 essentially overlap with each other when shifting the curves of the lower Si/Al ITQ-27 by $\sim 5^{\circ}$ C toward the higher temperature region. Since these two ITQ-27 materials have similar crystal morphology and size, this temperature difference is most likely attributed to the difference in acidity that is associated with their different Si/Al ratios. At the maximum isomer yield of \sim 75.5 mol%, the yield ratio of 2,2- to 2,3-dimethylbutane for ITQ-27 is \sim 1.7:1 and the yield ratio of dibranched isomers (2,2- and 2,3-dimethylbutane) to the monobranched isomers (2- and 3-methylpentane) is \sim 0.4:1.





Figure 9. Hydroisomerization of *n*-hexane over Pd/H-ITQ-27 with Si/Al = 14.8 (sample 1, top) and Pd/H-ITQ-27 with Si/Al = 23.2 (sample 2, bottom) at 170–300 °C, 1480 kPa, 1.0 h⁻¹ LHSV and 6:1 H₂/*n*-hexane.

The results obtained from this catalytic test reaction suggest that the effective pore size of ITQ-27 is similar to but slightly larger than that of ZSM-12, in fairly good agreement with the crystallographic data.

Conclusion

The facile synthesis of aluminosilicate IWV (ITQ-27) in both hydroxide and fluoride media has been demonstrated using simple, diquaternary OSDAs based on tetramethylimidazole. In hydroxide media, a product with Si/Al = 14.8-23.2 was found, and all the aluminum was in framework (tetrahedral) positions. The materials showed good microporosity. The solids produced in hydroxide media were tested for the hydroisomerization of *n*-hexane, and this test reaction suggests that the effective pore size of ITQ-27 is similar to but slightly larger than that of ZSM-12, in fairly good agreement with the crystallographic data. IWV materials can also be produced in fluoride media, as an aluminosilicate with Si/Al up to 82, and as a titanogermanosilicate material.

Experimental Section

OSDA synthesis: The diquaternary imidazolium OSDAs used in this work were synthesized by reacting 1,2,4,5-tetramethylimidazole (200 mmol; TCI Chemicals) with dibromoalkane (100 mmol) (all from Aldrich) at reflux in methanol overnight. The solvent was then removed using rotary evaporation and the product washed with ether. The products were verified using ¹³C NMR in D₂O with methanol added as an internal standard. Carbon NMR shifts are

∭ ★ Ch	emPubSoc
***	Europe



given in Table 3. The OSDAs were then converted from bromide to hydroxide form using Dowex Marathon A hydroxide exchange resin and then titrated to determine final concentration using a Mettler–Toledo DL22 autotitrator with 0.01 M HCl as the titrant.



diquaternary OSDAs

Microporous material synthesis: A general synthesis procedure for the microporous materials can be found below. In all situations the samples were spun at 43 rpm in a rotating oven. For all microporous material syntheses, aliquots of the material were taken periodically (generally every 3—4 days) by first quenching the reactor in water and then removing enough material for PXRD. Syntheses were considered to be finished when a crystalline product was observed via PXRD and the broad peak indicative of amorphous material, between 20 and 30° 2 θ , had disappeared. If incomplete crystallization or no crystalline product was observed in PXRD, the syntheses were replaced in the oven.

In this work all atomic ratios are on an atom basis, thus all compositions are given in terms of Si/Al ratios. In zeolite publications, both Si/Al ratio and silica to alumina ratio (SAR, SiO_2/Al_2O_3) are used; the SAR numerical value is twice the Si/Al ratio.

Fluoride-mediated reactions: A general procedure for a fluoridemediated synthesis was as follows. Tetraethylorthosilicate (TEOS) and aluminum isopropoxide (if necessary) were added to the OSDA in its hydroxide form in a Teflon Parr reactor liner. The container was closed and stirred for at least 12 h to allow for complete hydrolysis. The lid was then removed and the alcohol and an appropriate amount of water were allowed to evaporate under a stream of air. The composition was monitored gravimetrically. Additional water was added as necessary, and then aqueous HF (Aldrich) was added and the mixture was stirred by hand until a homogenous gel was obtained. (Caution: Use appropriate personal protective equipment, ventilation and other safety measures when working with HF.) The final molar ratios of the gel were: (1-x)SiO₂:xAI:0.5 ROH:0.5 HF:yH₂O. The parameters x and y were varied depending on the synthesis and the desired composition and can be found in Table S1, Supporting Information. For lowwater syntheses, a final evaporation step was used after the addition of HF to reach the desired water ratio. The Teflon-lined Parr reactor was sealed and placed in a rotating oven at 160 or 175°C. Complete results are given in Table S1, Supporting Information. The titanogermanosilicate material was prepared using germanium(IV) ethoxide and titanium(IV) butoxide.

Hydroxide-mediated reactions: For the hydroxide syntheses, several variations on gel Si/Al as well as the sources of silica and alumina were used. Specific synthesis preparations are reported below. For all hydroxide-mediated reactions, seeds were added after 1 day at reaction temperature, once a decrease in pH was observed. Normally seeds were added as a homogeneous aliquot of the contents of a previous, completed reaction (less than 0.3 mL) as these were found to be more active than seeds that had been washed. Aliquots were taken periodically, and crystallization was monitored by both PXRD and pH, as an increase in pH was generally observed when the product crystallized. After the product crystallized, the material was washed with DI water and then collected by centrifugation. This process was repeated at least three times, and a final wash was performed using acetone. The product was dried at 100 °C in air.

Table 2. Hydroisom	erization of <i>n</i> -hexane over ITQ-27 and so	me selected zeolites at maxim	num isomer yields (1480 kPa	ι, 1.0 h ⁻¹ LHS	V and 6:1 $H_{2^{\prime}}$	<i>n</i> -hexane)	[e] .			
Zeolite	Structural features	Tat max. isomer yield [°C]	Max. isomer yield [mol %]	Distribution 2,2-DMBu	[mol%] 2,3-DMBu	2-MPn	3-MPn	rield ratio 2,2-DMBu/2,3-DMBu	DMBu's/MPn's	Ref.
Y	3D, 12 MR (7.4 Å)	304	79.5	21.9	10	41.1	27	2.19	0.47	[26]
Beta	3D, 12 MR (6.6×6.7 Å)	266	81.5	21.4	11.3	41.2	26.1	1.89	0.49	this work
Mordenite	1D, 12 MR (6.5×7.0 Å)	293	78.6	21.5	10.8	40.7	27	1.99	0.48	[26]
ITQ-27 (sample 1)	2D, 12 MR (6.2×6.9 Å)	260	75.5	17.8	10.9	43	28.3	1.63	0.40	this work
ITQ-27 (sample 2)	2D, 12 MR (6.2×6.9 Å)	265	75.8	18.7	10.4	42.9	28.1	1.80	0.41	this work
ZSM-12	1D, 12 MR (5.6×6.0 Å)	260	72.7	16.2	9.6	44.8	29.4	1.69	0.35	[26]
ZSM-5	3D, 12 MR (5.1×5.5 Å and 5.3×5.6 Å)	260	74.4	0.2	с	59.6	37.2	0.07	0.03	[26]
At thermodynamic	I	277	I	37.8	18.5	30.6	13.1	2.04	1.29	[28]
equilibrium										
[a] DMBu stands for	dimethylbutane and MPn for methylpent	tane.								

Chem. Eur. J. 2016, 22, 4022 – 4029 www.ch



Table 3. ¹³ C NMR shifts for the diquats used in this work.	
Dibromoalkane	¹³ CNMR shifts (D ₂ O)
1,4-dibromobutane	7.56, 9.35, 21.21, 25.88, 30.17, 44.14, 124.60, 126.00, 141.89
1,5-dibromopentane	7.76, 7.82, 9.61, 22.82, 28.58, 31.42, 44.72, 124.84, 126.03, 141.95
1,6-dibromohexane	7.88, 7.95, 9.72, 25.42, 28.88, 31.51, 44.97, 124.96, 126.08, 142.01
1,8-dibromooctane	7.55, 7.59, 9.30, 25.46, 28.10, 28.76, 31.10, 44.83, 124.67, 125.70, 141.70
1,10-dibromodecane	7.66, 7.71, 9.45, 25.55, 28.21, 28.41, 28.83, 31.22, 44.92, 124.71, 125.73, 141.73

Sodium aluminate and Ludox AS-40 as an alumina and silica source: The OSDA in its hydroxide form, sodium hydroxide (if necessary), any necessary water, and sodium aluminate (Pfaltz & Bauer) were combined in a Teflon Parr reactor liner and stirred until the sodium aluminate completely dissolved. Ludox AS-40 (Aldrich) was then added and stirred until a homogenous gel was obtained. The gel pH was measured, and then the Teflon-lined Parr reactor was placed in a rotating oven at 160 °C. Molar ratios used are given in Table S2, Supporting Information.

CBV720 as an alumina and silica source: OSDA in its hydroxide form (3 mmol) was mixed with 1 M NaOH (1 g) and water was added to bring the total mass to 7 g. Then, CBV 720 HY (Zeolyst, Si/Al = 15) (1 g) was added. The solution was heated at $175 \degree$ C in a rotating oven.

CBV 760 as an alumina and silica source: OSDA in its hydroxide form (3 mmol) was mixed with 1 M NaOH (1 g) and water was added to bring the total mass to 7 g. Then, CBV 760 HY (Zeolyst, Si/Al=30) (1 g) was added. The solution was heated at 175 °C in a rotating oven.

Calcination and ammonium exchange: All products were calcined in breathing grade air. The material was heated to 150° C at 1° Cmin⁻¹, held for 3 h, then heated to 580° C at 1° Cmin⁻¹ and held for 6 h to assure complete combustion of the organic material. After calcinations, the materials produced in hydroxide media were exchanged to ammonium form using $1 \text{ M NH}_4\text{NO}_3$ (100 mL of solution per gram of catalyst) at 95 °C with stirring for 3 h, this was done a total of three times per sample. After ammonium exchange the materials were washed with water and dried in air at 100 °C.

Characterization: PXRD patterns were collected using a Rigaku Miniflex II diffractometer and $Cu_{K\alpha}$ -radiation. Liquid NMR spectra were recorded with a 500 MHz spectrometer. ¹³C, ¹⁹F, ²⁷Al, and ²⁹Si solid-state NMR were performed using a Bruker DSX-500 spectrometer (11.7 T) and a Bruker 4 mm MAS probe. The spectral operating frequencies were 500.2, 125.721, 470.7, 130.287, and 99.325 MHz for ¹H, ¹³C, ¹⁹F, ²⁷Al, and ²⁹Si nuclei, respectively. Spectra were referenced to external standards as follows: tetramethylsilane (TMS) for $^1\!H$ and $^{29}\text{Si},$ adamantane for ^{13}C as a secondary external standard relative to tetramethylsilane, CFCl₃ for ¹⁹F and 1.0 м Al(NO₃)₃ aqueous solution for ²⁷Al. Samples were spun at 14 kHz for ¹H, ¹⁹F, and ²⁷AI MAS NMR and 8 kHz for ¹³C and ²⁹Si MAS and CPMAS NMR experiments. For detection of the 27 Al signal, a short 0.5 μ s $-\pi/18$ pulse was used before FID was recorded in order to make quantitative comparison among resonances. Prior to ²⁷Al NMR analysis, the samples were hydrated by placing them in a desiccator containing a saturated aqueous solution of sodium chloride. TGA measurements were performed on a Perkin-Elmer STA 6000 instrument. Samples were heated in air to 900 °C at a rate of 10 °C min⁻¹. The micropore volume of the proton form of the zeolites was determined from nitrogen adsorption measurements using a Micromeritics Tristar 3000. All samples were heated at 400 °C in nitrogen for 24 h and then degassed for 0.5 h prior to measurement. SEM images were acquired on a ZEISS 1550 VP FESEM, equipped with in-lens SE. EDS spectra were acquired with an Oxford X-Max SDD X-ray Energy Dispersive Spectrometer system.

Hydroisomerization of *n*-hexane: The hydroisomerization of *n*-hexane was used as a catalytic test reaction to investigate the catalytic properties of ITQ-27. Each NH₄-ITQ-27 sample was loaded with 0.27 wt.% Pd via ion exchange. The 24–42 Tyler mesh (0.35–0.71 mm) particles of the calcined catalysts were used for the catalytic experiments. The reactions were carried out in a flow-type fixed bed reactor with pure *n*-hexane as a feed at temperatures between 170 and 310 °C, pressure of 1480 kPa, LHSV (Liquid Hourly Space Velocity) of 1 h⁻¹ and molar H₂ to *n*-hexane ratio of 6:1. More details about the catalyst preparations and pretreatment and catalytic testing are described in our previous publications.^[26,27]

Each experiment was started at 170 °C and the reaction temperature was then incrementally increased by 5.6 °C (=10°F) toward an end temperature of up to 310 °C. At least five data points for each temperature were collected to make sure that the results were reproducible and the catalyst was stable. The products were analyzed by online GC every hour. Each GC analysis took ~45 min to be sure that all the peaks (C₁–C₅ cracking products as well as 2,2dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, and *n*-hexane) were well separated in GC analysis. In addition, we also ran the experiment at the maximum isomer yield overnight, which is the best way to confirm the catalyst stability.

Acknowledgements

We would like to thank Chevron Energy Technology Company for providing funding for this work. J.E.S. would like to thank the NDSEG for their support through a fellowship. We would like to thank Dr. S. Hwang (Caltech) for his assistance with NMR data collection.

Keywords: heterogeneous catalysis • hydrothermal synthesis • isomerization • microporous materials • zeolites

- C. Baerlocher, L. B. Mccusker, "Database of Zeolite Structures, http:// www.iza-structure.org/databases/. Accessed December 8, 2014.," 2014.
- [2] M. Moliner, C. Martínez, A. Corma, Angew. Chem. Int. Ed. 2015, 54, 3560–3579; Angew. Chem. 2015, 127, 3630–3649.
- [3] Three-letter framework type codes for all zeolites mentioned in the text are given in parentheses.
- [4] S. I. Zones, Microporous Mesoporous Mater. 2011, 144, 1-8.
- [5] W. Vermeiren, J.-P. Gilson, Top. Catal. 2009, 52, 1131-1161.
- [6] J. Li, A. Corma, J. Yu, Chem. Soc. Rev. 2015, 44, 7112-7127.
- [7] Z. Wang, J. Yu, R. Xu, Chem. Soc. Rev. 2012, 41, 1729-1741.

Chem. Eur. J. 2016, 22, 4022 – 4029



CHEMISTRY A European Journal Full Paper

- [8] M. E. Davis, Chem. Mater. 2014, 26, 239-245.
- [9] M. E. Davis, R. F. Lobo, Chem. Mater. 1992, 4, 756-768.
- [10] A. Corma, J. Catal. 2003, 216, 298–312.
- [11] J. Jiang, J. Yu, A. Corma, Angew. Chem. Int. Ed. 2010, 49, 3120-3145; Angew. Chem. 2010, 122, 3186-3212.
- [12] D. W. Lewis, C. M. Freeman, C. R. A. Catlow, J. Phys. Chem. 1995, 99, 11194–11202.
- [13] D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas, G. J. Hutchings, *Nature* **1996**, *382*, 604–606.
- [14] D. W. Lewis, G. Sankar, J. K. Wyles, J. M. Thomas, C. R. A. Catlow, D. J. Willock, Angew. Chem. Int. Ed. Engl. 1997, 36, 2675–2677; Angew. Chem. 1997, 109, 2791–2793.
- [15] M. Moliner, P. Serna, A. Cantín, G. Sastre, M. J. Díaz-Cabañas, A. Corma, J. Phys. Chem. C 2008, 112, 19547 – 19554.
- [16] J. E. Schmidt, M. W. Deem, M. E. Davis, Angew. Chem. Int. Ed. Angew. Chem. Int. Ed. 2014, 53, 8372–8374; Angew. Chem. 2014, 126, 8512– 8514.
- [17] D. L. Dorset, G. J. Kennedy, K. G. Strohmaier, M. J. Diaz-Cabañas, F. Rey, A. Corma, J. Am. Chem. Soc. 2006, 128, 8862-8867.
- [18] A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, F. Rey, G. Sastre, K. G. Strohmaier, J. Am. Chem. Soc. 2008, 130, 16482 – 16483.

- [19] Y. Li, J. Yu, Chem. Rev. 2014, 114, 7268-7316.
- [20] M. Moliner, F. Rey, A. Corma, Angew. Chem. Int. Ed. 2013, 52, 13880– 13889; Angew. Chem. 2013, 125, 14124–14134.
- [21] C. Jo, S. Lee, S. J. Cho, R. Ryoo, Angew. Chem. Int. Ed. 2015, 54, 12805– 12808; Angew. Chem. 2015, 127, 12996–12999.
- [22] A. Corma, M.-J. Diaz-Cabañas, F. Rey, K. G. Strohmaier, D. L. Dorset, U. S. Pat. 7,527,782, 2006.
- [23] J. E. Schmidt, D. Xie, T. Rea, M. E. Davis, *Chem. Sci.* 2015, *6*, 1728–1734.
 [24] J. E. Schmidt, D. Xie, M. E. Davis, *J. Mater. Chem. A* 2015, *3*, 12890–
- 12897.
- [25] J. E. Schmidt, D. Xie, M. E. Davis, Chem. Sci. 2015, 6, 5955-5963.
- [26] C. Y. Chen, X. Ouyang, S. I. Zones, S. A. Banach, S. A. Elomari, T. M. Davis, A. F. Ojo, *Microporous Mesoporous Mater.* 2012, 164, 71–81.
- [27] S. Smeets, L. B. McCusker, C. Baerlocher, D. Xie, C. Chen, S. I. Zones, J. Am. Chem. Soc. 2015, 137, 2015–2020.
- [28] D. R. Stull, E. F. Westrum, G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, NY, 1969.

Received: November 23, 2015 Published online on February 2, 2016