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Synthesis, characterization, and catalytic properties of zeolites IM-5 and NU-88

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Abstract

The synthesis, characterization, and catalytic properties of two high-silica zeolites IM-5 and NU-88, whose structures still remain unresolved, are presented. When the 1,5-bis(*N*-methylpyrrolidinium)pentane and 1,6-bis(*N*-methylpyrrolidinium)hexane cations are used as organic structure-directing agents, respectively, crystallization of pure IM-5 and NU-88 was possible only from synthesis mixtures with a narrow range of SiO₂/Al₂O₃ and NaOH/SiO₂ ratios. The overall characterization results of this study strongly suggest that IM-5 is a new multidimensional large-pore zeolite, whereas NU-88 is a nanocrystalline material that could be an intergrowth of several hypothetical polymorphs in the beta family of zeolites. Despite its nanocrystalline nature, however, no detectable extraframework Al species were found to exist in H–NU-88, revealing excellent thermal stability. H–IM-5 and H–NU-88 both exhibit a very high 1-butene conversion compared to H–ZSM-35 over the period of time studied here, whereas the opposite holds for the formation of isobutene. This reveals that their pore topologies are large enough to allow undesired side reactions such as 1-butene dimerization followed by cracking to light olefins. They also show the initial *n*-octane cracking activity comparable to that on H–ZSM-5. However, a notable decrease in *n*-octane conversion on these two zeolites with increasing time on stream is observed. When the isomerization and cracking activities of all zeolites employed in this study are correlated with their coke-forming propensities, it can be concluded that both materials present a shape-selective character falling within the category of multidimensional, large-pore zeolites.

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1. Introduction

Since the first introduction of zeolites as solid acid catalysts by Mobil in the early 1960s, the use of this important class of microporous materials has continued to grow remarkably in the petrochemical and refining industries [1,2]. Indeed, the success of zeolites as commercial catalysts is largely due to the steady discovery of materials with novel pore topologies and thus new shape-selective properties that have offered valuable opportunities in developing new process technologies, as well as in improving the existing processes. Therefore, detailed knowledge of the physico-

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chemical and catalytic properties of newly discovered zeolites, together with their structure elucidation, is of fundamental importance in finding the successful industrial application of these materials.

IM-5 and NU-88 are two new, high-silica zeolites that have recently been reported by Benazzi et al. [3,4] and Casci et al. [5], respectively. Although the framework structures of these synthetic zeolites still remain undetermined, recent results from various catalytic test reactions have suggested that both materials may either contain the twodimensional pore system with two intersecting 10-ring channels or the one-dimensional pore system consisting of 10ring channels with large internal cavities [4–8]. If such is the case, they should be potentially useful as shapeselective catalysts in many hydrocarbon conversions, especially in isomerization, alkylation, and/or cracking of

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hydrocarbons catalyzed by medium-pore zeolites. According to the initial patents for IM-5 and NU-88, on the other hand, the synthesis of both materials include the use of diquarternary alkylammonium cations with formula $(C_5H_{11})N^+(CH_2)_nN^+(C_5H_{11})$ with n = 5 and 6, respectively [3,5], which are formed of two 1-methylpyrrolidinium groups connected by the polymethylene bridging unit. It has been repeatedly shown that the phase selectivity of zeolite syntheses in the presence of such flexible, linear organic cations as structure-directing agents (SDAs) is sensitive not only to the length of the central alkyl chain and the nature of the groups on the ammonium ion employed but also to the oxide composition of synthesis mixtures [9-14]. This has stimulated us to investigate the synthetic details on how to prepare zeolites IM-5 and NU-88 using the 1,5-bis(N-methylpyrrolidinium)pentane and 1,6bis(N-methylpyrrolidinium)hexane cations from synthesis mixtures having different oxide compositions, respectively.

In this paper we describe our attempts to synthesize pure IM-5 and NU-88 and their physicochemical properties that have been extensively characterized by using a number of analytical techniques including powder X-ray diffraction, elemental and thermal analyses, transmission electron microscopy, N₂ and Ar adsorption, ¹H, ¹³C, ²⁷Al, and ²⁹Si MAS NMR, IR, Raman, temperature-programmed desorption of ammonia, and IR measurements of adsorbed pyridine. In addition, we report the catalytic properties of H-IM-5 and H-NU-88 for the skeletal isomerization of 1-butene to isobutene and the cracking of *n*-octane. The catalytic results are compared to those obtained from H-ZSM-5, H-ZSM-35, H-EU-1, H-mordenite, and H-beta zeolites, which possess structural features considerably different from one another, to gain a better understanding of their pore structures.

2. Experimental

2.1. Synthesis

The divalent 1,5-bis(*N*-methylpyrrolidinium)pentane (MPP) cation was prepared by reacting 1,5-dibromopentane (97%, Aldrich) with an excess of 1-methylpyrrolidine (97%, Aldrich) in acetone as a solvent with rapid stirring at room temperature overnight. The excess amine was removed by extraction with diethyl ether and recrystallizations were performed in methanol–diethyl ether mixtures. The 1,6-bis(*N*-methylpyrrolidinium)hexane (MPH) dibromide salt was prepared by using 1,6-dibromohexane (96%, Aldrich) instead of 1,5-dibromopentane, respectively, with procedures similar to the MPP preparation. Due to the hygroscopic nature, after purification, these two diquaternary ammonium salts were stored in a desiccator prior to their use as organic SDAs.

The synthesis of zeolites IM-5 and NN-88 in the presence of MPP and MPH cations was carried out using aluminosilicate gels prepared by combining NaOH (50% aqueous solution, Aldrich), Al(NO₃)₃ · 9H₂O (98%, Junsei), fumed silica (Aerosil 200, Degussa), and deionized water. The final composition of the synthesis mixture was $3.0R \cdot x Na_2O$. $yAl_2O_3 \cdot 30SiO_2 \cdot 1200H_2O$, where R is the organic SDA prepared here, x is varied between $7.0 \le x \le 15.0$, and y is varied between $0 \le y \le 2.0$. When necessary, NaOH was replaced by the equivalent amount of LiOH · H₂O (98%, Aldrich) or KOH (45% aqueous solution, Aldrich). After being stirred at room temperature for 24 h, the synthesis mixture was charged into Teflon-lined 45-mL autoclaves and heated to 160 °C under rotation (100 rpm) for 14 days. The solid products were recovered by filtration, washed repeatedly with water, and then dried overnight at room temperature. As-synthesized zeolites were calcined under flowing air at 550 °C for 8 h to remove the organic SDA occluded. The calcined samples were then refluxed twice in NH₄NO₃ solutions for 6 h followed by calcination at 550 °C for 8 h to ensure that they were completely in their proton form. If required, the resulting solids were subsequently heated under flowing air at 600–800 °C for 4 h.

For comparison, ZSM-35 (SiO₂/Al₂O₃ = 27) and EU-1 (SiO₂/Al₂O₃ = 40) were prepared and converted into their proton form according to the procedures described elsewhere [15,16]. In addition to these zeolites, NH₄–ZSM-5 (SiO₂/Al₂O₃ = 27), H–mordenite (SiO₂/Al₂O₃ = 33), and NH₄–beta (SiO₂/Al₂O₃ = 25) were obtained from ALSI-PENTA Zeolithe, Tosoh, and PQ, respectively.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Miniflex or a Rigaku 2500H diffractometer with Cu-K_{α} radiation. Elemental analysis was carried out by the Analytical Laboratory of the Korea Institute of Science and Technology. Thermogravimetric analyses (TGA) were performed in air on a TA Instruments SDT 2960 thermal analyzer, where weight loss related to the combustion of organic SDA was determined from differential thermal analyses (DTA) using the same analyzer. Approximately 15 mg of sample was used at a heating rate of 10 °C min⁻¹. Crystal morphology and size were determined by a JEOL JSM-6300 scanning electron microscope (SEM) or a Carl Zeiss EM912 OMEGA transmission electron microscope (TEM). The Ar and N₂ sorption experiments were performed on a Micromeritics ASAP 2010 analyzer.

The ²⁹Si MAS NMR spectra were measured on a Bruker DSX 400 spectrometer at a spinning rate of 12.0 kHz. The operating ²⁹Si frequency was 79.492 MHz, and the spectra were obtained with an acquisition of ca. 800 pulse transients, which were repeated with a $\pi/5$ rad pulse length of 2.0 µs and a recycle delay of 60 s. The ²⁹Si chemical shifts are referenced to TMS. The ²⁷Al MAS NMR spectra were recorded on the same spectrometer with a spinning rate of 13.0 kHz at a ²⁷Al frequency of 104.269 MHz. The spectra were obtained with an acquisition of 2048 pulse transients, which were repeated with a $\pi/20$ rad pulse length of 0.5 µs

and a recycle delay of 1 s. The ²⁷Al chemical shifts are referenced to an Al(H₂O)₆³⁺ solution. The ¹H MAS NMR spectra at a spinning rate of 13.0 kHz were recorded at a proton Larmor frequency of 400.146 MHz with a $\pi/5$ rad pulse length of 2.0 µs, a recycle delay of 3 s, and an acquisition of 32 pulse transients. The ¹H–¹³C CP MAS NMR spectra at a spinning rate of 4.5 kHz were recorded at a ¹³C frequency of 100.623 MHz with a $\pi/2$ rad pulse length of 5.0 µs, a contact time of 1 ms, and a recycle delay of 3 s. Approximately 6500 scans were accumulated. Both ¹H and ¹³C chemical shifts are reported relative to TMS.

The IR spectra in the structural region were measured on a Nicolet Magna 550 FT-IR spectrometer using the KBr pellet technique. The IR spectra in the OH region were measured on the same spectrometer using self-supporting zeolite wafers of approximately 12 mg (1.3-cm diameter). Prior to IR measurements, the zeolite wafers were pretreated under vacuum at 500 °C for 2 h inside a home-built IR cell with CaF2 windows. For IR spectroscopy with adsorbed pyridine, the activated self-supporting wafer was contacted with a pyridine-loaded flow of dry He at room temperature, evacuated $(10^{-3}$ Torr) to remove physisorbed pyridine, and then heated at different temperatures. The Raman spectra were recorded on a Bruker RFA 106/S FT-Raman spectrometer equipped with a Nd:YAG laser operating at 1064 nm. The samples were exposed to a laser power of 200 mW at the spectral resolution of 2 cm⁻¹. Typically, 1024 scans were accumulated for obtaining the Raman spectra and 256 scans for the IR spectra. Temperatureprogrammed desorption (TPD) of ammonia was recorded on a fixed-bed, flow-type apparatus attached to a Balzers QMS 200 quadruple mass spectrometer, following the procedure described in our previous work [13].

2.3. Catalysis

All the catalytic experiments were conducted under atmospheric pressure in a continuous-flow apparatus with a fixed-bed microreactor. Prior to the experiments, the catalyst was routinely activated under flowing He (50 cm³ min⁻¹) at 500 °C for 1 h and kept at the desired temperature to establish a standard operating procedure, allowing time for the product distribution to stabilize. In the skeletal isomerization of 1-butene, a reactant stream with a He/ 1-butene molar ratio of 9.0 was fed into a quartz reactor containing 0.1 g of zeolite catalyst at 400 °C. The total gas flow at the reactor inlet was kept constant at 50 cm³ min⁻¹. The reaction products were analyzed online in a Chrompack CP 9001 gas chromatograph equipped with an Al₂O₃/KCl Plot capillary column (0.53 mm \times 50 m) and a flame ionization detector (FID), with the first analysis carried out after 10 min on stream. Conversion was calculated in terms of the mole percent of 1-butene, and selectivity to isobutene was calculated by dividing the isobutene yield by the 1-butene conversion. In the cracking of *n*-octane, a reaction stream with a fixed partial pressure of n-octane

(2.0 kPa) was passed over the same microreactor with 0.1 g of catalyst at 310–500 °C. In the absence of a catalyst, no conversion of *n*-octane was observed, even at 500 °C. He was used as a carrier gas with *n*-octane as a feed, and the total gas flow was fixed to 50 cm³ min⁻¹. The cracked products were analyzed online in a Chrompack CP 9001 gas chromatograph. Gaseous products with $< C_4$ were separated in a packed Porapak Q column (1/8 in. × 1.8 m) and analyzed in a thermal conductivity detector (TCD). Gaseous and liquid products with $\geq C_4$ were separated in a capillary PONA column (0.25 mm × 100 m) and analyzed in an FID. Conversion and selectivity to each product were calculated following the methods described elsewhere [13].

3. Results and discussion

3.1. Synthesis

Table 1 lists the results from syntheses using MPP as an organic SDA and aluminosilicate gels with different oxide compositions under the conditions described above. In each case, the zeolitic products listed were the only ones obtained in repeated trials. The powder XRD patterns of three IM-5 zeolites with different SiO_2/Al_2O_3 ratios in the as-synthesized form, which were obtained from runs 3, 1, and 5 in Table 1, respectively, are shown in Fig. 1. The positions and relative intensities of all the X-ray peaks from these IM-5 samples are in good agreement with those reported in the literature [3,6].

Table 1

Representative products obtained using 1,5-bis(N-methylpyrrolidinium)-pentane (MPP) as an organic SDA^a

Run	Gel com	position	Product ^b
	SiO_2/Al_2O_3	NaOH/SiO ₂	
1	60	0.73	IM-5
2	15	0.73	Analcime + IM-5
3	30	0.73	IM-5
4	40	0.73	IM-5
5	120	0.73	IM-5
6	240	0.73	Mordenite
7	∞	0.73	L ^c
8	60	1.00	Analcime
9	60	0.87	Mordenite + Analcime
10	60	0.60	Analcime + IM-5
11	60	0.47	ZSM-12
12	60	0.33	ZSM-12
13	60	0.73 ^d	ZSM-12
14	60	0.73 ^e	Mordenite

^a The oxide composition of the synthesis mixture is 4.5R:xNa₂O: yAl₂O₃:30SiO₂:1200H₂O, where *R* is organic SDA, *x* is varied between $5.0 \le x \le 15.0$, and *y* is varied between $0 \le y \le 2.0$. All the syntheses were carried out under rotation (100 rpm) at 160 °C for 14 days.

^b The phase appearing first is the major phase.

^c Unknown, probably layered material.

^d LiOH/SiO₂ ratio.

^e KOH/SiO₂ ratio.



Fig. 1. Powder XRD patterns of IM-5 and NU-88 zeolites prepared here: (a) IM-5(I), (b) IM-5(II), (c) IM-5(III), and (d) NU-88 in the as-synthesized form.

It can be seen from Table 1 that the oxide composition range yielding pure IM-5 in the presence of MPP is rather narrow. When the NaOH/SiO2 ratio in the synthesis mixture was fixed to 0.73, for example, the SiO₂/Al₂O₃ ratio leading to the successful IM-5 formation was found to be in the range 30-120. When using sodium aluminosilicate gels with $SiO_2/Al_2O_3 < 30$, however, we always obtained a mixture of analcime and IM-5, where the former material was the major phase from the gel with a lower SiO_2/Al_2O_3 ratio. In addition, mordenite was the phase that crystallized from the synthesis mixture with $SiO_2/Al_2O_3 = 240$ under the conditions described above. When the initial SiO₂/Al₂O₃ ratio in the synthesis mixture was fixed to 60, on the other hand, ZSM-12 with the one-dimensional 12-ring pore system was the phase formed from synthesis mixtures with NaOH/SiO₂ ≤ 0.5 . In contrast, the synthesis using aluminosilicate gels with NaOH/SiO₂ ≥ 0.8 again yielded mordenite or analcime rather than IM-5. These results indicate that the presence of Na⁺ ions with a certain level of concentration in the synthesis mixture, together with the organic MPP, is the major factor determining the phase selectivity of the crystallization. Therefore, it appears that the structure-directing ability of MPP itself is not strong enough to govern the crystallization of IM-5. We also note that the replacement of NaOH with the equivalent amount of LiOH under the conditions where the crystallization of IM-5 proved to be highly reproducible yielded ZSM-12, whereas the use of KOH gave mordenite that could also be prepared without using any organic SDA. This is not unexpected because the strong influence of the type of alkali metal cations on the product selectivity in zeolite syntheses is frequently observed, even in the presence of organic additives [12,13,17].

According to the original patent on the synthesis of IM-5 [3], on the other hand, this zeolite is claimed to crystallize in the presence of MPH, as well as MPP. Thus, we have carried out the synthesis using MPH, instead of MPP, as an organic SDA, under the conditions where the optimized gel $(SiO_2/Al_2O_3 = 60 \text{ and } NaOH/SiO_2 =$ 0.73) was employed. The powder XRD pattern of the solid obtained from this synthesis run is given in Fig. 1d. Notice that the positions and relative intensities of the observed X-ray peaks are notably different from those of any of the three IM-5 zeolites prepared here. For example, several peaks of medium intensity in the region $12^{\circ} \leq 2\theta \leq 18^{\circ}$ are present in IM-5 but absent in product synthesized with MPH. In particular, all the X-ray peaks of this solid are not well resolved compared to those of IM-5, despite the fact that their XRD patterns were measured with identical scan parameters. A comparison with the XRD patterns of zeolitic materials available in the literature reveals that the relative peak intensities and positions of the solid from the MPH-mediated synthesis is exactly the same as those of zeolite NU-88 recently patented by Casci et al. [5]. It should also be noted that the XRD pattern of NU-88 is similar to that of ITO-10 with some differences, one of recently reported intergrowths of several hypothetical polymorphs in the beta family of zeolites [18]. This led us to speculate that NU-88 may fall into the structural regime of largepore materials, although additional information regarding its pore topology cannot be readily obtained from its XRD pattern due to the very broad nature of X-ray peaks. Like those to IM-5, the reported synthesis routes to NU-88 also include the use of MPP and MPH as organic SDAs [5]. When MPP is used as a SDA, however, our attempts to reproduce the synthesis of this zeolite under the reported conditions were not successful: a mixture of IM-5 and analcime, instead of NU-88, was produced. The same result was observed from syntheses using aluminosilicate gels with a wide range of SiO₂/Al₂O₃ and NaOH/SiO₂ ratios (see Table 1). There is a large volume of work on the use of flexible diquaternary alkylammonium cations with aliphatic and/or cyclic moieties in the synthesis of zeolites and related materials, and it has been repeatedly shown that the phase selectivity of the crystallization depends highly on the length of the spacing alkyl chain and on the size and shape of the alkylammonium moieties [9–14]. We believe that this is the case for the synthesis of IM-5 and NU-88.

A summary of products from syntheses in the presence of MPH as an organic SDA is listed in Table 2. These data reveal that the SiO_2/Al_2O_3 ratio range of synthesis mixtures leading to pure NU-88 formation is much narrower than that found in the crystallization of IM-5. However, the general trend drawn from Table 2 is quite similar to that observed

Table 2 Representative products from syntheses using 1,6-bis(*N*-methyl-pyrrolidinium)hexane (MPH)^a

Run	Gel com	Product ^b	
	SiO_2/Al_2O_3	NaOH/SiO2	
15	60	0.73	NU-88
16	15	0.73	Mordenite
17	30	0.73	Mordenite
18	40	0.73	Mordenite
19	120	0.73	Mordenite + NU-88
20	240	0.73	D ^c
21	∞	0.73	D ^c
22	60	1.00	Mordenite
23	60	0.87	Mordenite
24	60	0.60	ZSM-12
25	60	0.47	ZSM-12
26	60	0.33	ZSM-12
27	60	0.73 ^d	D ^c
28	60	0.73 ^e	D ^c

 $^{\rm a}$ The synthesis conditions and oxide composition of the synthesis mixtures used are the same as those in Table 1.

^b The phase appearing first is the major phase.

^c Unknown, probably dense material.

^d LiOH/SiO₂ ratio.

^e KOH/SiO₂ ratio.

for the MPP-mediated synthesis of IM-5 in that MPH can also produce more than one zeolite structure (i.e., mordenite, ZSM-12, and NU-88), depending on the oxide composition of synthesis mixtures. The TGA/DTA curves (not shown) of as-synthesized mordenite and ZSM-12 clearly show the existence of MPH in their pores, where the decomposition pattern of the occluded organic SDA differs significantly according to the zeolite structure. A similar result was also obtained from IM-5, mordenite, and ZSM-12 prepared with MPP. This implies that the flexible organic cations (i.e., MPP and MPH) occluded within the voids of these three different products may adopt conformations distinctly different from one another, due to the difference in geometrical restrictions imposed by the particular framework topology of each zeolite. Very recently, we performed variabletemperature ¹H combined rotation and multiple-pulse spectroscopy (CRAMPS) and ²H NMR measurement on the ethylene glycol molecules in two sodalites with SiO₂/Al₂O₃ ratios of ∞ and ca. 10 [19]. The conformations of the encapsulated ethylene glycol molecules in these two materials were maintained even at 200 °C, which is higher than the crystallization temperature (175 °C) of the zeolite host, because the intermolecular hydrogen bonds between the framework oxygens and the OH groups of the encapsulated ethylene glycol, which appear only in the Al-substituted zeolite, are strong enough to overcome the thermal energy available at 200 °C. This strongly suggests that both conformations of ethylene glycol are actually relevant ones acting as SDAs at the nucleation stage in aluminosilicate and puresilica gels, respectively, which cannot happen without notable differences in the hydrogen-bonding interactions we proved, and more likely in the electrostatic interactions with the surrounding inorganic species at the crystallization temperature in these two synthesis mixtures. The synthesis results in Tables 1 and 2 demonstrate that there is a reasonable amount of lattice charge in the synthesis mixture, together with a certain level of Na⁺ concentration, in the crystallization of IM-5 and NU-88 using MPP and MPH, respectively. In our view this may make it possible to considerably differ the conformation of MPP or MPH from that in the synthesis mixture with a particular range of oxide compositions yielding the other zeolitic phase because the number of conformations available to such flexible organic SDAs and their geometric differences must be much larger than those for ethylene glycol or rigid polycyclic molecules with similar C/N⁺ values. In this regard, the synthesis results presented so far support our recent proposal [14,19] that the control of conformations of flexible, hydrophilic organic SDAs such as linear diquaternary alkylammonium ions with aliphatic and/or cyclic moieties by varying the concentrations of inorganic components in zeolite synthesis mixtures may be an area of considerable possibility for finding new materials.

3.2. Characterization

The powder XRD patterns (not shown) of the proton form of three IM-5 zeolites with different SiO₂/Al₂O₃ ratios and one NU-88 zeolite (i.e., the materials obtained from runs 3, 1, and 5 in Table 1 and run 15 in Table 2, respectively) agree well with those of the as-synthesized form of the corresponding materials given in Fig. 1, except the minor change in relative X-ray peak intensities and positions. This reveals that all IM-5 and NU-88 zeolites prepared here maintain their structures during the initial calcination at 550 °C to remove the organic SDAs occluded and the subsequent NH4+ ion exchange and calcination steps, which can be further supported by the N2 adsorption data (vide infra). The powder XRD pattern of the H-IM-5(II) sample was found to be successfully indexed on an orthorhombic cell, with a = 19.972(2) Å, b = 19.073(3) Å, and c = 14.172(2) Å, as given by Le Bail [20] profile matching in the space group Pnnm, which satisfactorily accounts for the systematically absent reflections. It is interesting to note here that these values are quite similar to those of ZSM-5 with the b and c parameters a little shorter and longer, respectively [21], although this does not mean that the framework topology of IM-5 is closely related to that of ZSM-5. We are carrying out the structure determination of IM-5 using synchrotron powder XRD and high-resolution TEM data, and the results will be described elsewhere. Due to the very broad feature of the X-ray peaks of NU-88, on the other hand, we were not able to reasonably index its XRD pattern. The chemical compositions of IM-5 and NU-88 zeolites prepared here, which were determined from a combination of elemental and thermal analyses, are given in Table 3. A considerable dissimilarity between the amount of Al and the sum of organic and alkali cations compensating for framework

Table 3 Chemical compositions of IM-5 and NU-88 zeolites prepared in this study^a

Zeolite	Run ^b	SiO ₂ / Al ₂ O ₃	$R^{c}/Al_{2}O_{3}$	Na_2O/Al_2O_3	$\frac{(R^{c} + Na_{2}O)}{Al_{2}O_{3}}$
IM-5(I)	3	18.8	0.84	0.41	1.25
IM-5(II)	1	25.3	1.24	0.28	1.52
IM-5(III)	5	32.2	1.28	0.17	1.45
NU-88	15	25.6	1.65	0.15	1.80

^a Determined from a combination of elemental and thermal analyses.

^b The same as the run numbers in Tables 1 and 2.

^c Doubly charged MPP and MPH cation.

charges is observed for all four zeolites. It thus appears that part of the N-methylpyrrolidinium moieties of the organic SDAs occluded within these materials exists in the form of bromide or hydroxide to serve as space-filling species rather than as charge-compensating cations. The data in Table 3 also show an enrichment of Al in all products with respect to their synthesis mixtures. This trend is more apparent to IM-5 zeolites obtained from synthesis mixtures with higher SiO₂/Al₂O₃ ratios, which allowed us to obtain IM-5 as a pure phase only at a very narrow range [19-32] of SiO₂/Al₂O₃ ratios under the synthesis conditions described above. Because the SiO₂/Al₂O₃ ratio (25.3) of the IM-5(II) sample is essentially the same as that (25.6) of NU-88, on the other hand, we have mainly used the characterization results from this IM-5 sample in comparison with the physicochemical properties of NU-88. For convenience sake, therefore, we will refer to the IM-5(II) sample simply as IM-5 from now on (unless otherwise stated).

Fig. 2 shows the TGA/DTA curves for as-synthesized IM-5 and NU-88. Zeolite IM-5 gives four stages of weight loss: 25-250, 250-440, 440-550, and 550-700 °C. The first loss is endothermic and can be assigned to the desorption of water. The other losses are accompanied by three exotherms around 420, 490, and 610 °C, respectively. Thus, they must be from the thermal decomposition of MPP. As seen in Fig. 2, by contrast, the decomposition of MPH in NU-88 is characterized by four weight losses at 250-340, 340-440, 440-530, and 530-700 °C that have distinct exothermic peaks in the DTA. We note here that the overall organic



Fig. 3. Pore size distribution curves for (a) H–IM-5 and (b) H–ZSM-5 calculated from their Ar adsorption isotherms using the Horvath–Kawazoe formalism. The inset shows the adsorption branch isotherms of the corresponding zeolites.

content (21.0 wt%) in NU-88 is approximately one and half times as large as that (14.7 wt%) in IM-5. The TGA/DTA curves (not shown) of both H–IM-5 and H–NU-88 gave no detectable exothermic peaks in the temperature region higher than 550 °C. This indicates that their hightemperature weight loss is not due to dehydroxylation of Brønsted acid sites, but is probably due to oxidation of products arising from incomplete combustion of organic SDAs below 550 °C.

The pore size distribution (PSD) curves of H–IM-5 and H–NU-88 calculated from their Ar adsorption isotherms using the Horvath–Kawazoe (HK) formalism [22] are shown in Figs. 3 and 4, respectively. Included for comparison are the curves for H–ZSM-5 and H–beta with a similar SiO_2/Al_2O_3 ratio (~ 25). The PSD curve for H–ZSM-5 with two intersecting 10-ring channels is characterized by one sharp maximum at 5.2 Å. As seen in Fig. 3, however, the curve for H–IM-5 shows signs of two components in the micropore size region: one feature around 5.3 Å and the other component around 5.9 Å. Notice that these values are quite similar to the effective sizes observed for the



Fig. 2. TGA/DTA curves for as-synthesized (a) IM-5 and (b) NU-88.



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Fig. 4. Pore size distribution curves for (a) H–NU-88 and (b) H–beta calculated from their Ar adsorption isotherms using the Horvath–Kawazoe formalism. The inset shows the adsorption branch isotherms of the corresponding zeolites.

medium-pore H–ZSM-5 and the large-pore H–beta zeolites, respectively. This led us to first postulate that IM-5 could contain a dual-pore system of two different sizes, one type of micropores with an effective size virtually identical to either the straight 10-ring or the sinusoidal 10-ring channels in ZSM-5 and the other type of pores whose size may rank this new zeolite in the structural regime of large-pore (i.e., 12ring) materials. If such is not the case, the other possibility could be that the IM-5 structure has two types of 12-ring pores in which one of them is very elliptical. The presence of two types of pores with different effective sizes in H-IM-5 can also be achieved by comparing the Ar adsorption isotherm of this zeolite with that of H-ZSM-5. As seen in Fig. 3, the pores in both materials start to fill up at a relative pressure of $P/P_0 \sim 5 \times 10^{-6}$. Unlike H–ZSM-5, however, H-IM-5 gives a second inflection point in the vicinity of $P/P_0 = 5 \times 10^{-4}$, which can be assigned to the filling of large 12-ring pores. On the other hand, H-NU-88 has essentially the same PSD curve as that of H-beta (Fig. 4). Also, no detectable differences in the Ar adsorption isotherm are observed for these two zeolites. Recent studies on the catalytic properties of IM-5 and NU-88 have suggested that both materials may contain either the two-dimensional pore system with two intersecting 10-ring channels or the onedimensional pore system consisting of 10-ring channels with large internal cavities [4-8]. Taking into account the PSD curves in Figs. 3 and 4, however, it is clear that these two zeolites with unknown framework structures cannot be regarded as medium-pore 10-ring materials. In our view, IM-5 may contain a multidimensional large-pore system with intersecting 12- and 10-ring windows, although the presence of strongly elliptical 12-ring pores, instead of 10ring pores, in this zeolite cannot be completely ruled out. In addition, it appears that NU-88 is a large pore material that could belong to the beta family of zeolites, as suggested above.

Table 4
N2 sorption data for various zeolites studied here

Zeolite	Run ^a	SiO ₂ / Al ₂ O ₃ ratio	BET surface area $(m^2 g^{-1})$	Micropore volume ^b (cm ³ g ⁻¹)	Mesopore volume ^c (cm ³ g ⁻¹)
H–IM-5(I)	3	18.8	375	0.14	0.06
H-IM-5(II)	1	25.3	460	0.18	0.11
H-IM-5(III)	5	32.2	559	0.22	0.26
As-syn. NU-88	15	25.6	97	0.04	0.34
H-NU-88	15	25.6	622	0.24	0.50
H-ZSM-5		27.0	398	0.14	0.02
H–beta		25.0	571	0.22	0.29

^a The same as the run numbers in Tables 1 and 2.

^b In the diameter range ≤ 20 Å.

 $^{\rm c}$ In the 20- to 500-Å diameter range. Calculated using the BJH formalism.

Table 4 shows the N₂ adsorption data for the proton form of all IM-5 and NU-88 zeolites prepared here. The H-IM-5(I) sample, which has the highest Al content among the three IM-5 zeolites prepared in this work, exhibits a BET surface area of $375 \text{ m}^2 \text{ g}^{-1}$. This value agrees well with that reported for this zeolite [7]. As seen in Table 4, however, the measured BET surface area increases remarkably with decreasing Al content in the zeolite. As a result, the BET surface area $(559 \text{ m}^2 \text{ g}^{-1})$ of the H–IM-5(III) with the lowest Al content was found to be approximately one and half times as large as that of the H-IM-5(I) sample. The same trend can be observed from the micropore volumes of these three IM-5 zeolites. Even in zeolites with the same framework structure and composition, on the other hand, their micropore volumes can differ considerably according to the procedure employed in the calculation [23]. Because the N₂ adsorption isotherms of all IM-5 and NU-88 prepared here is not flat at high relative pressures, we calculated their micropore volumes from the volumes of the adsorbed N₂ at $P/P_0 = 0.1$, corresponding to the pore diameter of ca. 20 Å. Table 4 shows that the H-IM-5(I) sample has a micropore volume of 0.14 $\text{cm}^3 \text{g}^{-1}$, which is quite similar to the reported value $(0.13 \text{ cm}^3 \text{ g}^{-1})$ [7], whereas the H–IM-5(II) and H– IM-5(III) samples exhibit considerably higher micropore volumes (i.e., 0.18 and 0.22 $\text{cm}^3 \text{g}^{-1}$, respectively). The ²⁷Al MAS NMR spectra of all H-IM-5 zeolites prepared here show a resonance around 0 ppm (vide infra), indicating the formation of extraframework Al species during the calcination and exchange steps. Because this ²⁷Al resonance did not appear in the spectra of their as-synthesized form, however, the observed increase in micropore volume for lower Al contents cannot be due to differences in the crystallinity. Furthermore, no noticeable differences in the intensity ratio of the two ²⁷Al resonances due to tetrahedral and octahedral Al species for the three H-IM-5 zeolites were found. Then, it can be expected that the amount of extraframework Al species formed should be smaller for the zeolite with a lower Al content, leading to a less serious pore blockage and thus to an increase in micropore volume. This seems to be a sensible hypothesis, if the IM-5 structure



Fig. 5. TEM photographs of as-synthesized (a) IM-5 and (b) NU-88.

is not a three-dimensional 12-ring pore system but a dualpore system of intersecting 12- and 10-ring windows. On the other hand, the micropore volume of H–NU-88 was calculated to be 0.24 cm³ g⁻¹ which, in principle, makes this zeolite to fall into the microporosity range of largepore zeolites. Table 4 also lists the micropore volumes of H–ZSM-5 and H–beta obtained from the adsorbed volumes at $P/P_0 = 0.1$. The values obtained in this work are in good agreement with those typically reported for these two zeolites [6,24], supporting the reliability of the micropore volumes of the H–IM-5 and H–NU-88 zeolites measured in this study. In parallel with the PDS data from Ar adsorption experiments, therefore, it is clear that both materials are large-pore materials rather than medium-pore ones.

Fig. 5 shows the TEM pictures of IM-5 and NU-88 zeolites synthesized in this study. IM-5 consists of needlelike crystallites approximately 0.6-1.0 µm in length and less than 0.1 µm in diameter. It should be noted here that the aspect ratio of IM-5 crystallites considerably decreases with decreasing Al content in the zeolite, although IM-5 can be obtained as a pure phase only in a narrow range of SiO₂/Al₂O₃ ratios (vide ante). As a result, most of the H-IM-5(III) crystallites with the lowest Al content among the three IM-5 zeolites prepared here are not elongated but appear to be cuboids of $0.2 \times 0.2 \times 0.2 \ \mu m^3$. Of particular interest is the extremely small crystal size (20-30 nm) of NU-88, although we were unable to determine its accurate crystal morphology. This strongly suggests that the very broad nature of its X-ray peaks (Fig. 1d) may originate from particle size effects rather than from poor crystallinity. In fact, we have found that no detectable line narrowing in the XRD pattern of NU-88 is caused by an additional 2 weeks of heating in the crystallization medium. When the Scherrer equation with K = 1 is applied to six different reflections in the 2θ region 7–45° [25], the average crystal size was calculated to be about 30 nm, which is in good agreement with the value estimated from TEM measurements. There is growing interest in the direct synthesis of uniform, nanocrystalline zeolites

because of potential crystal size effects on many important properties of these highly porous materials, most notably their adsorption and catalytic properties. However, only a handful of fullycrystalline but nanometer-sized zeolites (sodalite, A, X, ZSM-5, L, and beta) have thus far been reported [26–29].

To further investigate the nanocrystalline nature of NU-88, we have performed N₂ adsorption measurements on its as-synthesized and proton forms. Here, the as-synthesized NU-88 material was outgassed at 100 °C under vacuum to a residual pressure of 10^{-5} Torr for 4 h before measurement. This outgassing treatment, selected upon considering the TGA/DTA results in Fig. 2, yielded no noticeable removal of the occluded organic SDAs from the pores of NU-88 because a negligible microporous adsorption capacity (0.04 cm³ g⁻¹) was observed from the as-synthesized NU-88 crystallites. The N₂ adsorption–desorption isotherms for the as-synthesized and proton forms of NU-88 are shown in Fig. 6. The isotherms of both materials possess a steep step



Fig. 6. Pore size distribution curves for the (a) as-synthesized and (b) proton forms of NU-88 calculated using the BJH formalism from the N_2 desorption branch isotherm. The inset shows the N_2 adsorption–desorption isotherms of the corresponding zeolites.

at high relative pressures, together with a clear hysteresis loop, typical of mesoporosity. The corresponding parameters of the pore structure are summarized in Table 4. Note that the as-synthesized NU-88 exhibits a mesopore volume of 0.34 cm³ g⁻¹, suggesting significant interparticle adsorption. Barrett-Joyner-Halenda (BJH) analyses [30] show that this uncalcined material has an average pore size of ~ 110 Å. An important result is that the mesoporous capacity of NU-88 increases to a very large extent during the initial calcination at 550 °C for 8 h to remove the MPH cation and the successive NH_4^+ ion exchange and calcinations steps: H–NU-88 has a mesopore volume of $0.50 \text{ cm}^3 \text{ g}^{-1}$, which is approximately twice as large as its micropore volume. Comparison of the mesopore distribution of H-NU-88 with that of its as-synthesized form reveals a large increase in mesopore size together with a broadening of the distribution, which can be attributed to sintering effects during the calcination of NU-88 and subsequent treatments. We note here that several other H-NU-88 samples obtained from different synthesis batches gave a similar mesopore volume $(0.50 \pm 0.03 \text{ cm}^3 \text{ g}^{-1})$. Because H–NU-88 presents both a large interparticle mesoporosity and a relatively large zeolitic microporosity, and an excellent thermal stability (vide infra), therefore, this nanocrystalline material could have interesting applications in some shape-selective reactions such as gas oil cracking where the reactant diffusivity depends highly on both the crystal size and mesoporosity of the zeolite catalyst employed [31]. In addition, we believe that the nanocrystalline nature of NU-88 would be of considerable advantage for other important applications, for example, the synthesis of ultra-thin zeolite films [32] and the use as photochemical hosts [33].

Fig. 7 shows the ¹H-¹³C CP MAS NMR spectra of assynthesized IM-5 and NU-88. For the sake of comparison, the liquid ¹³C NMR spectra of D₂O solutions of the MPP and MPH bromide salts are also given in Fig. 7. These data clearly show that both the MPP and MPH cations are occluded intact in IM-5 and NU-88, respectively. When the MPP cation is trapped in the IM-5 pores, however, the splitting of the methyl carbon resonance of Nmethylpyrrolidinium moieties into two peaks around 48 and 53 ppm is observed. It thus appears that the considerable change in conformation is imposed on MPP upon occlusion into the IM-5 pores, which must be closely related to the structural aspects of the zeolite host. By contrast, the MPH in NU-88 gives only one methyl carbon resonance at 49.0 ppm that is shifted slightly downfield relative to that of free MPH. The same trend is also observed for the other ¹³C NMR resonances of the occluded MPH. It thus appears that unlike the organic in IM-5, the MPH occluded in NU-88 does not experience severe geometric constraints and van der Waals interactions with the zeolite framework. This can be further supported by the fact that all the carbon resonances observed for NU-88 are considerably narrower than those from IM-5. Additional evidence for the conclusion given above can be obtained from the ¹H MAS NMR spectra of as-synthesized



Fig. 7. 13 C NMR spectra of organic SDAs, (a) MPP and (b) MPH, showing the assignment of each resonance. The bottom traces are the Bloch decay 13 C NMR spectra of D₂O solutions of the bromide form of MPP and MPH, and the top traces are the 1 H $-{}^{13}$ C CP MAS NMR spectra of as-synthesized IM-5 with MPP and MPH occluded in their pores, respectively.



Fig. 8. ¹H MAS NMR spectra of as-synthesized (a) IM-5 and (b) NU-88.

IM-5 and NU-88 in Fig. 8. The intensities between 1.0 and 3.5 ppm are due to the resonance of the protons of organic SDAs; the signals are relatively sharp for NU-88, whereas they reveal one broad peak for IM-5. This suggests that the mobility of the occluded organic SDAs is higher in NU-88 than in IM-5.

Fig. 9 shows the ²⁷Al MAS NMR spectra of the assynthesized and proton forms of IM-5 and NU-88. The spectra of the as-synthesized IM-5 and NU-88 exhibit one resonance at 51–53 ppm, typical of tetrahedral Al in the zeolite framework. No signals corresponding to octahedral Al are observed for these materials. However, the ²⁷Al MAS NMR spectrum of H-IM-5 gives a small resonance around 0 ppm, indicating that a minor part of framework Al atoms has been extracted from the IM-5 framework during the calcination and exchange steps. The same result was also observed for the other two IM-5 zeolites prepared here, i.e., the IM-5(I) and IM-5(III) samples. An interesting result obtained from Fig. 9 is that, unlike H-IM-5, H-NU-88 exhibits no additional line around 0 ppm. In fact, we found that H-NU-88 gives only one ²⁷Al resonance around 55 ppm, even after heating at 800 °C for 4 h, revealing its remarkable thermal stability. This result is important in that the nanocrystallinity has little effect on the thermal stability of NU-88, despite its relatively high Al content. As shown in Fig. 10, on the other hand, the ²⁹Si MAS NMR spectra of as-synthesized IM-5 and NU-88 are characterized by a broad resonance around -110 ppm, which is indicative of the existence of multiple T-sites in these zeolite structures. Fig. 10 also shows that the subsequent calcination and exchange treatments caused no significant changes in the ²⁹Si MAS NMR spectra of IM-5 and NU-88, whereas some dealumination in IM-5 may have occurred according to the ²⁷Al MAS NMR results.

Fig. 11 shows the IR spectra in the structural region for the as-synthesized and proton forms of IM-5 and NU-88 prepared here. One significant difference between these two zeolites appears in the 500- to 650-cm^{-1} region. According to the IR investigations of zeolite frameworks reported thus far, the bands appearing in this region are attributed to external linkage vibrations [34–36]. As seen in Fig. 11, H–IM-5 exhibits one single band at 555 cm⁻¹, typical of 5-ring subunits for pentasil zeolites [36]. Unlike H–IM-5, however, H–NU-88 gives two bands at 536 and 570 cm⁻¹,



Fig. 9. ²⁷ Al MAS NMR spectra of (a) IM-5 and (b) NU-88 in the as-synthesized (bottom) and proton (top) forms. Spinning side bands are marked by asterisks.



Fig. 10. ²⁹Si MAS NMR spectra of (a) IM-5 and (b) NU-88 zeolites in the as-synthesized (bottom) and proton (top) forms.



Fig. 11. IR spectra in the structural region of (a) IM-5 and (b) NU-88 zeolites in the as-synthesized (bottom) and proton (top) forms. IR bands from the occluded organic SDAs are marked by asterisks.

suggesting that IR spectroscopy, as well as powder XRD, can be regarded as a means to distinguish between both zeolites.

Fig. 12 shows the Raman spectra of the as-synthesized and proton forms of IM-5 and NU-88 in the 200- to 1600-cm⁻¹ region. The Raman spectra of MPP and MPH in aqueous solution are also compared in Fig. 12. In agreement with the ¹H–¹³C CP MAS NMR data given above, Raman spectroscopy reveals that both organic SDAs remain intact upon their occlusion into the pores of IM-5 and NU-88, respectively. It can also be seen from Fig. 12 that many spectral changes take place as the organic cation is trapped inside the zeolite pores. The exact assignment and interpretation of most of these changes cannot be done without normalcoordinate calculations. However, some of them provide clear evidence for the existence of host–guest interactions occurring within zeolites prepared here. When compared with the Raman spectra of various tetraalkylammonium salts and pyrrolidine derivatives in the literature [37,38], for example, the band appearing at 731 cm⁻¹ in the Raman spectrum of MPP in aqueous solution can be tentatively assigned to the C–N stretching mode. As seen in Fig. 12, however, as-synthesized IM-5 gives this vibration at 726 cm⁻¹. The same trend can be observed for the C–N stretching mode of MPH (733 cm⁻¹ for free MPHBr₂; 728 cm⁻¹ for oc-



Fig. 12. Raman spectra in the 200- to 1600-cm⁻¹ region of (a) IM-5 and (b) NU-88 in the as-synthesized (middle) and proton (top) forms. The bottom traces are 0.5 M aqueous solutions of MPPBr₂ and MPHBr₂, respectively.

cluded MPH). Fig. 12 also shows that a strong band appearing at 558 cm^{-1} in the Raman spectra of free MPP and MPH, assignable to the C-N bending mode, is nearly missing in the Raman spectra of as-synthesized IM-5 and NU-88. In addition to perturbations on the C-N bond, the Raman signature of occluded organic molecules includes notable differences in the band position and intensity of the C-C stretching mode of the polymethylene bridging unit at 1040- $1080 \,\mathrm{cm}^{-1}$. These observations indicate that the mirror symmetry of flexible organic SDAs has been removed upon their occlusion into the resultant zeolite pores and thus the two halves of the molecules occluded are no longer equal to each other. It is thus clear that organic SDAs in zeolites prepared here adopt conformations distinctly different from those of the corresponding, free molecules. However, we note that the ring breathing vibration band of *N*-methylpyrrolidinium groups, which appears as a strong band at 900 cm^{-1} in the Raman spectra of both IM-5 and NU-88, is essentially unchanged relative to that of free MPP or MPH. This led us to speculate that changes in the conformation imposed on these doubly charged cations upon occlusion into the zeolite pores occur mainly in the flexible central alkyl chain rather than in the puckered pyrrolidinium rings, which might be sufficient to cause the considerable reduction of geometric constraints and van der Waals interactions with the particular zeolite structure formed. When the Raman spectrum of H-IM-5 is compared with that of H-NU-88, finally, notable differences in the number and position of structural Raman bands were found. H-IM-5 exhibits four well-resolved bands at 301, 362, 425, and 487 cm^{-1} . As seen in Fig. 12, however, the Raman spectrum of H-NU-88 is characterized by three main bands around 340, 390, and 467 cm^{-1} with

relatively poor resolution. Although the unequivocal assignment of the structural Raman bands of H–IM-5 and H–NU-88 cannot be made at this time, due to the lack of the reliable theoretical correlation between the specific structural units in zeolites and their Raman band positions, it is interesting to note that the general feature of the spectrum in the structural region of H–NU-88 is similar to that reported for H–beta [39], whereas there are notable differences in the number and position of structural Raman bands of H–IM-5 and H–ZSM-5 [40].

Fig. 13 shows the NH_3 TPD profiles obtained from H– IM-5 (i.e., H–IM-5(II) sample) and H–NU-88. The TPD profiles of the proton form of both zeolites are characterized by two desorption peaks with maxima in the temperature



Fig. 13. NH₃ TPD profiles from (a) H-IM-5 and (b) H-NU-88 zeolites.

regions 1700–190 and 360–410 °C. Despite the similarity in their SiO₂/Al₂O₃ ratios, the total area of NH₃ desorption (i.e., the density of acid sites), especially the area of the high-temperature desorption peak, was found to be much higher for H–IM-5 than for H–NU-88. Also, the temperature maximum of the high-temperature desorption peak from H–IM-5 is slightly higher than that from H–NU-88. This suggests that the number and strength of strong acid sites are higher in H–IM-5 than in H–NU-88. However, we cannot exclude the effects of the nanocrystallinity of H–NU-88 on its TPD profile because the extent of NH₃ re-adsorption from one acid site to another acid site during the TPD experiment is greatly influenced by the crystal size of zeolites [41].

Fig. 14 shows the IR spectra of H-IM-5 before and after pyridine adsorption followed by desorption at different temperatures. Three well-resolved bands at 3745, 3666, and 3608 cm^{-1} in the OH stretching region can be observed from the IR spectrum of dehydrated H-IM-5. The first band is attributed to silanol groups on the external surface of H-IM-5 crystallites, and the other two bands can be assigned to hydroxyl groups belonging to extraframework Al and those of the Brønsted acid sites, respectively [42]. The presence of a weak band around 3666 cm⁻¹ in the IR spectrum of dehydrated H-IM-5 indicates that partial dealumination has occurred during the SDA removal and successive NH₄⁺ ion exchange and recalcination steps, as evidenced by ²⁷Al MAS NMR measurements. After pyridine adsorption the broad band at 3608 $\rm cm^{-1}$ disappears completely and two bands associated with the pyridinium ion adsorbed at Brønsted acid sites and pyridine coordinated to Lewis acid sites appear at 1545 and 1455 cm⁻¹, respectively. With the increase of desorption temperature the intensity of the two bands at 1545 and 1455 cm^{-1} is reduced, but some fraction of both pyridinium ion and pyridine still remains adsorbed at

500 °C. This indicates that the IM-5 framework contains very strong acid sites. The IR spectra of H-NU-88 before and after pyridine adsorption followed by desorption at different temperatures are shown in Fig. 15. The spectrum of dehydrated H-NU-88 in the OH stretching region is characterized by two weak and broad bands around 3655 and 3570 cm^{-1} , as well as by one strong band at 3745 cm^{-1} , typical of surface SiOH groups not involved in hydrogen bonding. When compared to the spectrum of dehydrated H-IM-5, therefore, there are notable differences in the position and intensity of OH bands appearing below 3700 cm^{-1} . Fig. 15 also shows that pyridine adsorption gives rise not only to the notable decrease in intensity of the weak band around 3655 cm^{-1} but also to the disappearance of the very broad band around 3570 cm⁻¹, which is indicative of interaction of these OH groups with pyridine. Because the ²⁷Al MAS NMR spectrum of H-NU-88 shows no noticeable band around 0 ppm, even after heating at 800 °C for 4 h, as described above, the weak OH band around 3655 cm⁻¹ can be attributed to bridging OH groups in Si-(OH)⁺-Al Brønsted acid sites rather than to hydroxylated extraframework Al species. In contrast, assigning the broad band around 3570 cm⁻¹ simply to bridging Si-(OH)+-Al species appears to be unreasonable because its position does not fall into the known range $(3660-3600 \text{ cm}^{-1})$ of stretching for bridging OH groups in zeolites [42]. Although the exact origin of this band is not clear at this time, one possible explanation is that it could be due to hydrogenbonded Si-(OH)⁺-Al bridges with SiOH groups. It should be noted here that a similar OH band appearing below the typical stretching region ($< 3600 \text{ cm}^{-1}$), which disappears upon adsorption of pyridine, has also been observed for other zeolites such as SSZ-24 and ITQ-4 [43,44]. As seen in Fig. 15, on the other hand, the two bands at 1545 and



Fig. 14. IR spectra of H–IM-5 in the (A) 3300- to 3800-cm⁻¹ and (B) 1400- to 1700-cm⁻¹ regions (a) before and after pyridine adsorption followed by desorption at (b) 200, (c) 300, (d) 400, and (e) 500 °C for 2 h.



Fig. 15. IR spectra of H–NU-88 in the (A) 3300- to 3800-cm⁻¹ and (B) 1400- to 1700-cm⁻¹ regions (a) before and after pyridine adsorption followed by desorption at (b) 200, (c) 300, (d) 400, and (e) 500 °C for 2 h.

Table 5
Amounts of pyridine still retained on Brønsted and Lewis acid sites in H-
IM-5 and H–NU-88 after desorption at different temperatures ^a

Desorption	Amount (μ mol g ⁻¹) of pyridine retained					
temperature (°C)	H–IM-5		H–NU-88			
	Brønsted	Lewis	Brønsted	Lewis		
200	160	47	121	16		
300	133	33	57	5		
400	97	28	25	4		
500	31	3	7	1		

^a Determined from the intensities of the IR bands at 1545 and 1455 cm^{-1} , respectively, by using the extinction coefficients given by Emeis [45].

1455 cm⁻¹ due to pyridine species adsorbed on Brønsted and Lewis acid sites in H–NU-88, respectively, become considerably weak after desorption, even at 300 °C, unlike the trend observed for H–IM-5. Therefore, it is clear that the number and strength of both Brønsted and Lewis acid sites are higher in H–IM-5 than in H–NU-88. This can

Table 6 Physical properties of zeolite catalysts used in this study be further confirmed by the data in Table 5 where the amounts of Brønsted and Lewis acid sites in H–IM-5 and H–NU-88 zeolites as a function of temperature were determined from the intensities of the IR bands at 1545 and 1455 cm⁻¹, respectively, by using the molar extinction coefficients reported by Emeis [45].

3.3. Catalysis

Table 6 lists the physical properties of all zeolites employed in the skeletal isomerization of 1-butene to isobutene and the cracking of *n*-octane. Fig. 16 shows 1-butene conversion and selectivity to isobutene as a function of time on stream in the skeletal isomerization of 1-butene on H–IM-5, H–NU-88, H–ZSM-35, H–ZSM-5, H–EU-1, H–mordenite, and H–beta zeolites measured at 400 °C and 10.1 kPa 1-butene in the feed. Here, we have considered the results obtained at 5 min on stream as the intrinsic activities of zeolite catalysts, to minimize the well-known effect of coke deposition within the zeolite pores on the selectiv-

Zeolite	IZA	Pore topology	SiO_2/Al_2O_3	Crystal shape and size (µm)	BET surface
	code ratio		area ^a (m ² g ^{-1})		
H–ZSM-5	MFI	2D, 10-rings	27	Spherulites, 1–3	398
H-ZSM-35	FER	2D, 10- and 8-rings	27	Oval plates, 1×3	435
H-EU-1	EUO	1D, 10-rings $+$ side pockets	40	Rice-grains, 0.5–1.0	352
H-beta	BEA*	3D, 12-rings	25	Spherical agglomerates, 3-4	667
H-mordenite	MOR	2D, 12- and 8-rings	33	Small rods, 0.1×0.3	532
H-IM-5(I)	_	_	19	Rods, 0.1×0.5	375
H-IM-5(II)	-	_	25	Rods, 0.2×0.7	460
H-IM-5(III)	_	_	32	Cuboids, 0.1–0.2	559
H–NU-88	_	_	26	Very small spheres, < 0.05	571

^a BET surface areas calculated from nitrogen adsorption data.



Fig. 16. (a) 1-Butene conversion and (b) selectivity to isobutene as a function of time on stream in skeletal isomerization of 1-butene on H–IM-5 (\blacksquare), H–NU-88 (\blacktriangle), H–ZSM-35 (\bullet), H–EU-1 (\triangleright), H–mordenite (\blacktriangleleft), and H–beta (\triangledown) at 400 °C and 10.1 kPa 1-butene pressure.

ity to isobutene [13,46–51]. On the other hand, the acidity and pore size of zeolites and related materials are the two important factors determining their activity and selectivity during this isomerization [46–51]. Because there are no significant differences in the SiO_2/Al_2O_3 ratio of zeolite catalysts employed in this study (see Table 6), however, the catalytic results in Fig. 16, particularly those obtained at 5 min on stream, could be mainly regarded as a reflex of geometrical constraints imposed by the particular pore structure of each zeolite.

ZSM-35 is the high-silica analog of ferrierite, which contains a two-dimensional pore system consisting of 10ring $(4.2 \times 5.4 \text{ Å})$ channels intersected by 8-ring $(3.5 \times$ 4.8 Å) channels [21] and is known as the best catalyst for this reaction [46-51]. When H-IM-5 is compared with H-ZSM-35 under the same reaction conditions, the former zeolite gives a much higher initial 1-butene conversion (85% vs 42%). However, H-IM-5 produces a much larger amount of by-products (mainly propene and pentenes) than H-ZSM-35 from the beginning of the reaction, revealing its nonselective behavior for isobutene formation. This indicates that the free diameter of pores in H-IM-5 is considerably larger than that at the H-ZSM-35 intersection, giving rise to a more efficient accommodation of two n-butenes for side reactions such as their dimerization followed by cracking to light hydrocarbons. Fig. 16 also shows that 1-butene conversion on H-IM-5 decreases continuously with increasing time on stream, whereas the opposite holds for selectivity to isobutene. This trend is somewhat different from that found in H-ZSM-5 with an intersecting 10-ring pore system between the straight $(5.3 \times 5.6 \text{ Å})$ and the sinusoidal $(5.1 \times 5.6 \text{ Å})$ 5.5 Å) channels because the extent of changes in 1-butene conversion or selectivity to isobutene with time on stream is higher on H-IM-5 than on H-ZSM-5. In fact, it has been repeatedly reported that H-ZSM-5 with the uniform pore

size exhibits an excellent stability in time for the skeletal isomerization of 1-butene, regardless of its SiO₂/Al₂O₃ ratio [13,52]. The isomerization activities of the three H-IM-5 zeolites with different SiO₂/Al₂O₃ ratios [19-32] prepared here are compared in Fig. 17. A trend of decreasing 1-butene conversion with increasing time on stream is clearly observed for all the H-IM-5 zeolites. This led us to speculate that the pore topology of H-IM-5 is substantially different than that of H-ZSM-5. Fig. 17 also shows that H-IM-5 with a lower Al content gives a higher selectivity to isobutene, although the change in isobutene formation on H-IM-5 with its Al content is not so high. This is not unexpected because the extent of successive reactions leading to by-products such as propene and pentenes should decrease with decreasing the density of acid sites in the zeolite framework [48,49].

It is well-established that due to the inherently shapeselective nature of zeolites and molecular sieves, coke formation on these microporous materials is also a shapeselective process that depends highly on their pore architecture [31,53]. After the skeletal isomerization of 1-butene at 400 °C for 8 h, therefore, the amounts of coke deposited on all zeolites employed in this study have been determined by TGA/DTA and are given in Table 7. No significant differences in the amount (9-10%) of coke formed are observed for H-ZSM-5 and H-IM-5(I) with the highest Al content (or the lowest SiO_2/Al_2O_3 ratio) among the H–IM-5 zeolites prepared here. As seen in Table 7, however, the amount of coke deposited on H-IM-5 increases significantly with decreasing Al content in the zeolite. As a result, the amount (14.9%) of coke formed on H-IM-5(III) with the lowest Al content was found to be approximately one and half times larger than that (9.8%) on H-IM-5(I). Notice that this coke level is much higher than the amount (10.6%) of coke on H-mordenite, a two-dimensional pore system consisting of



Fig. 17. (a) 1-Butene conversion and (b) selectivity to isobutene as a function of time on stream in skeletal isomerization of 1-butene on H–IM-5 zeolites with different SiO_2/Al_2O_3 ratios: 19 (\blacksquare), 25 (\blacktriangle), and 32 (\bigcirc). The reaction conditions are the same as those given in Fig. 16.

intersecting 12-ring (6.5 \times 7.0 Å) and 8-ring (3.4 \times 4.8 Å) channels and is even higher than that (10.8%) observed for H-beta with mutually perpendicular intersecting 12-ring $(5.6 \times 5.6 \text{ and } 6.6 \times 6.7 \text{ Å})$ channels [21], despite the similarity in their Al contents. As described earlier, the amount of Al atoms removed from IM-5 framework sites during the calcination step is smaller for the zeolite with a lower Al content. Thus, if IM-5 is not a three-dimensional large-pore material like beta but a zeolite with intersecting 12- and 10ring pores, the possibility of blockage of the inner pores by extraframework Al species should be lower for the H-IM-5(III) zeolite. This appears to be reasonable because there is a notable increase in the amount of coke formed on H-IM-5, as well as in its N₂ BET surface area, with increasing the SiO_2/Al_2O_3 ratio (see Table 7). It is well known that the coke-forming propensity of medium-pore zeolites such as H-ZSM-5 and H-ZSM-11 is lower than that of zeolites with large 12-ring windows, due to the geometric constraints imposed by 10-ring pores [31,53]. Although coke formation during the skeletal isomerization of 1-butene occurs on the exterior surface of zeolite catalysts, as well as within their inner pores, therefore, the TGA/DTA results in Table 7 strongly suggests that IM-5 may belong to the structural regime of large-pore materials rather than of mediumpore zeolites.

Based on their results from several test reactions and adsorption of hydrocarbons with different sizes, Corma et al. [6] considered the possibility that IM-5 could possess a pore system of unidirectional 10-rings with large internal cavities. However, this can be ruled out by comparing the 1-butene isomerization activity of H–IM-5 with that of H– EU-1, whose structure consists of one-dimensional 10-ring (4.1×5.4 Å) pores in the main channel bounded by 12-ring pores leading to large side pockets (6.8×5.8 Å in cross section and 8.1 Å in depth) [21]. The initial 1-butene conver-

Table 7

Amounts of coke deposits formed on various zeolite catalysts during the 1-butene skeletal isomerization and n-octane cracking^a

Catalyst	SiO_2/Al_2O_3	SiO ₂ /Al ₂ O ₃ Amount (wt%) o		
	ratio	1-Butene skeletal isomerization	<i>n</i> -Octane cracking	
H–ZSM-5	27	9.0	3.2	
H-ZSM-35	27	4.1	_c	
H-EU-1	40	4.4	2.2	
H-beta	25	10.8	7.8	
H-mordenite	33	10.6	11.3	
H–IM-5(I)	19	9.8	2.8	
H-IM-5(II)	25	11.1	3.5	
H-IM-5(III)	32	14.9	7.0	
H–NU-88	26	12.2	10.0	

^a After 8 h on stream. The reaction temperatures for 1-butene skeletal isomerization and *n*-octane cracking are 400 and 500 $^{\circ}$ C, respectively. The other conditions for both reactions are the same as those stated in the text.

^b Determined from TGA/DTA.

^c Not reacted.

sion and selectivity to isobutene were found to be 67 and 20% for this one-dimensional medium-pore zeolite, respectively, which are in good agreement with the results reported by Guisnet et al. [54]. Thus, the initial 1-butene conversion on H-EU-1 is considerably lower than that on H-IM-5, and the opposite is observed for the selectivity to isobutene. As seen in Fig. 16, this trend remains unchanged during the period of 8 h on stream. Further support for the speculation that the IM-5 structure is not formed by unidirectional 10ring pores with large lobes can be obtained from the fact that the amount (4.4%) of coke formed on H-EU-1 is much smaller than that observed for any of the three H-IM-5 zeolites studied here (see Table 7). Like H-IM-5, on the other hand, H-NU-88 exhibits the initial 1-butene conversion similar to that of H-ZSM-5, revealing its nonselective behavior for isobutene formation. However, this zeolite shows a large decrease in 1-butene conversion during the first 1 h on stream. As seen in Table 7, in addition, the amount (12.2%) of coke on H–NU-88 is comparable to that formed on H– mordenite or H–beta. Therefore, it appears that H–NU-88 may meet the catalytic behavior of large-pore zeolites, which is in contrast to the proposal of Lacombe et al. [8].

Table 8 lists the conversions and product distributions from the catalytic cracking of *n*-octane on H-IM-5 and H-NU-88 with a similar SiO₂/Al₂O₃ ratio (\sim 25) measured at 500 °C, 2.0 kPa n-octane pressure in the feed and 500 s on stream. For comparison, the catalytic results from H-ZSM-5, H-EU-1, H-mordenite, and H-beta are also given in Table 8. These data reveal that the n-octane conversion (89%) on H-IM-5 is almost the same as that (90%) on H-ZSM-5, serving as a prime example of the uniqueness of medium-pore zeolites in the cracking of linear paraffins [31,55,56]. Thus, no severe spatial constraints for the free diffusion of n-octane molecules appear to exist within the pores of IM-5. This may also be the case of H-NU-88 because it yields an n-octane conversion of 91% that is very close to that on H-ZSM-5 but is considerably higher than the value observed for H-EU-1, Hmordenite, or H-beta. The catalytic data in Table 8 also show that ethylene, propane, and propylene are the three most dominant products observed for H-IM-5 and H-NU-88. The other major products include ethane, n-butane, isobutane, and butenes. These product distributions are somewhat

different from those for the other four zeolite catalysts with known structures in that H-IM-5 and H-NU-88 give a higher initial selectivity to propane, although the amount of propane produced becomes lower at higher times on stream. We also note that the production of aromatic hydrocarbons such as benzene, xylenes, and toluene is negligible for all zeolite catalysts studied here. To investigate the effect of reaction temperature on product selectivities, on the other hand, we have carried out the n-octane cracking reaction on H-IM-5 and H-NU-88 in the temperature region 310-500°C. Selectivities to ethylene and propylene on both zeolites were enhanced at higher temperature, whereas the opposite was observed for the selectivities to longer hydrocarbons, mainly, n-butane and butenes. This is not unexpected because the extent of secondary cracking activity of zeolites normally becomes larger at a higher temperature.

Fig. 18 shows *n*-octane conversion and selectivities to ethylene and propylene as a function of time on stream in *n*octane cracking on H–IM-5, H–NU-88, H–ZSM-5, H–EU-1, H–mordenite, and H–beta zeolites at 500 °C and 2.0 kPa *n*octane pressure in the feed. It can be seen that all the zeolite catalysts except H–ZSM-5 exhibit a continuous decrease in *n*-octane conversion during the period of 8 h on stream, although their initial conversions are different from one another. A similar result was observed when selectivities to ethylene on these five zeolites are plotted with time on stream. As shown in Fig. 18, however, differences in

Table 8

Conversion and product distribution from catalytic cracking of *n*-octane on various zeolite catalysts at 500 $^{\circ}$ C^a

	H–IM-5	H–NU-88	H-ZSM-5	H-EU-1	H-mordenite	H-beta
Conversion (mol%)	89.3	91.0	89.8	83.1	64.3	76.1
Selectivity (mol%) to						
Methane	2.6	3.6	2.7	2.4	2.8	6.0
Ethane	4.4	3.2	6.9	4.3	_	4.1
Ethylene	21.6	18.3	27.3	20.1	21.0	15.2
Propane	21.6	18.4	14.0	17.8	16.3	10.8
Propylene	23.0	23.9	27.7	28.0	26.0	25.4
<i>n</i> -Butane	6.5	7.7	5.8	6.0	6.6	7.3
Isobutane	6.5	8.8	1.5	4.5	8.3	6.2
1-Butene	3.9	5.0	4.3	6.3	6.9	8.1
cis-2-Butene	2.1	2.2	1.9	2.7	3.1	3.5
trans-2-Butene	1.4	1.5	1.3	1.9	2.2	2.6
<i>n</i> -Pentane	0.1	0.2	0.1	0.2	0.3	0.3
2-Methylbutene	0.6	0.9	0.2	0.3	0.9	0.8
1-Pentene	0.2	0.2	0.2	0.2	0.3	0.4
2-Pentene	1.3	1.5	2.0	1.7	1.6	3.2
cis-2-Pentene	0.1	0.1	0.1	0.1	0.2	0.2
trans-2-Pentene	0.5	0.4	0.3	0.5	0.8	0.9
<i>n</i> -Hexane	0.1	-	0.1	-	-	_
2-Hexene	-	0.1	0.2	0.2	0.2	0.4
3-Methylpentane	0.1	0.1	0.2	0.1	0.1	0.1
Benzene	0.8	0.9	0.7	0.5	0.4	0.9
Toluene	1.4	1.9	1.4	1.1	0.7	2.1
2-Methyheptane	0.1	-	0.2	0.2	0.4	-
o-Xylene	0.1	0.2	0.1	0.2	0.2	0.3
<i>m</i> -Xylene	-	-	0.2	0.2	0.1	0.1
<i>p</i> -Xylene	0.4	0.6	0.5	0.5	0.4	1.0
C9 >	0.6	0.3	0.1	_	0.2	0.1

^a Data are reported as the values of 500 s on stream at a total gas flow of 50 cm³ min⁻¹.



Fig. 18. (a) *n*-Octane conversion and selectivities to (b) ethylene and (c) propylene as a function of time on stream in *n*-octane cracking on H–IM-5 (\blacksquare), H–NU-88 (\blacktriangle), H–ZSM-5 (\blacklozenge), H–EU-1 (\diamondsuit), H–mordenite (\succ), and H–beta (\blacktriangleleft) at 500 °C and 2.0 kPa *n*-octane pressure.



Fig. 19. (a) *n*-Octane conversion and selectivities to (b) ethylene and (c) propylene as a function of time on stream in *n*-octane cracking on H–IM-5 zeolites with different SiO₂/Al₂O₃ ratios: 19 (\blacksquare), 25 (\blacktriangle), and 32 (\bigcirc). The reaction conditions are the same as those given in Fig. 18.

the initial selectivities to propylene on these zeolites and changes with time on stream are not so large as those observed for the selectivity to ethylene. Therefore, it is again clear that both IM-5 and NU-88 are not multidimensional medium-pore zeolites because they are much less stable than H–ZSM-5 with a similar SiO₂/Al₂O₃ ratio (\sim 25). It should also be noted here that the deactivation pattern and product distribution of H-NU-88 with time on stream are quite similar to those observed for H-beta. The cracking activities of three H-IM-5 zeolites with different SiO₂/Al₂O₃ ratios are shown in Fig. 19. When the IM-5(I) zeolite with the lowest SiO₂/Al₂O₃ ratio is compared with H-ZSM-5, *n*-octane conversions and selectivities to ethylene and propylene on both zeolites remain almost constant over the period of time studied here. However, the other two IM-5 zeolites with higher SiO₂/Al₂O₃ ratios (and hence with higher N₂ BET surface areas) deactivate continuously during the *n*-octane cracking. This is significantly different than the trend found in four H-ZSM-5 zeolites with a SiO₂/Al₂O₃ ratio ranging from 27 to 170 in that there is no noticeable decrease in *n*-octane conversion on these H–ZSM-5 zeolites with time on stream up to 8 h, although the level of conversion depends highly on their SiO₂/Al₂O₃ ratio [57]. The TGA/DTA results in Table 7 reveal that the amount of coke formed on H-IM-5 after the n-octane cracking at 500 °C for 8 h increases with increasing SiO₂/Al₂O₃ ratio in the zeolite, which is also opposite to the trend found in a series of used H-ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios [57]. These arguments taken in total led us to believe that the cracking behavior of IM-5 cannot be represented by a multidimensional, 10-ring system with the uniform pore size like ZSM-5. Due to the similarity

in the deactivation behavior of all zeolites employed in this study, except H–ZSM-5, however, it is very difficult to reasonably infer the pore structures of IM-5 and NU-88 from the catalytic results in Figs. 18 and 19. As stated earlier, the pore structure of zeolites exerts a very large effect on the rate of coke formation in a number of acid-catalyzed reactions. Therefore, we focused on the relationships between the structural features of H–mordenite, H–EU-1, and H–beta, and their amounts of coke formed after the *n*-octane cracking at 500 °C for 8 h. Based on the relationships drawn, we then attempted to estimate the most probable pore topologies of IM-5 and NU-88 from their coke-forming propensities.

Mordenite has a two-dimensional pore system consisting of 12-ring channels intersected by 8-ring channels. However, this zeolite should be effectively a one-dimensional 12-ring material as far as the n-octane cracking is concerned because its small 8-rings may slow down the overall diffusivity. Fig. 18 shows that H-mordenite exhibits a much lower *n*-octane conversion than H-IM-5 or H-NU-88 from the beginning of the reaction, revealing a much more severe diffusional limitation in the former zeolite. As seen in Table 7, in addition, the amount of coke deposited on Hmordenite is considerably higher than that not only on any of H-IM-5 zeolites studied here but also on H-NU-88. When H-EU-1 is compared with H-mordenite, on the other hand, the former zeolite exhibits a much higher n-octane conversion over the period of time studied here. Because the 10-ring $(4.1 \times 5.3 \text{ Å})$ pores in EU-1 are considerably smaller than the 12-ing $(6.5 \times 7.0 \text{ Å})$ channels in mordenite, however, the diffusion of *n*-octane molecules should be less favorable in the former zeolite. Thus, it is not difficult to speculate that the external acid sites on the H-EU-1 crystals, on which catalysis is not influenced by shape selectivity, may contribute mainly to the cracking of *n*-octane. This can be further supported the fact that the amount (2.2%) of coke on H-EU-1 for 8 h on stream is much smaller than that (11.3%) on H-mordenite, which is also considerably small compared to H-IM-5 or H-NU-88. Therefore, we can again rule out the possibility that the IM-5 and NU-88 structures consist of a pore topology of unidirectional 12-ring channels or 10-rings with large internal cavities. When H-beta, a three-dimensional large-pore material, is compared with H-NU-88, finally, the latter zeolite gives a higher amount of coke deposited, but its value is still smaller than the amount formed on H-mordenite (see Table 7). Clearly, it would be very difficult, or even impossible, to accurately determine the pore topologies of IM-5 and NU-88 from their isomerization and cracking activities alone. When correlated with the coke-forming propensities of these two zeolites with unknown structures, however, it can be concluded that both materials are identified as multidimensional, large-pore zeolites. Therefore, the overall catalytic results do support the conclusion that IM-5 is a new multidimensional largepore zeolite probably formed by intersecting 12- and 10ring windows, whereas NU-88 is an intergrowth of several hypothetical polymorphs in the beta family of zeolites.

4. Conclusions

Two new zeolites IM-5 and NU-88 were found to crystallize over a narrow range of SiO₂/Al₂O₃ and NaOH/SiO₂ ratios when the flexible, doubly charged ammonium cations 1,5-bis(N-methylpyrrolidinium)pentane and 1,6-bis(N-methylpyrrolidinium)hexane are used as organic SDAs together with Na⁺ ions, respectively. The physicochemical properties of IM-5 and NU-88 prepared here are investigated by powder XRD, elemental and thermal analyses, TEM, Ar and N₂ adsorption, multinuclear solid-state MAS NMR, IR, and Raman, NH₃ TPD, and IR spectroscopy of adsorbed pyridine. The overall characterization results suggest that IM-5 is a new multidimensional large-pore zeolite that probably consists of intersecting 12- and 10-ring windows, whereas NU-88 is a nanocrystalline material that is closely related to the beta family of zeolites. In addition, the strength of both Brønsted and Lewis acid sites was found to be stronger in H-IM-5 than in H-NU-88. Despite its nanocrystallinity, however, NU-88 exhibits a very high thermal stability. The catalytic properties of these two zeolites are evaluated for the skeletal isomerization of 1-butene to isobutene and the cracking of n-octane and compared to those from various zeolites with known structures. A combination of the catalytic results from all zeolites studied here with their coke-forming propensities allowed us to provide further evidence that both IM-5 and NU-88 are multidimensional, large-pore zeolites.

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