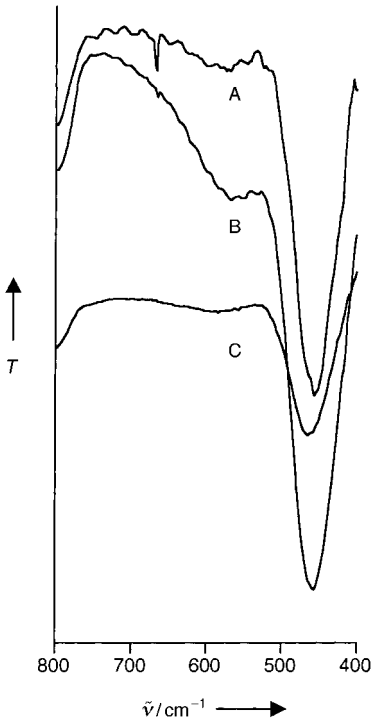

Figure 3. IR spectra of calcined mesostructures: A) 1.5 % Al-MSU-$S_{(MFI)}$ assembled from zeolite ZSM-5 seeds, B) 1.5 % Al-MSU-$S_{(BEA)}$ assembled from zeolite Beta seeds, and C) 1.5 % Al-MCM-41 formed from conventional aluminosilicate precursors.

two days. Al-MCM-41 (Si/Al = 67:1) also was assembled at 150 °C from conventional aluminosilicate precursors formed at 35 °C using tetramethylammonium (TMA^+) in place of TEA^+ and TPA^+.

X-ray diffraction patterns were recorded on a Rigaku Rotaflex diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.542$ Å). N_2 adsorption and desorption isotherms were determined on a Micromeritics ASAP 2000 sorptometer at -196 °C. The samples were outgassed under 10^{-5} Torr at 150 °C. ^{27}Al NMR spectra were recorded on a Varian VXR-400S spectrometer with a 7-mm zirconia rotor and a spinning frequency of 4 kHz. IR spectra of samples in the form of KBr pellets were recorded by using a Nicolet IR/42 spectrometer.

Cumene cracking reactions were performed in a 6 mm i.d. fixed bed quartz reactor with 200 mg catalyst. The cumene flow rate was 4.1 μmol min^{-1} in a 20 cm^3 min^{-1} carrier stream of N_2. Cumene conversions were reported under steady-state conditions after 60 min on stream at 300 °C.

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Strongly Acidic and High-Temperature Hydrothermally Stable Mesoporous Aluminosilicates with Ordered Hexagonal Structure**

Zongtao Zhang, Yu Han, Lei Zhu, Runwei Wang, Yi Yu, Shilun Qiu,* Dongyuan Zhao, and Feng-Shou Xiao*

Mesoporous molecular sieves such as hexagonally ordered MCM-41 have attracted considerable attention because of their potential use as versatile catalysts and catalyst supports for the conversion of large molecules.[1–16] However, the acidity and hydrothermal stability of these mesostructured materials are relatively low compared with those of zeolites, which strongly influences their practical applications in industrial catalytic reactions of petroleum.[1] Despite several successful examples of stabilizing aluminosilicate mesostructures at low temperatures (in boiling water, 100 °C), for example by synthesizing materials with thick pore walls by using triblock copolymers,[3] by removing silanol groups by silylation,[14] by employing salt effects,[15] by using the co-templating approach,[16] and by post-treatments,[5–8] the acidity and hydrothermal stability of these mesostructures at high temperature (800 °C) are still lower than those of microporous aluminosilicate zeolites.

It is well known that microporous zeolites are very stable, commercial catalysts, and the MFI-type and Beta zeolites, which contain structure building units of 5-rings (T-O-T, T = Si and Al), exhibit extremely high acidity and hydrothermal

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stability. Notably, several zeolite structure-directing agents (aluminosilicate nanoclusters) for syntheses with primary and secondary structure building units have been reported recently,[17–19] one of which has been shown to be particularly suitable for the synthesis of Beta zeolite.[19]

Here we demonstrate that strongly acidic and high-temperature hydrothermally stable mesoporous aluminosilicates with ordered hexagonal structure can be synthesized by self-assembly of preformed aluminosilicate nanoclusters with templating micella. Our results show that the materials obtained contain primary and secondary building units similar to those of microporous Beta zeolite. In addition the materials are highly active for the catalytic cracking of 1,3,5-triisopropylbenzene and have longer catalyst lifetimes for use in the alkylation of isobutane with butene than MCM-41 and HZSM-5. This should open the door for the application of mesoporous materials as acidic catalysts for the conversion of large molecules.

Strongly acidic and hydrothermally stable mesoporous aluminosilicates (denoted as MAS-5) with ordered hexagonal structures were hydrothermally synthesized from silica and sodium aluminate in the presence of co-templates of tetraethylammonium hydroxide (TEAOH) and cetyltrimethylammonium bromide (CTAB).

The small-angle X-ray diffraction (XRD) pattern for the as-synthesized sample of MAS-5 shows four well-resolved peaks (Figure 1 A) that can be indexed as (100), (110), (200), and (210) reflections associated with hexagonal symmetry. The (100) peak reflects a d spacing of 4.441 nm ($a_0 = 51.33$ Å). After calcination in air at 550 °C for 4 h, thermogravimetric analysis (TG) of the sample shows a weight loss of 51%, which was attributed to the removal of organic templates of TEAOH and CTAB, and the XRD pattern (Figure 1 B) shows that the four diffraction peaks are still observed, confirming that hexagonal MAS-5 is thermally stable. A similarly high degree of mesoscopic order is observed for hexagonal MAS-5 even after calcination to 900 °C. Interestingly, after treatment of the calcined sample in boiling water for 300 h (Figure 1 C), and even after treatment of the calcined sample at 600 °C for 4 h or at 800 °C for 2 h in flowing water vapor (Figure 1 D), the XRD patterns also show similar peaks assigned to hexagonal symmetry, suggesting that MAS-5 is extremely hydrothermally stable even at high temperature.

Figure 2 shows temperature-programed desorption of ammonia (NH_3-TPD) curves on MAS-5, MCM-41, H-ZSM-5, and H-Beta with similar SiO_2/Al_2O_3 ratios (78:1 – 84:1). Evidently, the desorption temperature for ammonia on MAS-5 is much higher than that on MCM-41 with a similar SiO_2/Al_2O_3 ratio, and the curve shape is very similar to that of H-Beta, indicating that the acidic strength and amount of

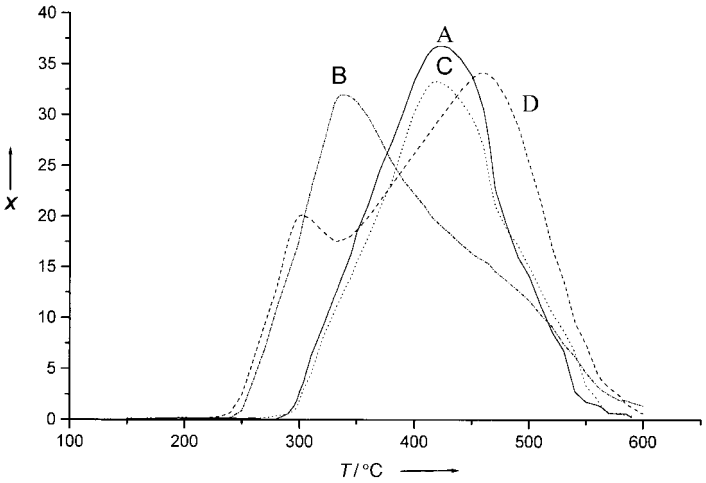

Figure 2. NH_3-TPD curves on A) MAS-5, B) MCM-41, C) H-Beta, and D) HZSM-5. X = amount of desorbed NH_3.

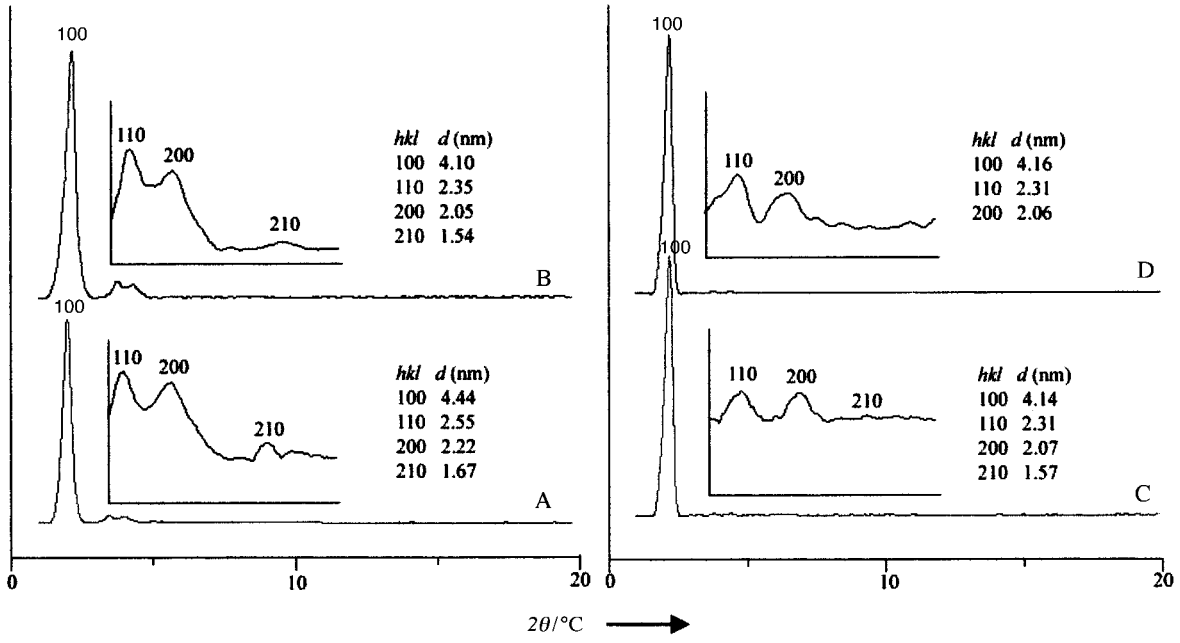

Figure 1. XRD patterns of A) as-synthesized MAS-5; B) calcined MAS-5 at 550 °C for 4 h; C) calcined MAS-5 after treatment in boiling water for 300 h; D) calcined MAS-5 after treatment with 100% water vapor at 600 °C for 4 h or calcined MAS-5 after treatment with 100% water vapor at 800 °C for 2 h. The XRD patterns were measured with a Siemens D5005 diffractometer.

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MAS-5 are similar to those of H-Beta zeolite, which is much stronger than that of MCM-41. Moreover, the IR spectrum recorded for pyridine adsorption over MAS-5 shows a much stronger band at 1545 cm^{-1} than that over MCM-41, indicating that MAS-5 has a much higher concentration of Brønsted acidic sites than MCM-41.

The transmission electron microscopy (TEM) image of calcined MAS-5 shows well-ordered hexagonal arrays of mesopores with one-dimensional (1D) channels, and further confirms that MAS-5 has a two-dimensional (2D) *p6mm* hexagonal mesostructure.[2] From the high dark contrast in the TEM image of this sample, the distance between mesopores is estimated to be 48 Å, which is in good agreement with that determined from XRD.

The N_2 adsorption – desorption isotherm of calcined MAS-5 exhibits a typical adsorption curve of type IV, which is attributed to the mesoporous structure. Correspondingly, the pore-size distribution for calcined MAS-5 shows narrow uniform pore with a mean value of 27 Å. Combined with the XRD results, we estimate that the thickness of the mesoporous wall is about 21 Å. Furthermore, a high BET surface area of 1150 $m^2 g^{-1}$ and a large pore volume of 1.17 $cm^3 g^{-1}$ were observed.[1, 2]

IR, UV-Raman, and NMR spectroscopy were used to characterize the primary and secondary building units (PSBU) of MAS-5. The IR spectrum of calcined MAS-5 (Figure 3) exhibits four sharp bands between 410 and

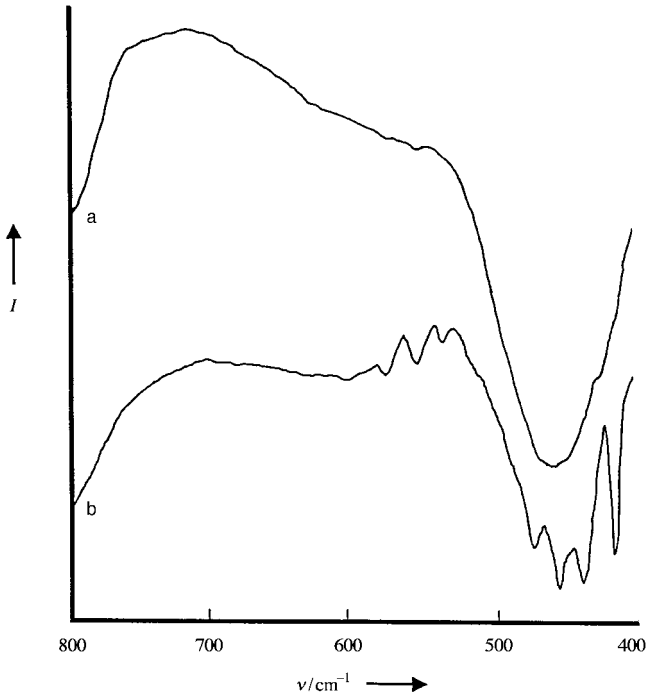

Figure 3. IR spectra of a) MCM-41 and b) MAS-5 after removal of organic templates.

480 cm^{-1} and other notable bands between 520 and 600 cm^{-1}, which are characteristic of 6- and 5-rings of T-O-T (T = Si or Al), respectively.[20] In contrast, MCM-41 only exhibits a broad band at 455 cm^{-1}; the UV-Raman spectrum of MAS-5 shows characteristic bands at 340 and 390 cm^{-1}, which are assigned to 5-rings of T-O-T (Figure 4),[21] in addition to the

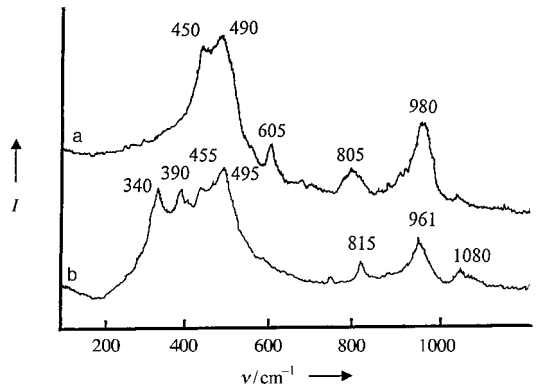

Figure 4. UV Raman spectra of a) MCM-41 and b) MAS-5.

bands at 455 and 495 cm^{-1} for the 4-rings of T-O-T. In contrast, MCM-41 exhibits bands at 450, 490, and 605 cm^{-1}, which are assigned to 4- and 3-rings in the amorphous phase of aluminosilicates;[12, 22] the ^{27}Al NMR spectrum shows that the full-width half-height (FWHH) of MAS-5 is similar to that of Beta zeolite, but much narrower than that of MCM-41. Additionally, the ^{27}Al NMR spectrum for MAS-5 displays a peak at $\delta = 61$; in contrast, this peak appears at $\delta = 55$ for MCM-41. These results suggest that the aluminum environment in MAS-5 is much more similar to that in Beta zeolite than in amorphous MCM-41.[23] All of these results indicate that MAS-5 contains PSBU of 5- and 6-rings of T-O-T,[20–23] similar to those in aluminosilicate zeolites such as Beta zeolite.

Catalytic activities determined for the cracking of 1,3,5-triisopropylbenzene over various catalysts are given in Table 1. HZSM-5 is almost inactive due to its relatively small pore size and the large diameter of the molecule to be cracked. MCM-41 shows high activity; however, it completely loses its activity after its treatment in boiling water for 6 h or at 600 °C for 2 h. Interestingly, our calcined MAS-5 displays both higher activity and longer catalyst lifetimes than those of MCM-41. Moreover, when MAS-5 is treated in boiling water for 300 h, or even when it is treated at 600 °C for 4 h or at 800 °C for 2 h, it still shows high catalytic activity. These results also confirm that MAS-5 is strongly acidic and is highly hydrothermally stable, suggesting that it is a good candidate catalyst for industrial cracking of petroleum.

Catalytic alkylation of isobutane with butene (Figure 5) shows that MAS-5 exhibits higher activity than calcined MCM-41 with a similar SiO_2/Al_2O_3 ratio. This is attributed to the strongly acidic sites of MAS-5. Furthermore, MAS-5 has the longest catalyst lifetimes of the catalysts studied, which is attributed to the relatively low coke formation. In addition, the products obtained over a MAS-5 catalyst display higher octane values than those obtained over the other samples measured.

MAS-5 is proposed to form by the self-assembly of aluminosilicate species co-templated by TEAOH and CTAB. In our case, the TEAOH template assembles aluminosilicates to form precursors in which the PSBU are similar to those in Beta zeolite. These precursors are further self-assembled with CTAB micella to give hexagonal mesoporous structures, which contain PSBU similar to those of Beta zeolite, that are

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Table 1. Catalytic activities in the cracking of 1,3,5-triisopropylbenzene on various catalysts.[a]

Sample	SiO_2/Al_2O_3	Treatment	Conversion [%]	Reaction temperature [°C]
HZSM-5	84:1	–	1.7	250
HMCM-41	80:1	–	65.8	250
HMCM-41	80:1	boiling water for 6 h	< 0.1	250
HMCM-41	80:1	treated with 100% water vapor at 600 °C for 2 h	< 0.1	250
MAS-5	81:1	–	78.8	250
MAS-5	81:1	boiling water for 300 h	79.1	250
MAS-5	81:1	treated with 100% water vapor at 600 °C for 4 h	78.9	250
MAS-5	80:1	treated with 100% water vapor at 800 °C for 2 h	77.5	250
MAS-5	123:1	–	87.0	320
MAS-5	81:1	–	90.1	320
MAS-5	59:1	–	95.2	320

[a] Catalytic reactions were performed by pulse injections, and the data presented are the results after 10 injections. In each run, 50 mg of catalyst was used, the pulse injection contained 0.4 μL of the reactant, and the reaction flow rate was 53.7 mL min^{-1}.

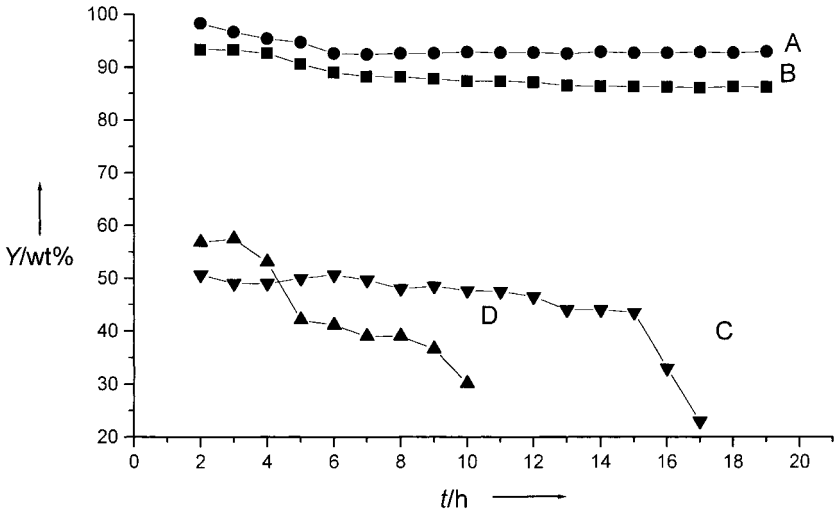

Figure 5. Catalytic conversion (Y) of 2-butene in the alkylation of isobutane with butene versus reaction time over various catalysts (each 0.5 g): A) MAS-5, B) H-Beta, C) MCM-41, and D) HZSM-5. Reaction temperature 25 °C; isobutane/butene ratio of 12:1; 1-butene/2-butene ratio of 8:1; WHSV = 9 h^{-1}.

hydrothermally stable even at high temperature, strongly acidic, resulting in excellent catalytic activity.

The aluminosilicate precursors were well characterized by IR spectroscopy. Prior to the formation of aluminosilicate precursors, the IR spectrum shows a broad band at 460 cm^{-1}, which is attributed to structure building units of amorphous aluminosilicates.[20] After the formation of these aluminosilicate precursors, the IR spectrum exhibits a notable bands between 520 and 600 cm^{-1}, which are characteristic of 5-rings.[20]

Experimental Section

Synthesis: Strongly acidic and hydrothermally stable mesoporous aluminosilicates (denoted as MAS-5) with ordered hexagonal structures were hydrothermally synthesized from silica and sodium aluminate in the presence of co-templates of tetraethylammonium hydroxide (TEAOH) and cetyltrimethylammonium bromide (CTAB) with a molar ratio of Al_2O_3/SiO_2/TEAOH/CTAB/H_2O at 1.0/7.0–350/10.0–33.0/12.0–32.0/500–2000. The molar ratio of SiO_2/Al_2O_3 in the products varied between 6.0:1–350:1.

Typical runs for the preparation of MAS-5: 1) Sodium aluminate (0.236–1.36 g), sodium hydroxide (0.11–0.4 g), and tetraethylammonium hydroxide (26–36 g; 20 wt% aqueous solution) were mixed in a plastic vessel. Then fume silica (10.086 g) was added, and the mixture was stirred for several hours. After the solution became homogeneous, the resulting mixture was transferred to a Teflon-lined stainless-steel autoclave and heated to 100–150 °C for several hours, which led to the aluminosilicate precursors. 2) CTAB (1.18–1.92 g) and deionized water (25 g) were mixed, and then added to the aluminosilicate precursors (9.8 g). The resulting mixture was transferred to a Teflon-lined stainless-steel autoclave, heated at 100–150 °C in an oven. 3) After crystallization for 48 h, the solid product was filtered, washed with water, and dried at 80 °C in air for 12 h. 4) The sample was calcined at 550 °C for 6 h in an oxygen flow to remove the templates TEAOH and CTAB. 5) The protonated form of the sample was prepared by ion-exchange with NH_4Cl, followed by calcination at 500 °C for 2 h.

Characterization: XRD patterns were obtained with a Siemens D5005 diffractometer using $Cu_{K\alpha}$ radiation. TEM images and electron diffraction (ED) patterns were recorded by using a Philips CM200FEG instrument with an acceleration voltage of 200 kV. The nitrogen isotherms of the sample were measured by using a Micromeritics ASAP 2010 system. The samples were outgassed for 2 h at 400 °C before the measurements. The pore-size distribution was calculated by using the Barrett–Joyner–Halenda (BJH) model. ^{27}Al NMR spectra were recorded on a Bruker MSL-300WB spectrometer, and chemical shifts were referenced to $[Al(H_2O)_6]^{3+}$. The Si/Al ratio of the samples was measured by using a Perkin–Elmer 3300 DV ICP, by NMR spectroscopy, and by chemical analysis.

IR spectra of the samples and IR spectra of pyridine adsorbed on the samples were recorded on an FT-IR spectrometer (PE 430) with a resolution of 1 cm^{-1}. Before measurement of the pyridine adsorption, the samples were pressed to thin wafers (5 mg cm^{-2}), and were placed into a quartz cell with CaF_2 windows. The sample disks were evacuated at 400 °C for 2 h (10^{-5} Torr) and cooled down to room temperature, then the disks were exposed to pyridine (10 Torr) at room temperature. The IR spectra were recorded after adsorption at room temperature for 1 h and evacuation at 150 °C for 1 h.

UV-Raman spectra were recorded on an UV-Raman spectrometer built at the State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics. The UV line at 244 nm was generated from a Coherent Ionva 300 Fred ultraviolet laser equipped with an intracavity frequency-doubling system based on a β-barium borate (BBO) crystal. The laser power at the sample was kept below 4.0 mW. The scattered Raman light was collected at 180°. The spectral resolution was estimated to be 1.0 cm^{-1}. Powders of samples were pressed into pellets with diameters of 1.0 cm and then placed in the sample holder.

TPD-NH_3 curves were performed in the range of 120–600 °C; the temperature was increased at a rate of 15 °C min^{-1}. The adsorption of

ammonia on the sample was performed at room temperature; the subsequent removal of ammonia was carried out at 120 °C for 1 h in flowing pure nitrogen.

Catalytic reactions: Two catalytic reactions were used to characterize the catalytic performance of the prepared materials, and analyses of the catalytic products were carried out using GC-8A and GC-17A (Shimazu Co.) instruments equipped with TCD and FID detectors. Catalytic cracking of 1,3,5-triisopropylbenzene was performed by the pulse method. Samples were calcined at 600 °C for 5 h to burn off any residual organic template. The catalytic testing was performed according to the following standard conditions: catalyst mass: 0.051 g; reaction temperatures in the range of 250–320 °C (no thermal cracking); the ratio of catalyst to 1,3,5-triisopropylbenzene or isopropylbenzene at 0.4 μL per 0.051 g. Nitrogen was used as carrier gas; flow rate 0.92 mL s^{-1}.

The catalytic alkylation of isobutane with butene was investigated at 2 MPa by using a stainless-steel apparatus equipped with a one-through stainless-steel flow reactor. Typical reactions were carried out with 0.5 g of catalyst and an isobutane/butene ratio of 12:1, and a 1-butene/2-butene ratio of 8:1; the WHSV was 9 h^{-1} at a reaction temperature of 25–100 °C.

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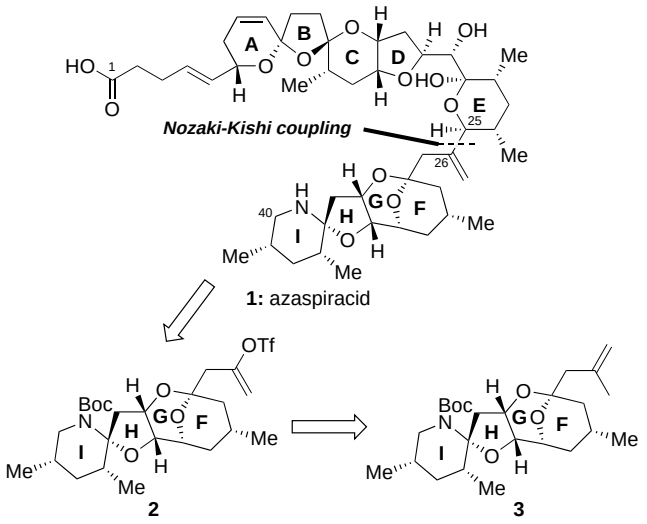
Synthesis of the FGHI Ring System of Azaspiracid**

K. C. Nicolaou,* Petri M. Pihko, Nicole Diedrichs, Ning Zou, and Federico Bernal

Azaspiracid (**1**, Scheme 1), a novel marine toxin isolated from the mussel *Mytilus edulis* in Killary Harbor, Ireland, represents a new class of marine metabolites unrelated to any



Scheme 1. Structure of azaspiracid (**1**) and retrosynthetic analysis leading to FGHI ring framework **3** via key intermediate **2**.

previously known agents of diarrhetic shellfish poisoning.[1] This seasonally occurring toxin displays an unusually complex molecular assembly – it harbors a total of nine rings, eight of which are part of acetal or ketal structures – namely, an azaspiro ring system fused to a 2,9-dioxacyclo[3.3.1]nonane ring and a trioxadispiroketal fused to a tetrahydrofuran ring. Adding to the serious challenge posed by such a molecular framework, the absolute stereochemistry of the molecule and the relative stereochemistry between the ABCDE and the

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