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Synthesis, Characterization, and Catalytic Activity of a Large-Pore Tridirectional Zeolite, H-ITQ-7**

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Zeolites are probably the most widely used solid catalysts in refining, petrochemistry, and fine chemical production. This is especially true for the acid zeolites, (H-zeolites). Their success is derived from properties such as high surface area, high adsorption capacity, molecular sieve characteristics, and the possibility of preparation with a well defined number of uniformly active sites;[1] these sites are introduced by direct synthesis or by postchemical treatment.[2] Considering the channel size, zeolites are classified as ultralarge (>12 membered rings (MR)), large (12-MR), medium (10-MR) or small (8-MR) pore materials depending on the number of T atoms that limits the pore aperture of their largest channels (T represents atoms from the aluminum and silicon families). While zeolites with small pores have found some specific applications in, for instance, the conversion of methanol to olefins[3], the most successful zeolitic catalysts are those based on zeolites with medium and large pores. More specifically, large-pore zeolites have unique properties for dealing with many of the oil fractions involved in refinery processes (cracking, hydrocracking, hydroisomerization, among others), in petrochemistry (including benzene alkylation with olefins, isomerization and disproportionation of alkylaromatic species), and in fine chemical production (such as alkylation, acylation, isomerization, and esterification).

It must be noted, for many of the processes named above, a rapid diffusion of the reactants and products is desired and this is better achieved with large-pore tridirectional zeolites. Until recently, however, only two large-pore tridirectional zeolites were synthesized, faujasite and Beta, and of these only the Beta zeolite can be directly synthesized with a high Si:Al ratio and therefore does not need, unlike the faujasites, a postsynthesis dealumination. Therefore, owing to the large catalytic interest and very limited number of large-pore tridirectional zeolites, a considerable effort has been devoted in the last decade to produce such structures[4]. Very recently,[5] the pure silica form of a new large-pore tridirectional zeolite has been presented, named ITQ-7 (Instituto de Tecnología Química-7). Unfortunately, the authors were unable to introduce acidity into ITQ-7 by direct synthesis with the trivalent (Al and Ga family) atoms in an isomorphically substituted zeolite[6]. Therefore, this large-pore tridirectional zeolite have had no possibilities in catalysis since only the purely siliceous form was available. Herein, we present the possibility to synthesize ITQ-7 with different T^{III} and T^{IV} elements isomorphically incorporated into the framework and, in this way, acidic, catalytically active ITQ-7 materials have been prepared.

The synthesis of isomorphically substituted zeolites was attempted following two strategies. The first strategy consists of synthesizing a boron-containing ITQ-7 (B-ITQ-7) sample which already should present some weak acidity and then, in a further step, to exchange B with Al to yield materials, named B/Al-ITQ-7, with a much greater acidity than the B-ITQ-7 precursor. The second strategy involves the direct synthesis of Al-ITQ-7. The two synthesis routes will be described below.

B-ITQ-7: Boron-containing ITQ-7 was formed from a gel with the composition SiO_2:B_2O_3:$C_{14}H_{26}NOH$:HF:H_2O in a molar ratio 1.0:0.01:0.50:0.50:3.0, where $C_{14}H_{26}NOH$ is 1,3,3-trimethyl-6-azonium-tricyclo[3.2.1.4^{6,6}]dodecane hydroxide. The gel was prepared by dissolving H_3BO_3 (0.08 g) in a solution of $C_{14}H_{26}NOH$ (0.99 M, 31.98 g). Tetraethylorthosilicate (TEOS, 13.46 g) was then hydrolyzed in the solution and the mixture was stirred gently to completely evaporated the ethanol formed. Finally, HF (1.34 g as 48.1 % in water) and purely siliceous ITQ-7 crystals (0.20 g) were added and the mixture was homogeneized. After 7 days crystallization at

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423 K in a PTFE-lined stainless steel autoclave rotating at 60 rpm, the powder obtained was washed, dryed at 373 K, and calcined at 853 K for 3 hours to yield a material whose X-ray diffraction (XRD) pattern closely corresponds to that obtained for the purely siliceous ITQ-7 (Figure 1 a). The ^{11}B MAS NMR spectra of the uncalcined sample showed the

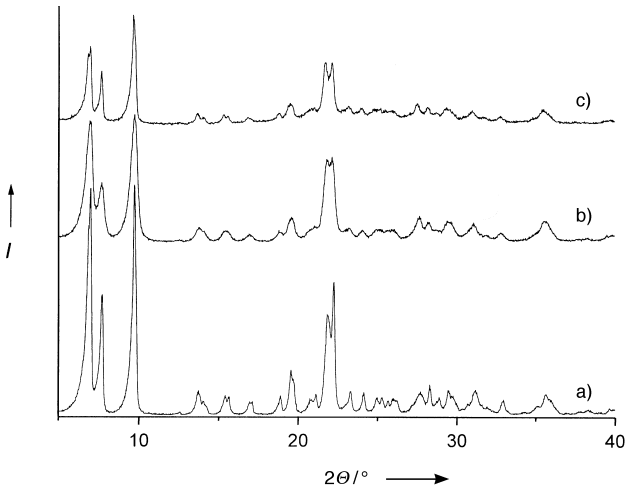

Figure 1. XRD patterns of calcined ITQ-7 samples: a) B-ITQ-7; b) Ge-ITQ-7; c) Al/Ge-ITQ-7.

presence of tetrahedrally coordinated boron (−3 ppm, spectrum not shown).[7] During the activation of the sample by calcination, the thermal decomposition of the structure directing agent (SDA; in this case $C_{14}H_{26}NOH$) was followed by IR spectroscopy. A 10 mg cm^{-2} self-supported wafer of the as-synthesized sample was introduced in an IR cell and the sample was heated to effect the complete disappearance of the IR bands of the SDA. Figure 2 shows the IR spectra of the ITQ-7 sample, in which of IR bands at 2955 cm^{-1} (ν_{asym}), 2873 cm^{-1} (ν_{sym}) and 1460 cm^{-1} (δ_{sciss}) are assigned to CH_2 groups and a shoulder at 2972 cm^{-1} (ν_{asym}) and a band at 1398 cm^{-1} (ν_{asym}) correspond to terminal CH_3 groups. Upon heating in vacuum (10^{-3} Pa), a slow and homogeneous decrease of the IR intensities occur. At 573 K, a new band appears at 1685 cm^{-1} while the intensity of the bands assigned to CH_3 groups decreases. The intensity of this new band increases with temperature up to 673 K and, at the same time, the bands of the methyl groups vanish and the total intensity of the IR spectrum strongly decreases. This change must be related to the partial decomposition of the SDA. The presence of the 1685 cm^{-1} band, tentatively assigned to an imine $\nu_{-C=N-}$ stretching vibration[8], suggests the formation of these compounds during the process. It seems reasonable to assume that the elimination mechanism occurs by breaking the SDA, at the C–N bond, into the five member ring imine and the remainder of the molecule, which includes all of the CH_3 groups. The imine moiety remains in the zeolite structure and the rest of the SDA decomposes. The imine moiety is fully lost at 773 K.

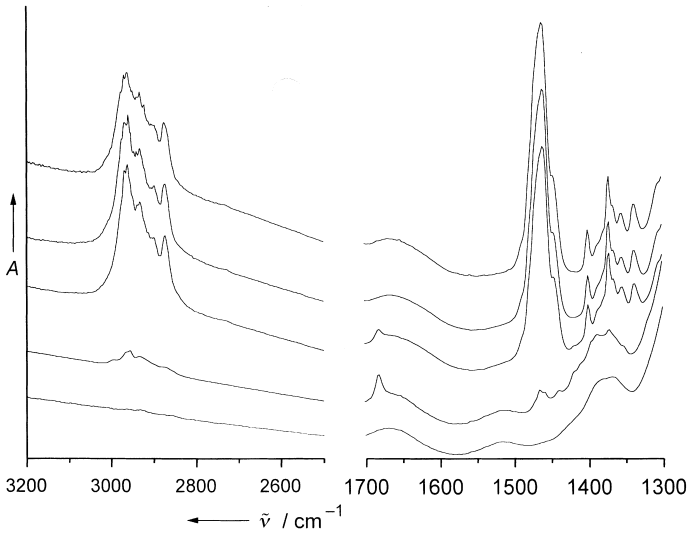

Figure 2. Infrared spectra of as-synthesized B-ITQ-7 sample. From top to bottom, the spectra are at room temperature and heated under vacuum at temperatures of 473, 573, 673, and 773 K.

The B-ITQ-7 sample was calcined and boron was exchanged with aluminum to form B/Al-ITQ-7 by following the procedure of Lobo and Davis[9]. The exchanged sample has a bulk Si:Al ratio of 90:1, as determined by elemental analysis, and the ^{27}Al MAS NMR spectrum (Figure 3 a) shows that most of the Al atoms occupy framework positions (54 ppm).

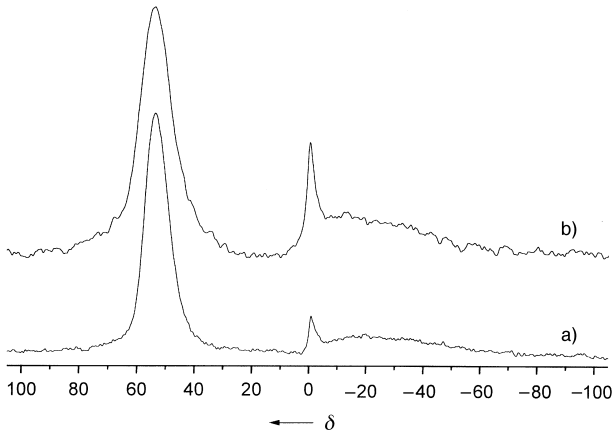

Figure 3. ^{27}Al MAS NMR spectra of calcined ITQ-7 samples: a) B/Al-ITQ-7, b) Al/Ge-ITQ-7.

To determine the Brønsted and Lewis acidities of the aluminum-exchanged sample, pyridine adsorption/desorption experiments were performed. The IR spectrum of the B/Al-ITQ-7 sample in the ν_{OH} region shows (Figure 4 a 1) the presence of three bands at $\tilde{\nu} = 3745$, 3628, and 3595 cm^{-1}. The first band is assigned to silanol groups, while the other two bands should be attributed to exposed hydroxyl groups of the acidic sites, as they vanish upon pyridine adsorption (Figure 4 a 2). The IR spectra of the adsorped pyridine in the 1350–1750 cm^{-1} region (Figure 4 b) show the relative intensities of the 1545 cm^{-1} (Brønsted) and 1455 cm^{-1} (Lewis) acid sites after desorption at different temperatures. This temperature-dependant desorption indicates that the majority of the Brønsted acid sites are of medium strength (423 K) while

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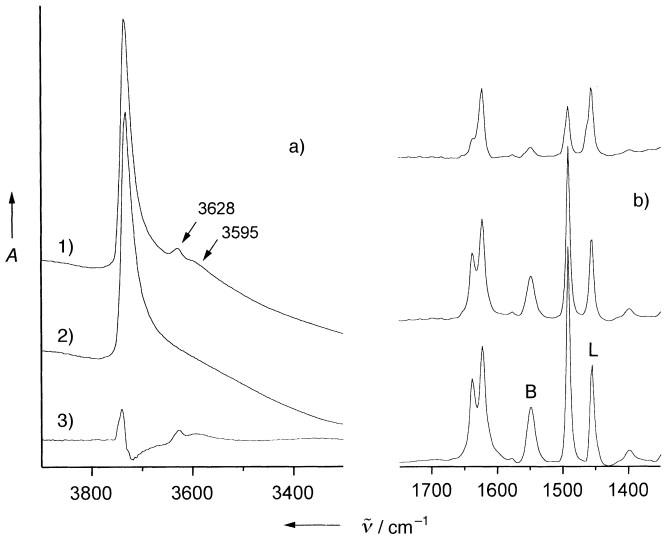

Figure 4. a) IR spectra in the OH stretching region of Al-ITQ-7: 1) after treatment at 673 K in vacuum, 2) after adsorbing pyridine at 523 K and 3) the differential spectrum. b) IR spectra of the adsorbed pyridine, which is then desorbed at (bottom to top) 423, 523, and 623 K. The IR spectra are offset for clarity. Labels B and L represent Brønsted and Lewis acid sites, respectively.

some remaining sites are of high strength (pyridine signal at >623 K). Lewis acid sites are strongly acidic, since pyridine remains adsorbed at temperatures as high as 623 K.

The presence of sites with medium and strong acidities in the B/Al-ITQ-7 sample opened the possibility of using this material as acid catalyst. In order to estimate its catalytic behaviour, the sample was tested by the catalytic cracking of *n*-decane and the conversion was compared with that obtained with a Beta zeolite with the same Si:Al ratio. The results, given in Figure 5, clearly show that the B/Al-ITQ-7 is active and its activity is close to that of Beta zeolite.

Al-ITQ-7: When we have attempted to introduce Al under the synthesis conditions reported previously,[6] an amorphous material was obtained even when using Si:Al ratios of 100:1 in the synthesis gel. When seeded with purely siliceous ITQ-7, an amorphous material with some XRD peaks of ITQ-7 was obtained after 30 days crystallization, while under other synthesis conditions, Beta zeolite was produced when Al was added to the gel. It seems that the distortion created in the framework by introducing Al may complicate the nucleation and growth of the ITQ-7 structure.

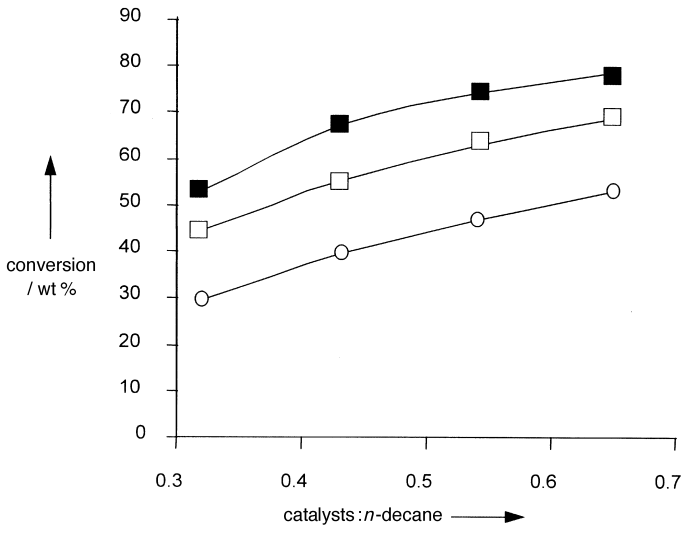

Figure 5. Cracking of *n*-decane on (□) B/Al-ITQ-7, (○) Al/Ge-ITQ-7, and (■) Beta zeolites at atmospheric pressure, 773 K, and 60 s on stream.

Recently, it has been proposed[10] that the addition of T atoms to the synthesis gel that are not Si but which can also coordinate tetrahedrally can produce different zeolitic structures, even when using the same organic SDA. It appears then that the effect of added heteroatoms on the structure of the zeolite should be due to the T-O-T′ bond lengths and angles which can direct the formation of particular secondary building units. In a recent theoretical study,[11] we found, by using periodic models and ab initio methods, that the introduction of germanium in the zeolite framework produces an increase in the framework flexibility because of the less rigid GeO_4 units and, as a consequence, we concluded that structures containing Ge could stabilize other, non-silicon framework cations, such as Ti and Al. Following this concept, we thought that a Si/Ge-ITQ-7 sample, if it could be synthesized, may be better able to cope with the framework distortions created by introducing Al.

The following synthesis gel of composition SiO_2:GeO_2:$C_{14}H_{26}NOH$:HF:H_2O in a molar ratio 1.0:0.10:0.55:0.55:3.30 was thus prepared. A quantity of GeO_2 (0.71 g) was dissolved in a solution of $C_{14}H_{26}NOH$ (1.06 M, 38.60 g). Then, TEOS (14.18 g) was added, allowed to hydrolyse, and the ethanol formed was left to evaporate. Finally, HF (1.56 g as 48.1 % in water) was added. After 7 days crystallization at 423 K, Ge-ITQ-7 was obtained (Figure 1 b) as the unique phase. The ^{29}Si MAS NMR spectra of the calcined sample (Figure 6) shows, in addition to a small concentration of defects (denoted by a resonance around -100 ppm due to Q_3 species), a marked decrease in the resolution of the bands corresponding to Q_4 species as

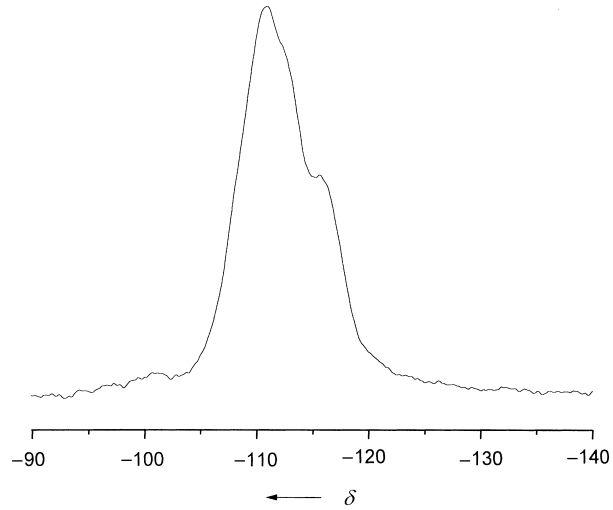

Figure 6. ^{29}Si MAS NMR spectrum of calcined Ge-ITQ-7.

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compared with those reported for the purely siliceous ITQ-7[5]. This can probably be attributed to the presence of Ge in the framework. An interesting observation is that while the purely siliceous sample presents crystallite sizes of ~ 2.0 μm, Ge-ITQ-7 forms very small crystallites with dimensions (> 0.1 μm) close to those of nanocrystalline zeolites (Figure 7). This result is extremely interesting, from the catalytic point of view, when treating molecules with smaller diffusion coefficients.

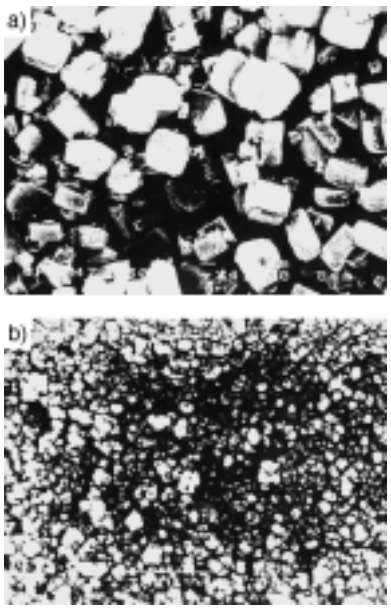

Figure 7. Scanning electron micrographs of a) purely siliceous ITQ-7 and b) Ge-ITQ-7.

After succeeding in the synthesis of Ge-ITQ-7, the incorporation of Al was attempted by preparing a gel with of composition SiO_2:GeO_2:Al_2O_3:$C_{14}H_{26}NOH$:HF:H_2O in a molar ratio 1.0:0.10:0.02:0.55:0.55:3.30. After 7 days crystallization at 423 K, Al/Ge-ITQ-7 was obtained (Figure 1c). The Al content was 1.2 wt % in the form of Al_2O_3. The ^{27}Al MAS NMR spectrum (Figure 3b) indicates that the majority of Al is tetrahedrally coordinated ($\delta = 54$) but some octahedral Al ($\delta = 0$) is present. In the IR spectrum of Al/Ge-ITQ-7 after pyridine adsorption (spectrum not shown), a $\tilde{\nu} = 1545$ cm^{-1} band attributed to pyridinium ions is observed, which indicates that this sample possesses a strong acidity.

The catalytic behaviour of the Al/Ge-ITQ-7 was tested by means of the catalytic cracking of *n*-decane and the results (Figure 5) indicate that the activity of this sample is lower than the B/Al-ITQ-7. This is in agreement with the greater amount of extra-framework Al present in Al/Ge-ITQ-7.

In conclusion, the T^{III}- and T^{IV}-substituted ITQ-7 zeolites have been synthesized and acid catalysts could be derived. For B-ITQ-7, boron occupies framework positions and generates mildly acid sites. The B can be exchanged with Al and, in the resultant B/Al-ITQ-7, the Al is in mostly in tetrahedral framework positions, to generate strongly acid sites that are very active for the cracking of *n*-decane. Germanium can also be introduced in the framework by direct synthesis, with a concomitant modification in the morphology of ITQ-7. When Ge is present in the synthesis gel, Al can be directly introduced in the framework of ITQ-7. The resultant Al/Ge-ITQ-7 zeolite is also acidic and catalyticaly active.

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Infinite, Linear, Unbranched Borynide Chains in LiB_x—Isoelectronic to Polyyne and Polycumulene**

Michael Wörle* and Reinhard Nesper*

Dedicated to Professor Peter Paetzold on the occasion of his 65th birthday

One of the great challenges in carbon chemistry is the synthesis of unbranched, linear chain modifications of carbon, the carbynes. Such carbynes are expected to have interesting physical properties like exceptional mechanical strength as well as one-dimensional conductivity and display an unusual variety of soliton and polaron states under appropriate doping conditions.[1] An infinite, linear, unbranched carbon chain can adopt the acetylenic $-[C{\equiv}C-]_nC{\equiv}$ (α carbyne) or the cumulenic form $=[C{=})]_nC=$ (β carbyne).[1–3] A main problem in synthesizing these carbon chains is their tendency to undergo interchain polymerization reactions of the Diels–Alder type.[2, 4, 5]

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