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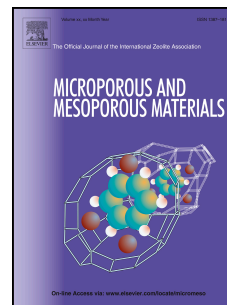
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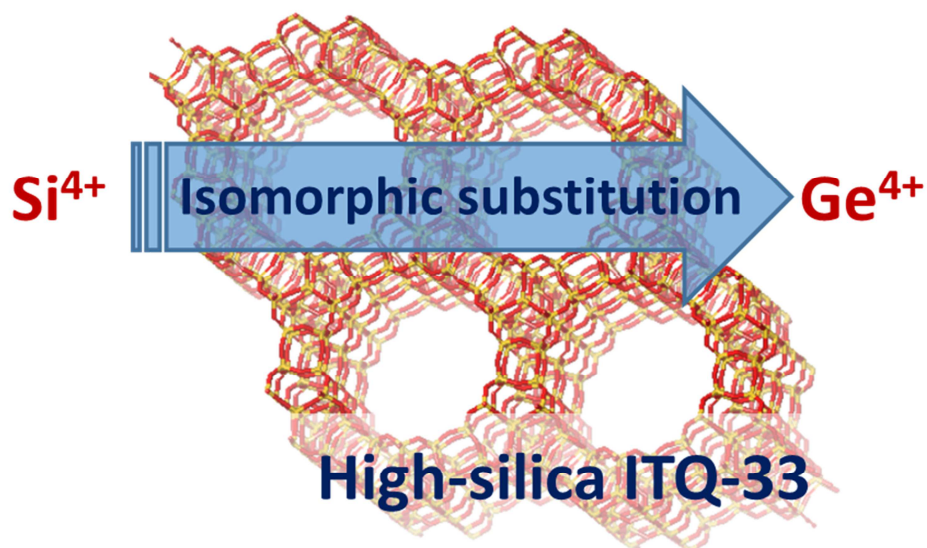
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Graphical abstract:



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Increasing the stability of the Ge-containing extra-large pore ITQ-33 zeolite by post-synthetic acid treatments

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Abstract

Extra-large pore ITQ-33 zeolite (ITT, 18x10x10-rings) is a very promising catalyst for the catalytic cracking of gasoil but, unfortunately, this material shows a limited hydrothermal stability due to the large germanium content present in the ITQ-33 structure. Taking this into account, the Ge-containing extra-large pore ITQ-33 zeolite has been post-synthetically modified using different acid procedures with the aim of studying the effect of these treatments on the overall hydrothermal stability of this extra-large pore zeolite. In this sense, the as-prepared ITQ-33 has been treated with different HCl solutions in ethanol (from 0.1 to 1 M), containing also tetraethylorthosilicate (TEOS) as silicon precursor, at different temperatures (150-175°C). From the different acid treatments, it is observed that treating ITQ-33 with a TEOS-containing 1 M HCl solution in ethanol at 150°C for 24 h, allows increasing the Si/Ge ratio from 2 to 3.2, mostly preserving the crystalline structure. If this acid-treatment is repeated three consecutive times, the Si/Ge can be increased up to 7.5, resulting in a highly stable extra-large pore zeolite. This post-synthetically modified ITQ-33 zeolite has been characterized by different techniques, including PXRD, FESEM, N₂ and Ar adsorption, ICP and ²⁷Al MAS NMR to unravel its physico-chemical properties. Finally, the catalytic behavior of the treated ITQ-33 zeolite has been tested for the catalytic cracking of gasoil, confirming in this way a remarkably higher hydrothermal stability than the as-prepared Ge-rich ITQ-33, permitting its regeneration for successive catalytic cycles.

Keywords

Extra-large pore zeolite, germanium, isomorphic substitution, catalytic cracking of gasoil

1.- Introduction

The introduction of germanium in the synthesis media has allowed the crystallization of several new zeolite structures in the last fifteen years,⁽¹⁾ particularly zeolites presenting very low framework densities and, in some cases, extra-large pores (openings above 8 Å).⁽²⁻⁷⁾ All these new germanosilicate structures have one thing in common, the presence of a particular secondary building unit (SBU) in their frameworks, which is the double four member ring (D4R).⁽¹⁾ In addition, some of them also contain 3-rings (3R) or double-3-rings (D3R).^(4, 6) The inorganic directing effect of germanium towards zeolite structures containing D4Rs was theoretically predicted and, later, experimentally proved by Corma et al.,⁽⁸⁾ based on the fact that Brunner and Meier proposed years before that the synthesis of very open zeolite structures should favour the formation of 3- and 4-rings in their frameworks.⁽⁹⁾

However, the incorporation of germanium into a high-silica framework negatively influences its hydrothermal stability and, in this sense, an increasing germanium content results in a very unstable crystalline material in the presence of water.⁽¹⁰⁾ In the last years, diverse authors have described different post-synthetic treatments in order to selectively substitute germanium from lattice positions by silicon and/or aluminium atoms.⁽¹¹⁻¹⁴⁾ The idea behind these post-synthetic treatments is to obtain stable high-silica zeolites with an analogous crystalline structure to the former silicogermanate zeolites.⁽¹¹⁻¹⁴⁾ The reported zeolites that have been post-synthetically degermanated maintaining the initial crystalline structure are ITQ-17 (BEC, 12x12x12-rings),^(11, 13) ITQ-15 (UTL, 14x12-rings), or ITQ-24 (IWR, 12x10x10-rings).⁽¹⁴⁾ Among the different post-synthetic treatments, it seems that those performed in an acid alcoholic media, containing a silicon soluble source, i.e. tetraethylorthosilicate, could be considered as the most versatile procedure to perform the isomorphic substitution of germanium by silicon species.⁽¹⁴⁾ In addition, alternative severe acid treatments have also been reported in the literature, such as the so-called ADOR or inverse sigma-inversion,^(15, 16) but they are accompanied by a phase transformation, allowing the crystallization of new crystalline structures.⁽¹⁷⁻¹⁹⁾

From the different germanium-containing zeolites described in the literature, the crystalline structure of ITQ-33 (ITT, 18x10x10-rings) is one of the most interesting topologies.⁽⁴⁾ This multipore zeolite combines the presence of extra-large pores (18-rings, openings above 10 Å, see Figure 1) with interconnected medium pores (10-rings, pore openings of ~5.5 Å, see Figure 1), favoring unique molecular diffusion pathways that can result in unique product selectivities when applied as catalyst to some industrially-relevant chemical processes, such as catalytic cracking of

gasoil.(4, 20) However, the ITT framework contains small subunits, D4R and 3R units (see Figure 1), where the lattice atoms (T) conforming these sub-units require T-O-T angles in the range of $\sim 130^\circ$.(21) These low T-O-T angles can be more easily afforded when germanium is present in, at least, one of the vertices of these sub-units, since the Ge-O-Ge or Ge-O-Si angles are closer to 130° than those of Ge-free conformations, such as Si-O-Si or Al-O-Si ($\sim 145^\circ$). (8, 21) According to these structural features, the syntheses of the as-prepared ITQ-33 zeolites reported in the literature are limited to low Si/Ge ratios (below 2). (4, 20, 22) These Ge-rich zeolites are very unstable after being calcined, even under mild conditions, such as being exposed to wet atmospheric conditions. Herein, we have studied different post-synthetic acid treatments on the as-prepared ITQ-33 zeolite to selectively substitute part of the initial tetrahedrally-coordinated Ge atoms by Si, with the principal aim of enhancing its hydrothermal stability. The resultant post-synthetically treated ITQ-33 samples have been properly characterized by different techniques to evaluate their physico-chemical properties, including Powder X-Ray Diffraction (PXRD), Field Emission Scanning Electron Microscopy (FESEM), N_2 and Ar adsorption, chemical analysis by Inductively Coupled Plasma (ICP) and, ^{27}Al and ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR), among others. When testing this optimized ITQ-33 zeolite for the catalytic cracking of gasoil, it presents a remarkable hydrothermal stability improvement as compared to the parent Ge-rich ITQ-33.

2.- Experimental

2.1.- Synthesis of the ITQ-33 zeolite and post-synthetic treatments

The ITQ-33 zeolite has been synthesized according to the synthesis procedure described in the literature.(4, 20)

For the post-synthesis acid treatments of the as-prepared ITQ-33 zeolites, 1.0 g of solid is mixed with 30 ml of an HCl solution in ethanol (0.1 or 1M) containing 1 mmol of tetraethylorthosilicate (TEOS) as additional silicon source, and the resultant mixture is autoclaved and introduced at 150 or $175^\circ C$ for 24 h under rotatory conditions (Note: the HCl-ethanol solutions are prepared from a commercially-available 1.25 M hydrogen chloride – ethanol solution, Sigma-Aldrich, containing $<0.5\%$ wt of water). This post-synthetic acid-treatment can be repeated up to 3 times. Finally, the modified ITQ-33 samples are calcined at $540^\circ C$ in air using a fixed-bed reactor.

2.2.- Characterization

Powder X-ray diffraction (PXRD) measurements were performed with a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 35 mA, and using Cu K α radiation ($\lambda = 0,1542$ nm). The chemical analyses were carried out in a Varian 715-ES ICP-Optical Emission spectrometer, after solid dissolution in HNO₃/HCl/HF aqueous solution.

The morphology of the samples was studied by field emission scanning electron microscopy (FESEM) using a ZEISS Ultra-55 microscope.

Textural properties were determined by N₂ and Ar adsorption-desorption isotherms measured on a Micromeritics ASAP 2020 at 77 and 87 K, respectively. The ASAP 2020 analysis program V4.01 has been used to calculate the pore size distribution from the Ar adsorption isotherm data based on the Horvath-Kawazoe method.

Solid NMR spectra were recorded at room temperature with a Bruker AV 400 MAS spectrometer. ²⁹Si MAS NMR spectra were recorded with a spinning rate of 5 kHz at 79.459 MHz with a 55° pulse length of 3.5 μ s and repetition time of 180 s. ²⁷Al MAS NMR spectra were recorded at 104.2 MHz with a spinning rate of 10 kHz and 9° pulse length of 0.5 μ s with a 1 s repetition time. ²⁹Si and ²⁷Al chemical shifts were referred to tetramethylsilane and Al³⁺(H₂O)₆, respectively.

2.4.- Catalytic tests

Catalytic cracking of a vacuum gasoil, whose main properties are presented in Table 1, was carried out in an automated microactivity test (MAT) unit (ASTM D-3907), at 520°C and 15 s time on stream (TOS), and different catalyst-to-oil ratios (cat/oil expressed as weight of zeolite/weight of feed). For testing in the MAT unit, the zeolite was pelletized, crushed and sieved to a particle size in the range of 0.42–0.59 mm in diameter. 0.5 g of this sample was mixed with SiO₂ (2.5 g), which was previously sieved to a particle size in the range of 0.25–0.42 mm. The reaction system, fully automated, can be operated in a continuous way up to eight cycles, i.e. stripping-reaction-regeneration. Before starting the series of experiments, the catalyst was activated under a 100 cm³/min air flow at 540°C for 3 h. Then, before each reaction, the system was purged with a 30 cm³/min N₂ flow for 30 min at the reaction temperature. After reaction, stripping of the catalyst was carried out for 15 min using a N₂ flow of 30 cm³/min. During the reaction and stripping steps, the liquid products were collected in the corresponding glass receivers located at the exit of the reactor, kept at 15°C by means of a computer controlled bath, and the gaseous products were collected in a gas burette by water displacement. After stripping, the catalyst was regenerated at 540°C for 3 h, in a 100 cm³/min stream of air. This cyclic operation enables the study of the catalysts' hydrothermal stability during the different reaction/regeneration steps. More details are given in ref. (23).

3.- Results

3.1.- Synthesis of the ITQ-33 zeolite

The ITQ-33 zeolite has been prepared according to the synthesis procedure described in the literature using hexamethonium as organic structure directing agent (OSDA).^(4, 20) The PXRD pattern of the as-prepared ITQ-33 material shows the crystallization of the ITT structure as pure phase (see ITQ-33_a.p. in Figure 2), whereas FE-SEM microscopy indicates the formation of homogeneous crystals of 0.2x1 μm along the entire solid (see ITQ-33_a.p. in Figure 3). The elemental analysis of the as-prepared ITQ-33 zeolite allows quantifying the presence of ~15% of organic moieties within the zeolite pores. The ICP analysis indicates that the Si/Ge and (Si+Ge)/Al molar ratios in the original ITQ-33 zeolites are ~2 and ~20, respectively (see Table 3), in good agreement with previous descriptions in the literature.^(4, 20)

If the as-prepared Ge-rich ITQ-33 zeolite is calcined and exposed to moisture at ambient conditions, the crystalline structure collapses with time. However, if the calcined Ge-rich ITQ-33 sample is immediately introduced under an inert atmosphere (N_2 or Ar) after the calcination treatment, the crystalline structure is preserved and, then, the textural properties of this material can be measured by N_2 adsorption. As seen in Table 4, the ITQ-33 zeolite after being calcined and stored in a moisture-free atmosphere, shows a BET surface area and a micropore volume of 631 m^2/g and 0.28 cm^3/g , respectively. However, if this calcined Ge-rich ITQ-33 zeolite is exposed to ambient conditions in presence of moisture for 7 days, the crystalline structure collapses, resulting in a BET surface area and a micropore volume of 200 m^2/g and 0.08 cm^3/g , respectively (see Table 4, and the N_2 adsorption isotherm of ITQ-33_7d in Figure 4).

3.2.- Post-synthetic acid treatments

Different post-synthetic acid treatments have been proposed to attempt the selective removal of, at least, part of the germanium atoms present in the structure of the Ge-rich ITQ-33 zeolite with the aim of increasing its hydrothermal stability. For this purpose, two different HCl solutions in ethanol have been selected (0.1 M and 1 M) to evaluate the effect of the acid concentration on either the germanium extraction or the crystalline framework damage. It is worth noting that since the Si/Ge ratio of the original ITQ-33 zeolite is very low, a silicon source soluble in ethanol, such as tetraethylorthosilicate (TEOS), has also been incorporated in the acid solutions to favor the

insertion of isolated silicon species in the framework vacancies created by the germanium extraction. The influence of the temperature of the post-synthetic acid treatments has also been studied (i.e. 150 or 175°C).

Therefore, three different acid treatments have been carried out to evaluate the post-synthetic modification of the Ge-rich ITQ-33: (A) 1 M HCl in ethanol at 175°C, (B) 0.1 M HCl in ethanol at 175°C, and (C) 1 M HCl in ethanol at 150°C. All these three treatments have been performed for 24 hours at the selected temperatures in autoclaves under tumbling conditions. After these procedures, the treated ITQ-33 zeolites have been recovered by filtration, and the resultant solids were structurally and texturally characterized.

The PXRD pattern of the acid-modified ITQ-33 solid, obtained by treatment with a 1 M HCl solution at 175°C, shows the formation of a dense crystalline phase (see the peak at $\sim 26^\circ$ in the PXRD pattern of ITQ-33_A_1T in Figure 2). Since this peak is characteristic of quartz, it could be speculated that these post-synthetic conditions are excessively severe for the Ge-rich ITQ-33 zeolite, resulting in an undesired crystalline phase transformation. In contrast, the other two procedures performed at either lower acid concentration (0.1 M HCl at 175°C) or lower temperature (1 M HCl at 150°C), mostly preserve the ITQ-33 crystalline structure while avoiding the undesired formation of a quartz-related phase (see PXRD patterns of ITQ-33_B_1T and ITQ-33_C_1T in Figure 2). The ICP analysis of these acid-treated ITQ-33 reveals a significant increase of the Si/Ge ratio from 2.2 to 3.2 (see Table 3), which corresponds to a decrease of the initial 32% germanium content in the as-prepared ITQ-33 to a germanium content below 24% in the treated ITQ-33 samples. In addition, the aluminum content within the acid-treated ITQ-33 zeolites mostly remains unaltered after these individual acid procedures ($T^{\text{IV}}/\text{Al} \sim 20$, see ITQ-33_B_1T and ITQ-33_C_1T in Table 3). Moreover, the ^{27}Al MAS NMR spectrum of the ITQ-33 treated with the 1 M HCl solution at 150°C confirms the exclusive presence of a single peak centered at ~ 55 ppm, which can be assigned to tetrahedrally coordinated aluminum species (see ITQ-33_C_1T in Figure 5). These results undoubtedly indicate that the selected acid treatments, at least those performed under milder conditions (i.e. lower acidity and/or temperature), favors the selective removal of germanium from tetrahedral positions and mostly preserves the original ITT framework structure. Although these preliminary results are very interesting, the germanium content within the ITQ-33 should be further reduced to enhance its hydrothermal stability. Considering that the use of severe post-synthetic acid treatments (i.e. 1 M HCl at 175°C) results in a permanent structure damage by the recrystallization of a dense phase, we decided to carry out successive post-

synthetic treatments (up to three), under milder conditions (i.e. 1 M HCl at 150°C). Then, the previously treated ITQ-33_C_1T sample has been submitted to one or two additional acid treatments using a TEOS-containing 1 M HCl solution in ethanol at 150°C for 24 hours, resulting in the ITQ-33_C_2T and ITQ-33_C_3T samples, respectively. The PXRD patterns of the recovered solids after each post-synthetic acid treatment show that the crystalline structure of the ITQ-33 is mostly preserved, and the presence of an additional crystalline dense phase is not observed (see ITQ-33_C_2T and ITQ-33_C_3T in Figure 6). ICP analyses reveal an increasing Si/Ge molar ratio as the number of acid treatments also increases, achieving a Si/Ge molar ratio of 7.4 after three post-synthetic acid procedures (see ITQ-33_C_3T in Table 3), which corresponds to a final germanium content below 11% in the treated ITQ-33 sample. Interestingly, the ^{29}Si MAS NMR spectrum of the three-time treated ITQ-33 shows a remarkable increase of the intensity of the peaks in the range -110 and -116 ppm, and a decrease of the peaks in the range -102 and -105, which could be mostly associated to Si(4Si) and Si(2Ge, 2Si), respectively, compared to the as-prepared ITQ-33 (see Figure 7). These results would suggest that, at least partially, the selective isomorphous substitution of the initial tetrahedrally-coordinated germanium by silicon is adequately occurring.

The ICP analyses also indicate that there is a slight decrease of the aluminum content in the ITQ-33 after three post-synthetic treatments ($\text{T}^{\text{IV}}/\text{Al} \sim 26$, see ITQ-33_C_3T in Table 3) but, interestingly, the ^{27}Al MAS NMR spectrum confirms that all remaining aluminum species are in tetrahedral coordination (see the single peak at ~ 55 ppm in the ^{27}Al MAS NMR spectrum of the ITQ-33_C_3T in Figure 5).

The N_2 adsorption characterization on the successively treated ITQ-33 materials shows a slight and continuous decrease of the measured micropore volumes after each acid treatment, resulting in a micropore volume value of $\sim 0.20 \text{ cm}^3/\text{g}$ for the ITQ-33 treated three times (see ITQ-33_C_3T in Table 4). This decrease of the textural properties could be explained either by the partial collapse of the crystalline structure or by the incorporation of low-polymerized silicon species within the pores of the zeolite during the different post-synthetic treatments. In this sense, the FE-SEM images show that the modified ITQ-33 zeolites maintain the initial crystal morphology of the as-prepared ITQ-33 without an apparent “amorphization” of the solids (see Figure 3), and, in addition, the pore distribution of the ITQ-33_C_3T measured by Ar adsorption clearly indicates the presence of the extra-large pores within the modified ITQ-33 zeolites (see Figure 8). These characterization techniques, together with the PXRD patterns, would suggest that the crystalline structure of the ITQ-33 could be mostly preserved after being acid treated, and thus, the presence

of some silicon species within the pores could not be ruled out. Nevertheless, it is very important to note that textural properties of the ITQ-33_C_3T remain intact after being exposed seven days to wet ambient conditions, confirming the improvement of the hydrothermal stability achieved after undergoing the post-synthetic acid treatments (see the N₂ adsorption isotherm for ITQ-33_C_3T_7d in Figure 4).

3.3.- Catalytic application: catalytic cracking of a vacuum gasoil

The catalytic cracking of gasoil is a main conversion process within a refinery, where the use of zeolite-based catalysts, particularly FAU-related materials, has permitted efficient transformations of high-molecular weight hydrocarbons into more valuable fractions, such as gasoline, diesel or light olefins gases, mainly propylene. During the catalytic process, the zeolitic material is quickly deactivated by the formation of coke within the pores of the zeolite, and a continuous regeneration of the catalyst at high temperatures is required for successive uses. These severe reaction/regeneration cycles enforces the design of highly stable zeolite catalysts to prevent the permanent catalyst deactivation, mainly by collapse of the structure.

Preliminary results on the use of the Ge-rich ITQ-33 as catalyst for the catalytic cracking of gasoil showed excellent initial catalytic activities (see results for ITQ-33 at a cat-oil ratio of ~0.5 g/g in Table 5), and good selectivities towards highly desired products, as diesel or olefins within the liquefied petroleum gases fraction (LPG). In fact, VGO conversion (~76%) is comparable to that obtained with a commercially-employed FAU-related zeolite of similar Si/Al molar ratio tested under the same conditions (see USY_CBV760 in Table 5), and the yield to diesel obtained with ITQ-33 is higher in more than 5 points. However, when the exhausted Ge-rich ITQ-33 catalyst is “in-situ” regenerated and tested at the same cat-oil ratio (~0.5 g/g), a remarkably lower VGO conversion is obtained, as compared to the originally fresh Ge-rich ITQ-33 zeolite (~25% loss of catalytic activity, see results corresponding to ITQ-33-REG in Table 5). This behavior can only be attributed to a permanent catalyst deactivation occurred during the regeneration process, maybe associated to the low-hydrothermal stability of the Ge-rich ITQ-33 zeolite, and resulting in a partial annihilation of the crystalline structure.

The “degermanized” ITQ-33 zeolite, ITQ-33_C_3T, presents a lower VGO conversion than the fresh parent ITQ-33 zeolite when tested at a cat-oil ratio of ~0.5 g/g (see ITQ-33_C_3T in Table 5), a result that can be related to the lower Al content and/or micropore volume of the treated ITQ-33. However, despite its initially lower activity, ITQ-33_C_3T does not deactivate after being tested for three consecutive reaction-regeneration cycles (see ITQ-33_C_3T-REG in Table 5), and the VGO

conversion obtained with the regenerated zeolite when repeating the test at a cat/oil of 0.5 g/g is maintained as compared to the one given by the fresh sample. Yield to diesel obtained for the fresh treated ITQ-33 zeolite, ITQ-33-3T, is lower than that obtained for the non-treated parent ITQ-33, but this can be explained by the lower conversion given by the former. In fact, when ITQ-33_C_3T is tested at a higher cat/oil ratio of 0.83 (g/g) and conversion is increased to 76.6%, the degermanized ITQ-33 is more selective to diesel than the commercial CBV760 zeolite, and it yields more propylene (5.2 wt%) than the USY or the fresh Ge-rich ITQ-33 (4.8 and 3.2, respectively) at similar propene/propane ratios. Olefinicity in the C₄ fraction is also higher for the treated ITQ-33_C_3T than for the USY zeolite and the parent ITQ-33 (see C_4^-/C_4 and iC_4^-/iC_4 ratios in Table 5).

4.- Conclusions

The post-synthetic modification of the Ge-rich ITQ-33 zeolite by different acid treatments with tetraethylorthosilicate (TEOS)-containing HCl solutions in ethanol, has allowed notoriously increasing the hydrothermal stability of this extra-large pore zeolite with a pore system composed by interconnected 18x10x10-rings. The three-time treated ITQ-33 with a TEOS-containing 1 M HCl solution in ethanol at 150°C for 24 h, allows increasing the Si/Ge ratio from 2 to 7.5, while preserving almost intact the crystalline structure. This post-synthetically modified ITQ-33 zeolite results in a highly-stable extra-large pore zeolite, as it has been revealed by different characterization techniques. Finally, the optimized ITQ-33 zeolite has been evaluated for the catalytic cracking of gasoil, yielding to a very active and stable catalyst that can be regenerated for many consecutive catalytic cycles.

Acknowledgements

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Figure 1. Crystalline structure of the ITQ-33 zeolite (ITT)

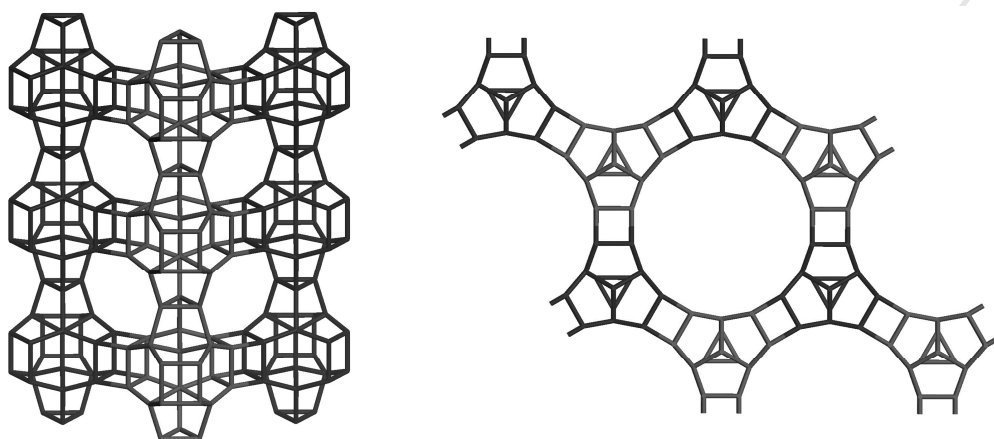


Figure 2. PXRD patterns of the as-prepared ITQ-33, and after being treated with an acid solution under different conditions: (A) 1 M HCl in ethanol at 175°C; (B) 0.1 M HCl in ethanol at 175°C; and (C) 1 M HCl in ethanol at 150°C

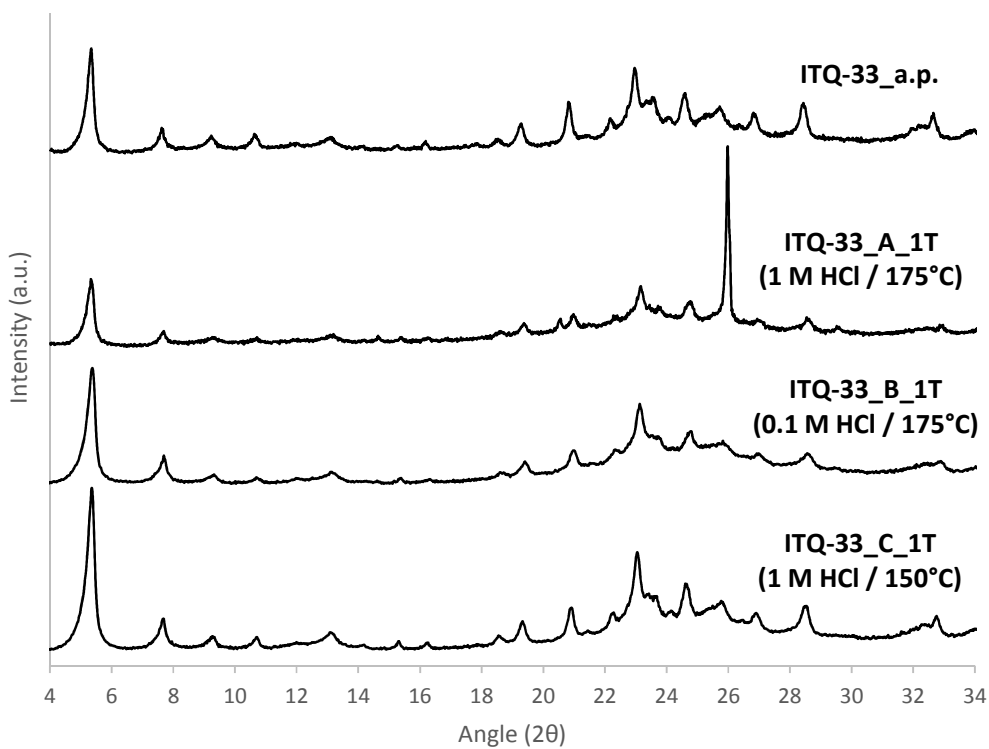


Figure 3. FESEM images of the as-prepared ITQ-33, and after being successively treated with a 1 M HCl solution in ethanol at 150°C (1T, 2T or 3T, corresponds to 1, 2 or 3 consecutive acid treatments)

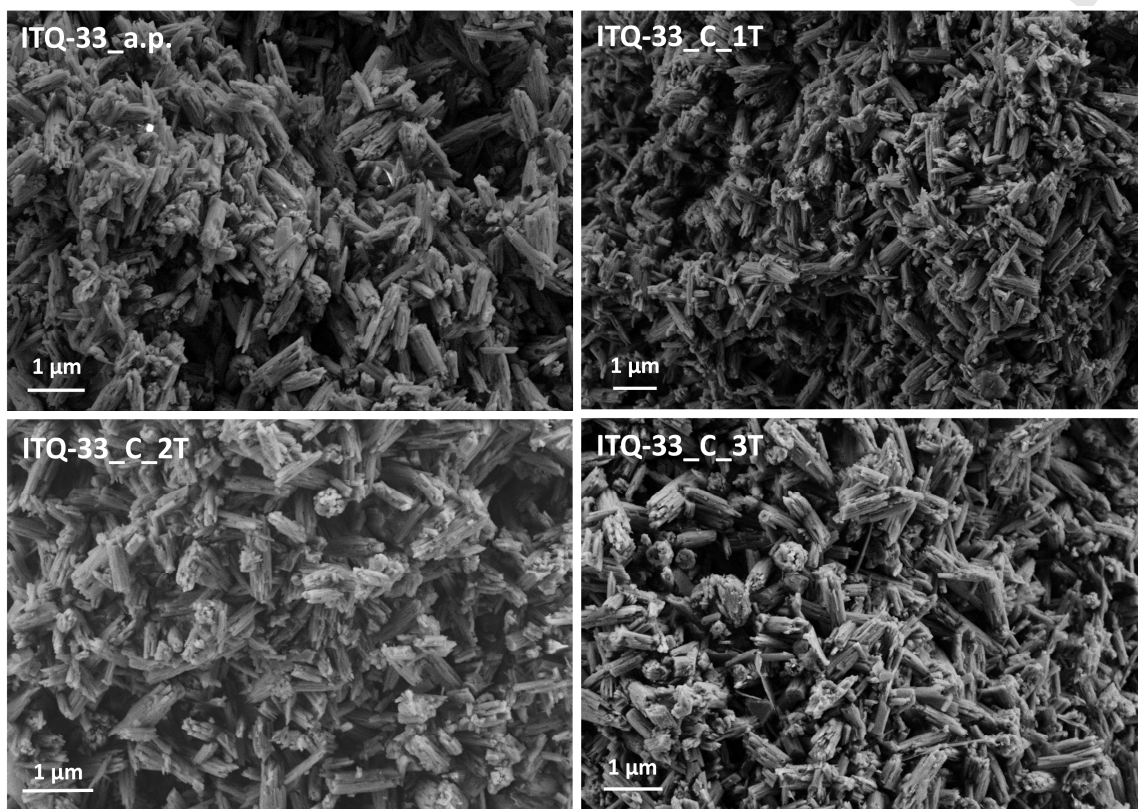


Figure 4. N_2 adsorption isotherms of the non-treated ITQ-33 after being calcined (ITQ-33_calc) and exposed to ambient conditions 7 days (ITQ-33_7d), and the three-time acid treated ITQ-33 after being calcined (ITQ-33_C_3T) and exposed to ambient conditions 7 days (ITQ-33_C_3T_7d)

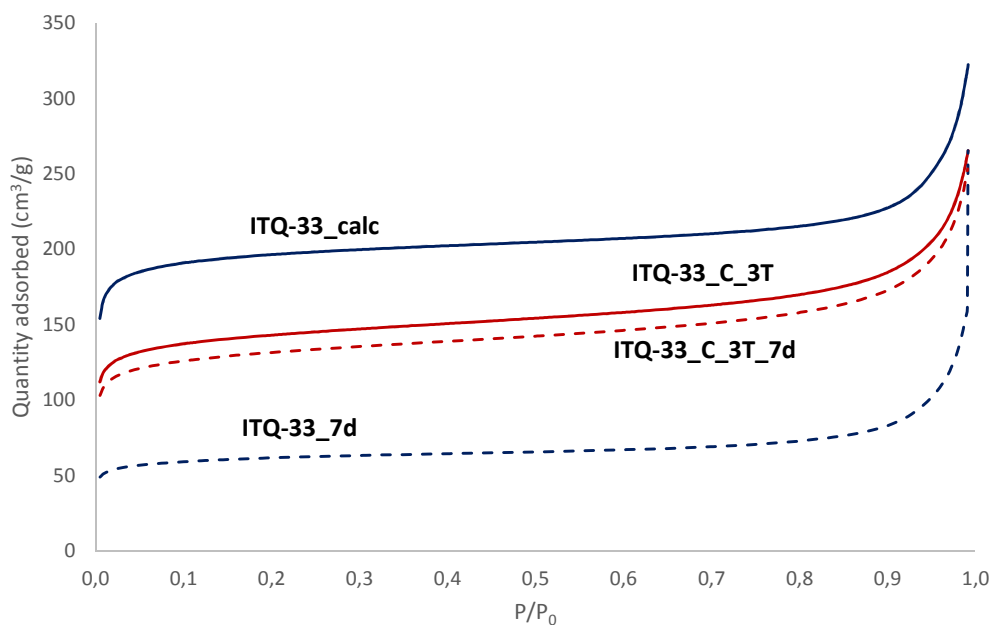


Figure 5. ^{27}Al MAS NMR spectra of the as-prepared ITQ-33 zeolite and after being post-synthetically treated with a 1 M HCl solution in ethanol at 150°C, one-time (1T) and three-time (3T), respectively

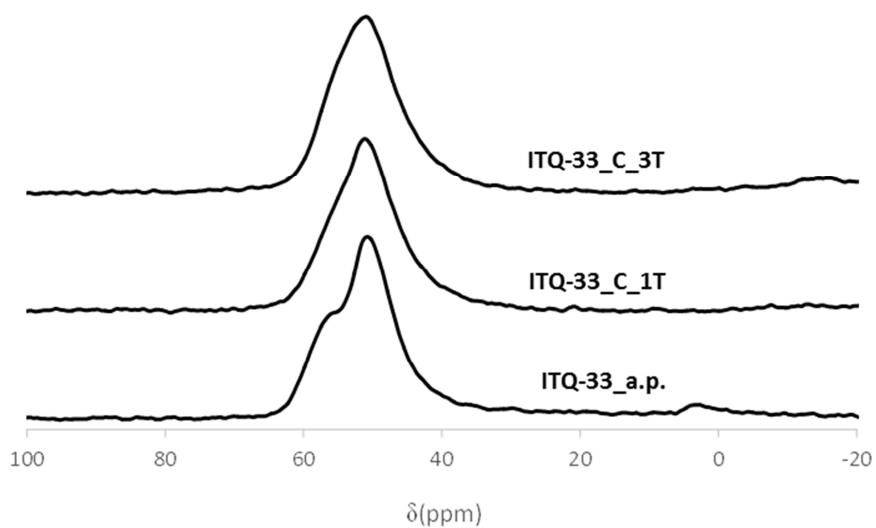


Figure 6. PXRD patterns of the as-prepared ITQ-33, and after being successively treated with a 1 M HCl solution in ethanol at 150°C (1T, 2T or 3T, corresponds to 1, 2 or 3 consecutive acid treatments)

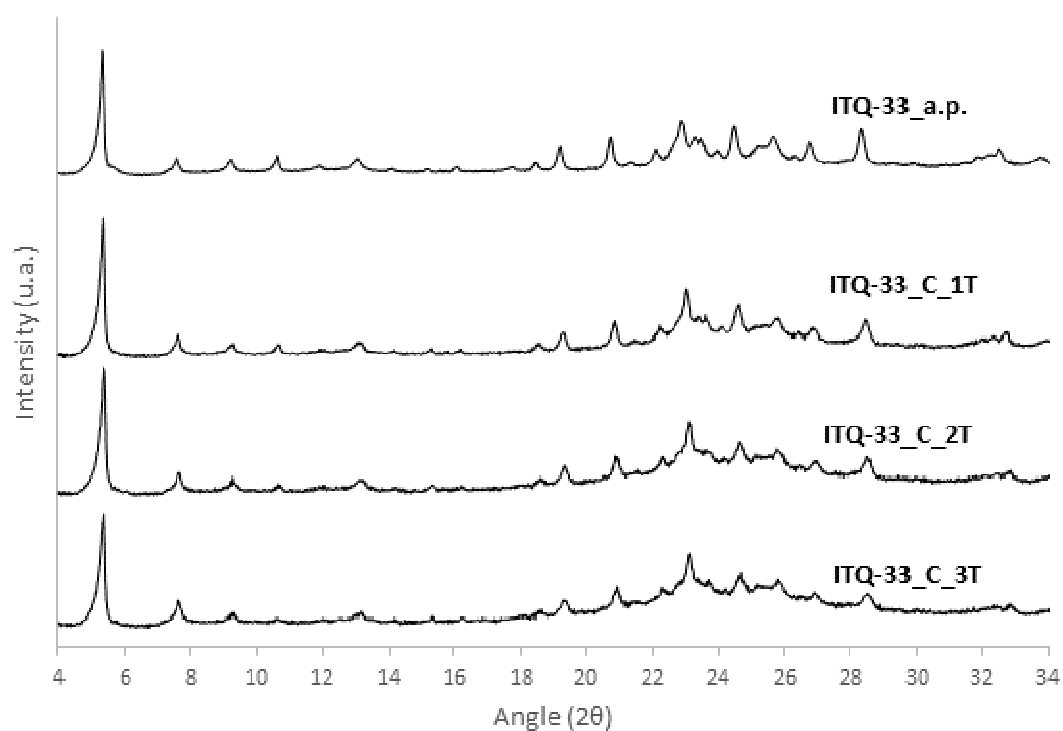


Figure 7. ^{29}Si MAS NMR spectra of the as-prepared ITQ-33 zeolite (ITQ-33_a.p., Top) and after being three-time post-synthetically treated with a 1 M HCl solution in ethanol at 150°C (ITQ-33_C_3T, Bottom)

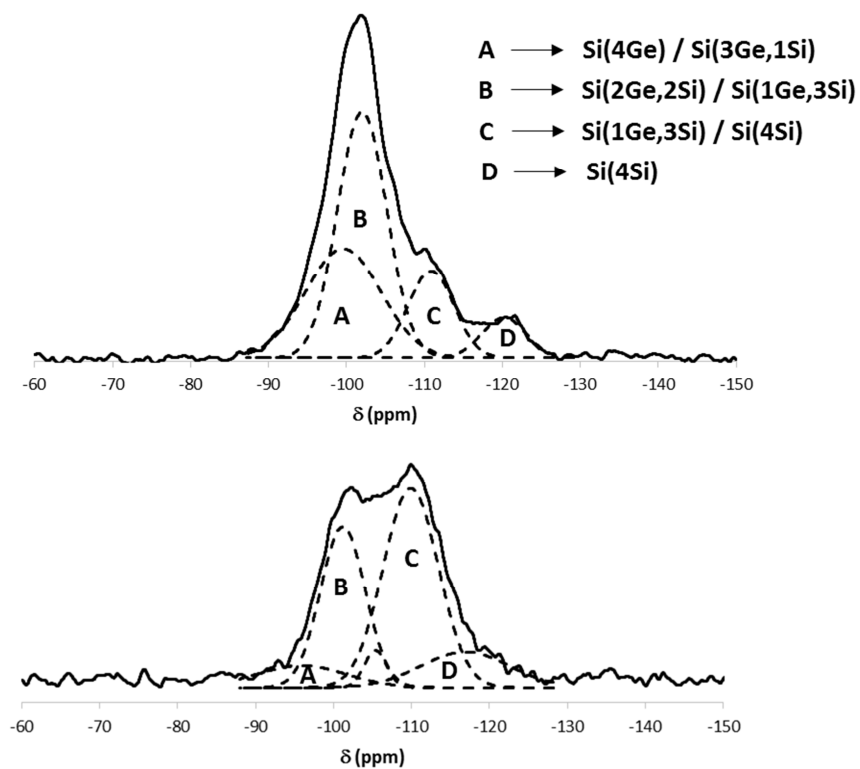


Figure 8. Pore distribution, measured by Ar adsorption, of the post-synthetically treated ITQ-33_C_3T after being treated with a 1 M HCl solution in ethanol at 150°C three consecutive times

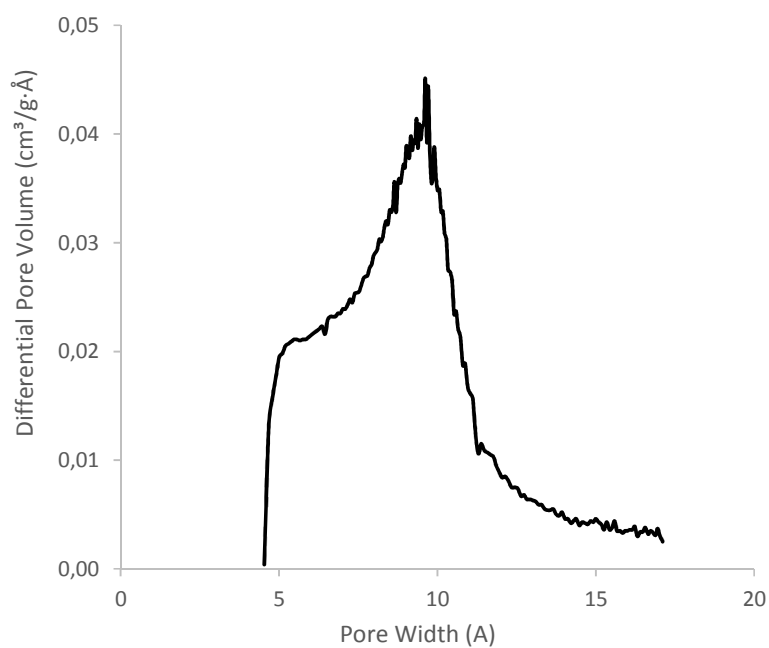


Table 1: Characteristics of the vacuum gas oil

DENSITY(15°C)g/cc	0.9258
ANILINE POINT	90.8
K(UOP)	11.907
SULFUR(%wt)	0.488
NITROGEN(ppm)	1876
Na (ppm)	0.3
Cu (ppm)	<0.1
Fe (ppm)	<0.1
Ni (ppm)	<0.1
V (ppm)	0.1
AVERAGE MOLECULAR WEIGHT	474
AROMATIC CARBON (ndM)%	22.32
NAPHTHENIC CARBON (ndM)%	19.19
PARAFFINIC CARBON (ndM)%	58.48
AROMATIC RINGS/MOLECULE (ndM)	1.33
NAPHTHENIC RINGS/MOLECULE (ndM)	1.68
ASTM 1160 (°C)	
5%	402
10%	414
30%	438
50%	464
70%	496
90%	543

Table 2: Elemental analyses of the ITQ-33 materials

Sample	Treatment	Number of treatments	%wt N	%wt C	%wt H	%wt Total	C/N (molar ratio)
ITQ-33_a.p.	As-prepared	---	1.93	9.47	2.31	13.71	5.7
ITQ-33_C_1T	1 M HCl, 150°C	1	1.26	6.13	1.90	9.29	5.7
ITQ-33_C_3T	1 M HCl, 150°C	3	0.58	2.70	1.08	4.36	5.5

Table 3: ICP analyses of the ITQ-33 materials

Sample	Treatment	Number of treatments	Si/Ge	(Si+Ge)/Al
ITQ-33_a.p.	As-prepared	---	2.2	20.4
ITQ-33_B_1T	0.1 M HCl, 175°C	1	3.2	23.7
ITQ-33_C_1T	1 M HCl, 150°C	1	3.2	21.9
ITQ-33_C_2T	1 M HCl, 150°C	2	5.8	24.7
ITQ-33_C_3T	1 M HCl, 150°C	3	7.4	26.4

Table 4: Textural properties of the different ITQ-33 zeolites measured by N₂ adsorption

Sample	Treatment	BET surface area (m ² /g)	Micropore area (m ² /g)	External area (m ² /g)	Micropore volume (cm ³ /g)
ITQ-33_calc	Calcined "in-situ"	631	588	43	0.28
ITQ-33_7d	Calcined "in-situ" + 7 days ambient	200	176	23	0.08
ITQ-33_C_1T	1 treatment (1 M HCl, 150°C) + calcination	575	532	43	0.26
ITQ-33_C_2T	2 treatments (1 M HCl, 150°C) + calcination	523	458	65	0.22
ITQ-33_C_3T	3 treatments (1 M HCl, 150°C) + calcination	464	398	66	0.19
ITQ-33_C_3T_7d	3 treatments (1 M HCl, 150°C) + calcination + 7 days ambient	427	362	65	0.18

Table 5: Catalytic results for cracking of a VGO in a MAT unit at 520°C and 15 s time on stream (TOS)

Catalyst	Cat/oil ratio (g/g)	Conversion (%)	Yields (wt%)			Olefin/paraffin ratios in LPG (wt/wt)		
			Diesel	Gasoline	C ₃ ⁼	C ₃ ⁼ /C ₃	C ₄ ⁼ /C ₄	iC ₄ ⁼ /iC ₄
USY-CBV760*	0.25	59.9	19.4	28.2	2.5	4.5	1.44	0.59
USY-CBV760*	0.50	78.8	18.9	39.0	4.8	4.7	1.16	0.42
ITQ-33	0.50	75.6	23.8	31.0	3.4	3.2	1.15	0.44
ITQ-33-REG	0.50	59.3	19.7	24.8	2.1	3.7	1.95	0.95
ITQ-33_C_3T	0.50	65.0	17.5	26.0	4.3	3.2	1.15	0.46
ITQ-33_C_3T-REG	0.50	65.9	19.2	26.4	3.5	3.6	1.53	0.66
ITQ-33_C_3T	0.84	76.6	21.2	30.0	5.2	3.3	1.23	0.51

*CBV760 (Zeolyst Int.): bulk Si/Al=28, unit cell size of 24.26 Å

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Highlights:

- The hydrothermal stability of ITQ-33 has been improved by post-synthetic acid treatments.
- Different characterization techniques reveal the isomorphic substitution of Ge by Si.
- High-silica ITQ-33 shows good activity and enhanced stability for the cracking of gasoil.