

MWW monolayers obtained by direct dual template synthesis.

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Abstract: A two dimensional zeolite with the topology of MWW sheets has been obtained by direct synthesis with a combination of two organic structure directing agents. The resultant material is formed in about 70% by single and double layers with a well structured external surface area of about 300 m²·g⁻¹. The delaminated zeolite prepared by means of this single step synthesis route presents not only a high delamination degree, but a well preserved structural integrity of the MWW layers. It presents an excellent activity, selectivity and catalyst life for alkylation of benzene with propylene, being better than catalysts used today for producing cumene.

The importance of zeolites as adsorbents and heterogeneous catalysts is well recognized [1]. When used as catalysts, the microporous structure of these crystalline solids confers the reactants a confined environment that, besides pre-activating the molecules, may direct the reaction towards the formation of the desired products by stabilizing the reaction transition states. However, the narrow pore dimensions of most of the zeolites, in the range of 4 to 7 Å, limit their use to processes involving relatively small molecules. Many efforts have been directed to increase the accessibility to the active sites, and to reduce the diffusional problems of bulkier reactants while preserving a degree of confinement. Traditionally, the accessibility to the active sites has been increased by means of post-synthesis methods that combine acid and hydrothermal treatments, such as in ultra-stabilized Y based catalysts for FCC [2] or mordenite based catalysts for hydroisomerization [1, 3], or by combining acid and basic treatments [4]. These top-down procedures are effective but enclose several steps and, depending on the conditions employed, may result in crystallinity and micropore volume loss. Addition of soft or hard templates to the synthesis gel has also been described as a possible route to obtain hierarchical zeolites presenting micro and mesoporosity [4b, 5]. Direct synthesis of single layers of ZSM-5 was achieved by using diquatery ammonium surfactants and tetra-alkylphosphonium as directing agents (OSDA) [6]. The use of these type of OSDAs has also allowed the synthesis of other micro- mesoporous zeolites, with structural mesoporosity [7] or intercrystalline mesoporosity due to small crystallite size [8].

A different approach for increasing zeolite's accessibility was described in the middle 1990's, and consisted in the delamination of layered zeolite precursors. The concept was proved to be applicable to different structures, and new delaminated zeolites ITQ-2 [9], ITQ-6 [10] [10], ITQ-18 [11] and ITQ-20 [12] were prepared starting from MCM-22(P), PRE-FER, NU-6(1), and ITQ-19, respectively [13]. The resultant zeolitic materials showed very high accessible surface areas and interesting catalytic properties for a large number of reactions [14]. The first of those delaminated zeolites described, ITQ-2, is formed by disordered MWW layers in a "house of

cards" disposition. The layers, with a 2.5 nm thickness, present an hexagonal array of "cups" penetrating into the sheets from both sides, formed by a 12-membered ring and connected by a 10-ring channel running through the center of the layer [9a]. Preservation of the layers' structure was improved by delaminating under milder conditions [15]. A certain degree of delamination of zeolite precursor MCM-22(P) has recently been achieved by treating the layered precursor in the presence of cetyltrimethylammonium bromide, tetrabutylammonium fluoride, and tetrabutylammonium chloride at a mild pH of 9 [16]. The material obtained, UCB-1, presents high structural integrity and formation of amorphous silica phase has not been detected.

In this paper we present a single step direct synthesis of a material containing a large proportion of MWW monolayers. The layered zeolite, named as DS-ITQ-2, has been obtained by combination of hexamethylenimine (HMI), the traditional organic compound used for synthesis of MWW materials, with a bifunctional OSDA, N-hexadecyl-N'-methyl-DABCO, C16DC1 (see Figure 1). We were expecting HMI to direct the crystallization of the MWW layers, whereas the cationic head of the C16DC1 molecule, which, according to ¹³C-MAS NMR, remains stable under the synthesis conditions employed (see Figure S1), was expected to be located in the hemi-cavities of the layers, while the alkyl chain would avoid the layers to grow and order along the c-axis. We will show that this synthesis route allows the one-step preparation of a delaminated zeolite, with a high delamination degree and a high structural preservation of the microporous layers.

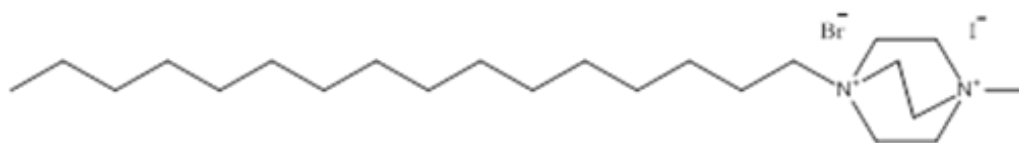


Figure 1. C16DC1 OSDA used for the direct synthesis of delaminated MWW DS-ITQ-2

The layers arrangement in MWW materials and their inter-layer interactions can be deduced from the 6-10° 2θ range (Cu Kα radiation) of their powder XRD patterns [17], which are shown in Figure 2 for the as prepared (continuous lines) and calcined (dotted lines) samples. The MCM-22(P) presents a doublet in the lower 6.5-7° 2θ region ((002) inter-layer and (100) intra-layer reflections). Upon calcination the 002 peak is shifted to higher 2θ angles, and overlaps the (100) peak. Both, MCM-22(P) and MCM-22, present two discrete peaks at 8.1 and 10° 2θ due to inter-layer reflections (101) and (102), indicating stacking with 3D order. The XRD pattern obtained for MCM-56 [18], one of the disordered materials of the MWW family obtained by direct synthesis, corresponds to that of a zeolite with partial condensation of the MWW sheets and a large proportion of layers randomly translated in the ab plane and submerged within each other [17b]. In the case of ITQ-2 the XRD patterns present a unique broad band in the 7.5-10° 2θ range confirming the disordered arrangement of their layers and a high delamination degree. However, with the direct synthesis presented here, structural integrity of the MWW layers of the highly delaminated zeolite, associated with the intensity of the 7.1° 2θ peak (100), is clearly higher than for the delaminated ITQ-2 prepared by post-synthesis methods. Thermal stability of the new material is high, as can be deduced from the preservation of the XRD patterns corresponding to the as prepared and the calcined samples.

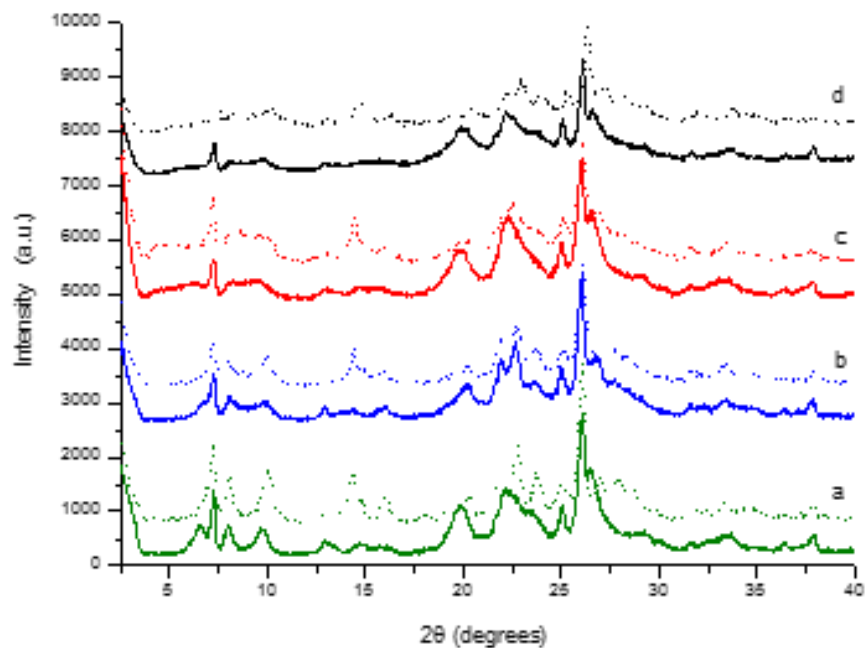


Figure 2. XRD patterns for MCM-22 (a), MCM-56 (b), DS-ITQ-2 (c) and ITQ-2 (d). Continuous and dotted lines correspond to as-prepared and calcined materials, respectively.

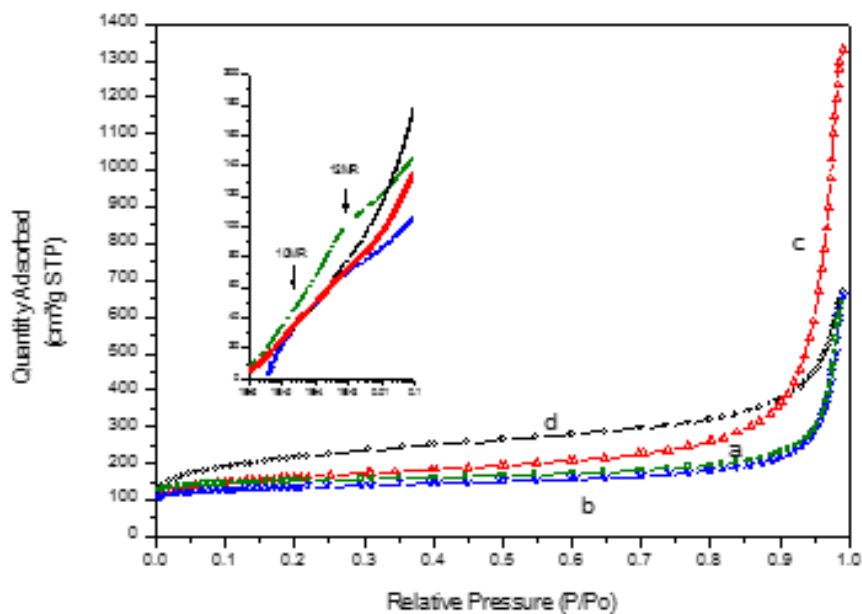


Figure 3. Argon adsorption isotherms of the calcined MWW materials: (a) MCM-22, (b) MCM-56, (c) DS-ITQ-2 and (d) ITQ-2. Inset enlarges the low relative pressure region.

The higher crystallinity degree of the material prepared here as compared to conventional ITQ-2 is also evidenced by the shape of the Ar and N₂ adsorption isotherms of the corresponding calcined samples (see Figure 3 and S2, respectively), closer to a type I, representative of

microporous materials (MCM-22), than to a type IV typical of disordered mesoporous materials (ITQ-2) at relative pressures up to 0.5. However, at $P/P_0 > 0.8$ the sharp adsorption increase indicates an extremely high total pore volume of the one step prepared material ($2.06 \text{ cm}^3/\text{g}$) that doubles the value obtained for MCM-56 or conventional ITQ-2 (see Table S1). Moreover, at low relative pressures the Ar adsorption isotherms show the inflection points corresponding to 10-ring channels and 12-ring supercages for MCM-22, and the absence of the latter in the case of the conventional ITQ-2, as described previously [9c] (see Figure 3, inset). Regarding the newly prepared material, the inflection at the lowest P/P_0 is more intense than that of ITQ-2, indicating a better preservation of the layers' structure when the delaminated MWW is obtained by this new one-step procedure, and the high delamination degree is confirmed by the significant reduction of the 12-MR cavities' inflection.

The DS-ITQ-2 material presents an increased external surface area as compared to MCM-22 and MCM-56, although it is lower than for ITQ-2. However, its higher micropore volume is an additional indication of the larger structural integrity of the MWW layers as compared to the delaminated zeolite obtained by post-synthesis treatments.

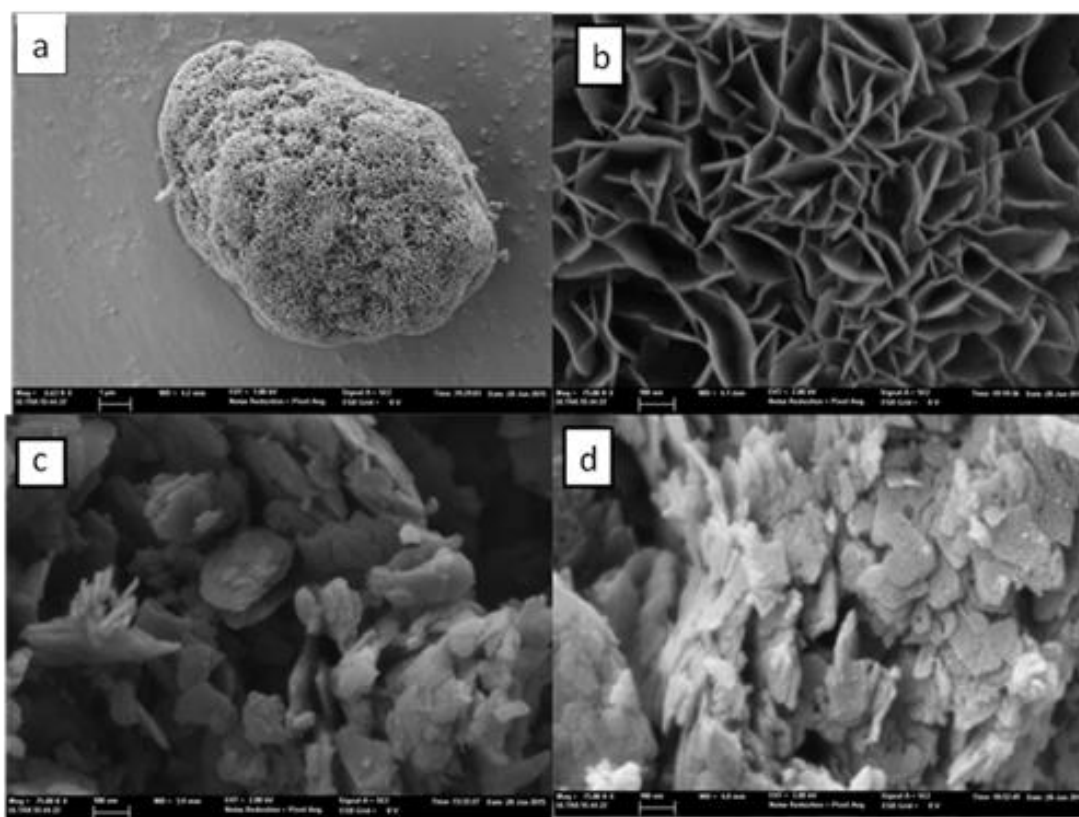


Figure 4. SEM images corresponding to calcined MWW materials: (a, b) DS-ITQ-2, (c) MCM-22 and (d) ITQ-2.

The morphology of the zeolite material prepared here is different from that of MCM-22 or the post-synthesis delaminated ITQ-2 according to the SEM images enclosed in Figure 4. Although the crystals have a platelet shape in all cases, DS-ITQ-2 presents an open and vertical

disposition of well-defined small crystallites, whereas they are more agglomerated for conventional ITQ-2.

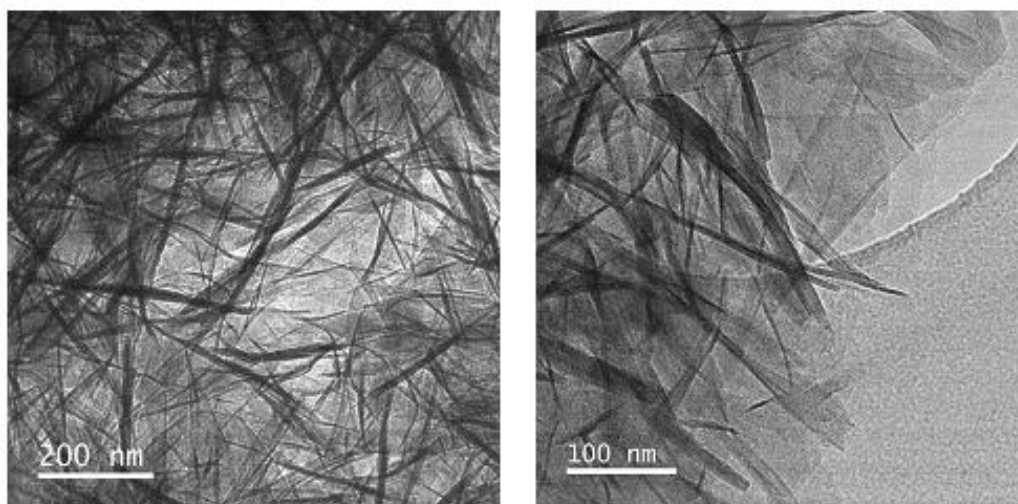


Figure 5. HR-TEM images corresponding to DS-ITQ-2.

The definite evidence for the presence of individual layers is given by the HR-TEM images shown in Figure 5, where the high delamination degree is clearly visible. In order to evaluate the degree of delamination of this new material, a detailed inspection of 30 different HRTEM images and 275 different crystals, gives the distribution presented in Figure S3, which has been obtained considering a layer thickness of 2.5 nm. Most of the crystals are mono- (34%) or bi-layered (36%), whereas only 9% of the crystals measured are formed by more than three sheets.

The thermal stability of the DS-ITQ-2 zeolite can be deduced from the preservation of the structure according to the XRD patterns of the calcined sample (Figure 2) and its micropore volume (see Table S1). The proportion of Al remaining in framework positions in the calcined sample is close to 80% as per ^{27}Al -MAS NMR, in the same range as that observed for MCM-22 or conventional ITQ-2 (Figure S4-a). This is significantly higher than for the disordered zeolite MCM-56, where 30% of the Al is in octahedrally coordinated extra-framework positions after thermal treatment.

The Brønsted acidity related to presence of framework Al has been studied by FT-IR spectroscopy combined with the adsorption of two probe molecules of different size. The smaller pyridine is able to enter the micropores of all the samples, it can interact with all the Brønsted acid sites of the zeolites, and will give information on the total Brønsted acid site density (see Figure S5-a). The bulkier di-tert-butyl-pyridine (DTBP) will be able to interact only with the external sites, located at the external cups, but not with the acid sites within the circular 10R or with the acid sites located within the large 12R cavities connected by 10R (see Figure S5-b).

Figure 7 shows the FT-IR spectra of the four MWW samples derived after pre-treatment at 400°C under vacuum (continuous lines) and after absorption of the basic probe (dashed lines). Results obtained by adsorption of pyridine and DTBP are enclosed in Figure 7-left and 7-right,

respectively. Two main bands are observed for the four zeolites before absorption of the probes, at 3750 and at 3620 cm^{-1} , assigned to external silanols and acidic hydroxyls, respectively.

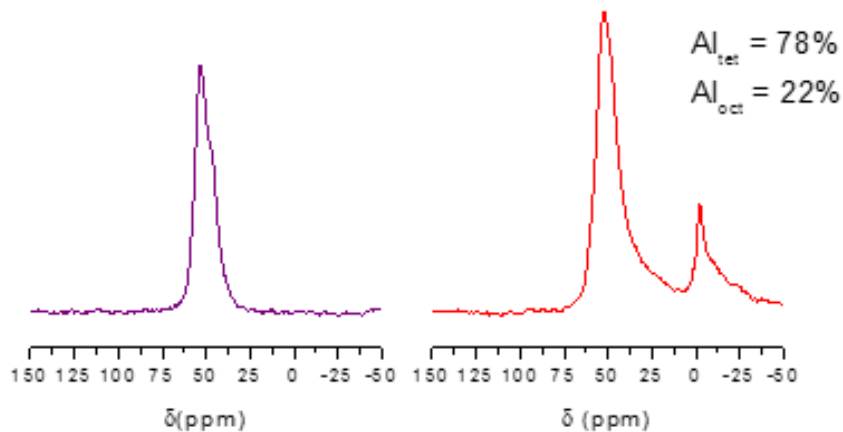


Figure 6. ^{27}Al -MAS NMR spectra corresponding to as prepared (left) and calcined (right) DS-ITQ-2

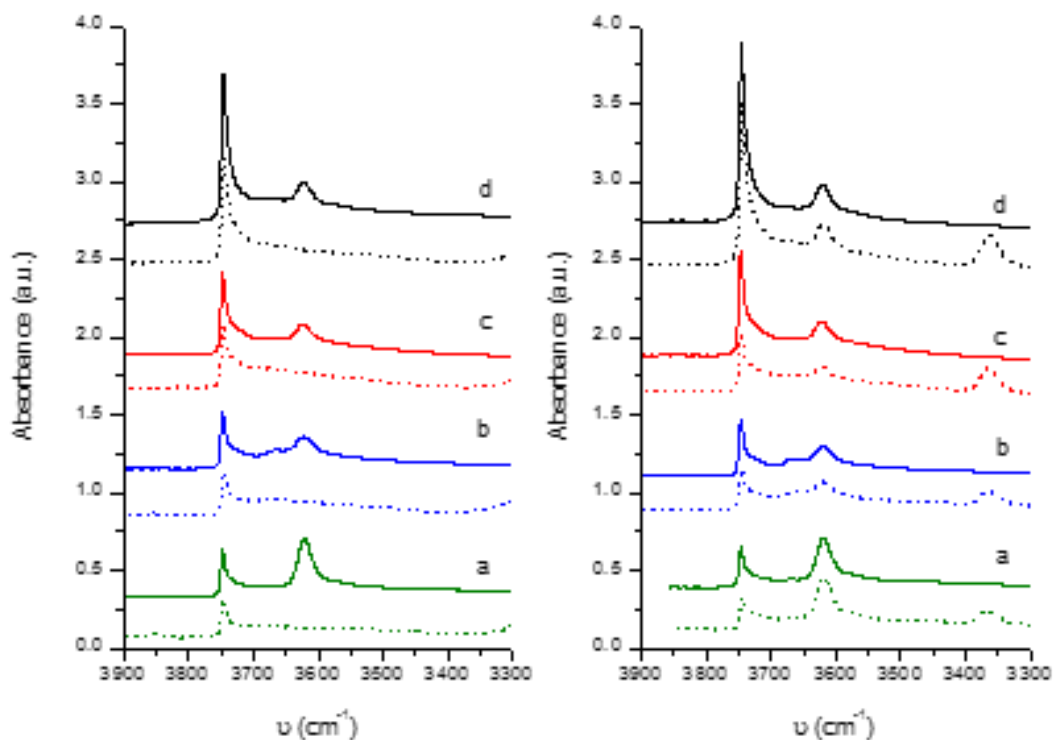


Figure 7. FT-IR spectra of the calcined MWW materials pretreated at 400°C under vacuum (continuous lines) and after absorption with the probe molecules (dotted lines), pyridine (left) and DTBP (right). (a) MCM-22, (b) MCM-56, (c) DS-ITQ-2, (d) ITQ-2.

The new DS-ITQ-2 sample presents a similar Brønsted acid site density as conventional ITQ-2 according to the intensity of the latter (see Figure 7 and Table S2), but less external silanols.

This confirms a larger layer structure preservation for the former, and a lower amount of defects, but also a lower external surface area, in agreement with the textural properties given in Table S1.

Interaction of pyridine with the Brønsted acid sites is confirmed by disappearance, in all cases, of the 3620 cm^{-1} band assigned to acid hydroxyls. However, the improved accessibility of ITQ-2 and the new delaminated material is confirmed by the interaction of a larger amount of Brønsted acid sites with the bulkier DTBP as compared to MCM-22 or MCM-56, where the decrease of the 3620 cm^{-1} band after adsorption of the bulkier basic molecule is considerably smaller (see Figure 7 and Table S2).

Alkylation of benzene with propene is an industrial process for obtaining cumene, an intermediate in the production of phenol and acetone [1, 19]. The current trend is to operate in liquid phase and in the presence of zeolite based catalysts. The zeolites employed are generally large pore materials, such as Beta zeolite, with no restrictions for cumene diffusion through the 12MR pores. MCM-22, which presents an unexpected good catalytic behavior, comparable, if not better, than that of the large pore zeolites, is also employed. Different studies proved that only the external surface of MCM-22 was participating in the reaction [20] and, in fact, delaminated ITQ-2 was shown to present higher activity and especially improved catalyst life as compared to MCM-22 [21].

The catalytic behavior of the new MWW material in the liquid phase alkylation of benzene with propene to cumene is the final confirmation of the exceptional properties of this delaminated zeolite obtained by a single-step procedure. Figure 8-a shows that its initial activity is comparable to that of conventional ITQ-2 in a wide range of space velocities, despite its lower external surface area, and significantly higher than that of MCM-22 or MCM-56, especially at the highest space velocities considered. The main difference when compared with MCM-22 and MCM-56 is the deactivation rate (see Figures 8-b and Figure S6).

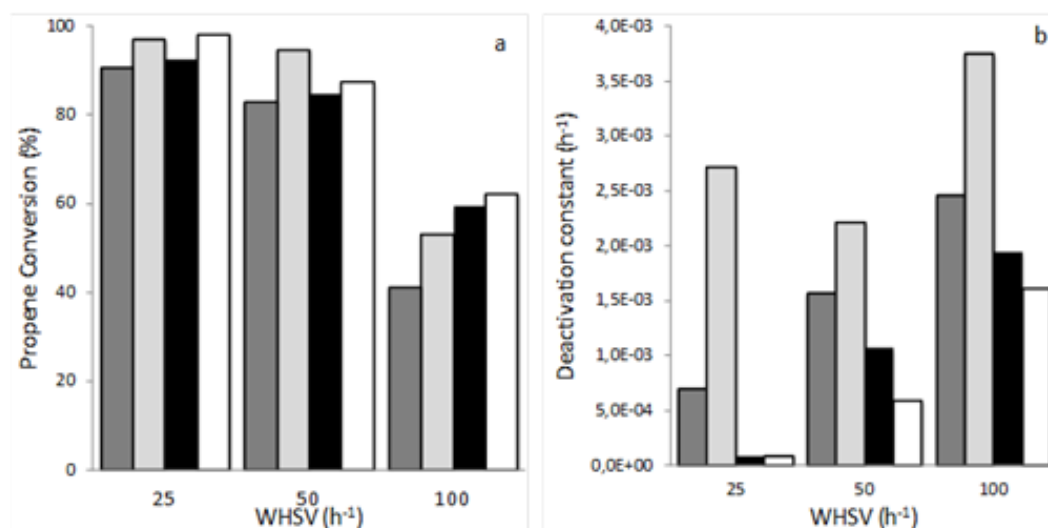


Figure 8. Initial activity (left) and deactivation constant (right) for MCM-22 (), MCM-56 (), DS-ITQ-2 () and ITQ-2 () for the liquid phase alkylation of benzene with propene at different space velocities, $\text{WHSV}=50$ and 100 h^{-1} , $T=398\text{K}$, $P=3.5 \text{ MPa}$.

The variation of conversion with time on stream (see Figure S6 for two different space velocities, 50 and 100 h⁻¹) can be described by the first-order deactivation relation given in Eq. (1)[22], where X and X₀ are the initial and subsequent propene conversion values, t is the time on stream and k_D is the deactivation constant.

$$X = X_0 \exp(-k_D t) \quad (1)$$

The deactivation constant obtained in this way, plotted in Figure 8-b, are significantly lower for the delaminated DS-ITQ-2 and ITQ-2 materials than for MCM-22 or MCM-56.

Regarding product selectivity, the results for the four samples fall on the same curve when plotted vs. conversion (see Figure S7). This goes in line with the fact that only the external sites are involved in the acid alkylation reaction.

In summary, we have presented a new single-step route for directly synthesizing a delaminated MWW material, with a high delamination degree and high structural preservation of the microporous layers. For the first time a MWW material has been obtained by direct synthesis with high yields (78%) and more than 70% of mono- and bi-layered crystals, and it has been possible thanks to the combination of two different OSDA, HMI for crystallization of the microporous layers, and a bifunctional biquaternary ammonium surfactant for avoiding the growth and stacking of the layers along the c-axis. DS-ITQ-2 has shown the same catalytic activity, selectivity and stability towards deactivation on stream than the reference ITQ-2 obtained following the traditional post-synthesis delamination procedure, but presents the advantage of a single step synthesis procedure and larger zeolite yield.

Experimental Section

DS-ITQ-2 was prepared by dissolving 0.846g of NaAlO₂ (47% Al₂O₃, 34.4% Na₂O, 18.6% H₂O, Carlo Erba) and 10.460g of NaOH (10% in water) in 46.428g of double distilled water. Then, 6.713g of C16DC1 were added to the solution while stirring. When surfactant was completely dissolved, 3.713g of Hexamethyleneimine (Sigma-Aldrich) and 7.210g (Sigma-Aldrich, particle size = 0.007 μm) were added to the mixture and stirred vigorously for 1h obtaining a gel with a molar composition 0.15 Na₂O : 1 SiO₂ : 0.033 Al₂O₃ : 0.3 HMI : 0.1 C16DC1 : 40 H₂O. Finally, the gel was transferred to 35mL PTFE lined stainless-steel autoclaves, rotated at 60rpm and heated at 423K for 7 days. After quenching the autoclaves with cold water, the product was filtered, washed with distilled water until pH < 9 and dried at 373K overnight. Organic material was removed by calcination in air at 813K for 12 hours.

MCM-22, MCM-56 and ITQ-2 were synthesized following the procedures described in the literature [22].

The acid zeolites were used to catalyze the liquid phase alkylation of benzene with propene at 398K, 3.5 MPa and a space velocity varied in the range of 25-100 h⁻¹. The reaction was performed in a stainless steel fixed bed reactor and composition of outlet stream was analyzed

on-line on a Varian-450 gas chromatograph equipped with a 30 m 5%phenyl-95%dimethylpolysiloxante capillary column connected to a flame ionization detector.

Acknowledgements

Financial support by the Spanish Government-MINECO through "Severo Ochoa" (SEV 2012-0267), Consolider Ingenio 2010-Multicat and MAT2012-31657 is acknowledged. M.E. M-A thanks MINECO for economical support through pre-doctoral fellowship (BES-2013-066800).

Keywords: MWW zeolite, layered zeolite, ITQ-2, direct synthesis of monolayered MWW, cumene production, benzene alkylation.

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