KINETICS AND DYNAMIC BEHAVIOUR OF TOLUENE DESORPTION FROM ZSM-5 USING *IN SITU* HIGH-TEMPERATURE SYNCHROTRON POWDER X-RAY DIFFRACTION AND CHROMATOGRAPHIC TECHNIQUES

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Abstract

In situ high-temperature (HT) synchrotron X-ray powder diffraction (XRPD), was used in this study as a tool to understand the adsorption/desorption process features of toluene adsorbed in organophilic ZSM-5 zeolite (SiO_2/Al_2O_3 ~ 280), as well as framework structural modifications upon thermal treatment from room temperature to 600°C. Rietveld refinements showed that toluene release starts in the 75°C< T < 200°C temperature range. Furthermore, extraframework structural changes take place when toluene removal starts. Significant internal pressure is developed with the composition product diffusion causing a corresponding transient expansion in the 10-ring channels. Our results clearly demonstrated that ZSM-5 regeneration is effective when it is thermally treated at about 400°C. Above this temperature, when all the organic have been ejected, non-equilibrium distortions in the framework are relaxed and channel apertures become more circular. ZSM-5 shows no significant difference in saturation capacity once regenerated after toluene reloading, thus

demonstrating that thermal regeneration under mild conditions appears to be both very effective even after several cycles of adsorption/desorption.

1. Introduction

Zeolites are microporous materials which are widely used in many industrial adsorption and catalytic processes due to their excellent thermal and chemical resistance. Furthermore, great potential is offered by zeolites in terms of tailoring their structure and physical-chemical properties. To date, organic compound adsorption in zeolites has been widely studied [1-4], especially in vapour or gas systems, since this process is relevant in many catalysed reactions, organic synthesis and depollution processes. In particular, the characteristics of zeolites - such as high organic contaminant selectivity, high specific capacity, rapid kinetics, absence of salt and humic substance interference and excellent resistance to chemical, biological, mechanical or thermal stress - make these materials particularly suitable as adsorbents for water treatment plants [5-11]. With regard to the latter application, a variety of organic compounds are potential water pollutants. Among these, BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) constitute one of the main marine environment pollutants due to accidental spills or leaks. The US environmental protection agency (USEPA) has classified BTEX as priority pollutants and has fixed concentration levels in water and wastewater [12]. According to the World Health Organization (WHO) guidelines, the maximum permissible concentration of benzene, toluene, ethylbenzene and xylene in drinking water is 0.01, 0.7, 0.3 and 0.5 mg/l, respectively [13]. Indeed, BTEX compounds can cause adverse health effects on humans, including central nervous system impairment, respiratory problems and liver and kidney damage [14-15]. Therefore, BTEX removal from water and wastewater is an important issue. Adsorption based treatment technology offers several advantages, such as low operation costs and reduced waste generation in as much as adsorbent reuse is possible. In several cases, zeolites were

proved to be easily thermally regenerated without changing their initial adsorption or catalytic properties [16-19]. However, these studies are rather limited and most deal with organic compound adsorption in gas phase systems. Zeolite ZSM-5 (MFI topology) is an important member of a class of high silica zeolites. It has been largely exploited due to its shape selectivity, solid acidity, ion exchangeability, pore size and high thermal stability. Moreover, ZSM-5 is the synthetic counterpart of the mineral mutinaite, $(Na_{2.76}K_{0.11}Mg_{0.21}Ca_{3.78})$ $(Al_{11.20}Si_{84.91}) \cdot 60$ H_2O, [20], a very rich calcium zeolite with a 7.6 Si/Al ratio, the highest ever found in natural zeolites.

Its MFI topological symmetry is orthorhombic *Pnma*. However, a polymorphic monoclinic (*P2$_1$/n*) - to- orthorhombic (*Pnma, Pn2$_1$a* or *P2$_1$2$_1$2$_1$*) phase transition was reported with varying framework defect density, temperature, or nature and amount of guest compounds in the channel systems [21-25]. Usually low-loaded ZSM-5 (4 or less sorbate per unit cell) are orthorhombic, with a *Pnma* or *Pn2$_1$a*[21, 26-28] space group. On the contrary, high-loaded ZSM-5 (over 4 sorbate per unit cell) is orthorhombic, with a *P2$_1$2$_1$2$_1$* space group [29]. This latter was also reported for a high-loaded ZSM-5 with 6.4 toluene molecules per unit cell on the basis of single-crystal XRD data by Nishi et al. [30].

Very recently, Ardit et al. [31] reported on spontaneous strain variation analysis across ferroelastic (monoclinic) and paraelastic (orthorhombic) phases in the ZM-5 zeolite transition using *in situ* synchrotron XRD data. The authors highlighted the tricritical character of this transition from ferroelastic to paraelastic phases in ZSM-5. The adsorption properties of a hydrophobic ZSM-5 zeolite compared to a toluene aqueous solution (TOL) were investigated in this work in order to obtain information on the kinetic and thermodynamics of the adsorption process. Additionally, *in situ* high-temperature (HT) synchrotron X-ray powder diffraction (XRPD) was carried out on ZSM-5 after toluene adsorption (known as ZSM-5-TOL to follow). Saturated material was used as a key to continuously monitoring TOL decomposition process, as well as structural modifications on ZSM-5 upon temperature-programmed treatment. Understanding the features of both adsorption and

desorption processes can help in the opting and design water treatment appliances based on microporous materials, as well in their catalytic applications. Furthermore, it can provide insight for the reuse of adsorbing material.

2. Material and methods

2.1 Materials

The zeolite sample used in this study is a hydrophobic ZSM-5 (CBV28014, Zeolyst International) characterized by SiO_2/Al_2O_3 ~ 280, Na_2O content <0.05 wt.% , NH_4^+ content <0.1% w/w, with a 400 m^2/g surface area. The TOL-loaded form of ZSM-5 was obtained by preparing TOL aqueous solutions and mixing them with the zeolite powder in a 1:4 (mg mL^{-1}) solid/solution ratio as detailed in the following sections.

2.2 Gas Chromatography

The TOL concentration in the aqueous solutions was determined by a Gas Chromatography – Flame Ionization Detector (GC- FID). Prior to this, TOL was extracted from the water sample by Head Space - Solid Phase Micro Extraction (HS-SPME). The head space mode was used to extract TOL from 10 ml of solution in 25-ml glass flasks sealed with Teflon screw caps. 2 mL of a 300 g L^-^{1}NaCl solution were added to the sample. Samples were immersed in a thermostatic water bath at 40 °C (±0.5 °C) and maintained under controlled agitation with a magnetic stirrer (300 rpm) for 10 min to reach equilibrium conditions before SPME insertion. The fibre was inserted into the GC injector for analysis and kept at 250 °C. Desorption time was 1 min. The GC used in this work was an HRGC 5160 MEGA SERIES Instrument (Carlo Erba, Mi, I) equipped with a split/splitless injector and an FID detector. A fused-silica capillary column OV-1 (30 m x 0.32 mm I.D:, 0.1 μm film thickness; MEGA, MI, I) was used. Helium (99.999%) was used as a carrier gas at 30 kPa constant head pressure. The detector temperature was kept constant at 250°C. The GC oven was programmed as follows: 40°C (5 min), 5°C min^{-1} to 80°C (5 min), 30°C min^{-1} to 100°C (5 min).

2.3 Adsorption Isotherm

The adsorption isotherm was determined using the batch method. Batch experiments were carried out in duplicate in 20 ml crimp top reaction glass flasks sealed with PTFE septa (Supelco, PA, USA). The flasks were filled in order to have minimum headspace, a solid/solution 1:4 (mg mL^{-1}) ratio was employed. The solids were separated from the aqueous solution using centrifugation (14000 rpm for 30 min) after equilibration, for 24 hours at a temperature of 25.3 ± 0.5 °C under stirring. TOL concentrations in solutions with regenerated zeolite were read before and after equilibration by HS-SPME-GC-FID in order to determine the adsorbed quantities (q) and the equilibrium concentrations (Ce).

2.4. Synchrotron powder XRD data collection and Rietveld refinements

A TOL-loaded zeolite ZSM-5 powder sample (ZSM-5-TOL) was used for in situ time-resolved XRPD. XRD data were collected at the European Synchrotron Radiation Facility (ESRF) ID31 beam line, Grenoble, using a fixed wavelength of 0.40003(1)Å. A series of XRD patterns were measured through nine parallel scintillation counters behind Si (111) analyser crystals in the 0.5–19.5 2θ range, in steps of 25°C as a function of temperature while the sample was heated from room temperature to 600°C in air with a heating rate of 0.083 K s-1. Rietveld refinements were performed using the Larson and Von Dreele [32] General Structure Analysis System (GSAS) with an EXPGUI graphical interface [33]. After toluene adsorption, automatic peak indexing was performed using High Score Plus v.3.0 software, revealing the presence of several doublets (i.e. 131 + 13-1 and 311 + 31-1, and 133 + 13-3 and 313 + 31-3) suggesting monoclinic symmetry. As a consequence, structure refinement of this sample (TOL-ZSM-5) was then performed in the *P2$_1$/n* space group starting from the framework atom site positions reported by Pasti et al. [7] for the initial unloaded sample. The refined β (90.545 (1)) value confirms the assumption of the monoclinic symmetry after toluene adsorption (Table 1S).

Extra-framework sites were located by difference Fourier synthesis. H-atoms were not considered within the structure refinement due to their low scattering factors. Refined structural parameters for each data histogram were the follows: fractional coordinates and isotropic displacement factors for all atoms (one for each tetrahedral site and framework oxygen atom, one for each toluene molecule). Toluene occupancy factors were refined in blocks e.g. all the carbon atoms for each toluene molecule were constrained to have same value. The occupancy and isotropic displacement factors were varied in alternate cycles. Figure 1, shows the powder pattern evolution of the investigated ZSM-5-TOL sample when close to the monoclinic ($P2_1/n$) to orthorhombic ($P2_12_12_1$) phase transition at a Tc $\approx 75°C\pm5$ in the 1.7 – 4.7 (a) and 4.7 – 7.1 (b) °2θ ranges. The symmetry change was marked by the gradual merging of several peaks doublet into single ones . The Rietveld refinement in the orthorhombic s.g. was carried out starting from the framework atomic coordinates reported by Nishi et al [30]. The structural model obtained after the phase transition was then used for the ZSM-5L high temperature (HT) patterns, by adopting the same structure refinement strategies. After the desorption of the organic molecules (Tc close to 400°C±5), the slope variation of the unit cell volume suggested a new displacive phase transition from orthorohombic $P2_12_12_1$ to *Pnma*. As a consequence, all Rietveld refinements up to 400°C were performed in this latter space group, starting from the atomic model of van Koningsveld et al24]. Using the this crystal structure model, based on the latter space group, appreciably improved the quality of the Rietveld refinement, as testified by the lower R_{wp} and R_p parameters. Soft constraints were imposed on Si-O (1.60(1) Å), O-O (2.60(1) Å) and C-C (1.34Å) distances and their weight was gradually released after the initial refinement stages of rement. The instrumental background was empirically fitted using a Chebyschev polynomial of the first kind with 16 variable coefficients for room temperature and 24 variable coefficients for HT data set. The 2θ-zshift, scale factor and unit-cell parameters were accurately refined and the reflection intensity were was preliminary refined with Le Bail extraction method and then kept fixed at the mean value in all patterns of the data set. Peak intensity profiles (0.01% cut-off peak intensity) were modelled by means of a pseudo-Voigt profile function using Gaussian U,

V, and W coefficients, which is a Lorentzian particle-size broadening term. All positional parameters, site occupancy and isotropic atomic displacement parameters (ADPs) were refined in the final cycles. Lattice parameters and refinement details have been summarized for four selected temperatures (30°C, 75°C, 400°C and 600°C) in Table 1S, the corresponding refined atomic parameters for both framework and extraframework atoms are given as Supporting Information (Tables 2SI-7SI, respectively).

3. Results and Discussion

3.1 Adsorption kinetics

The effect of contact time on TOL adsorption onto ZSM-5 was studied at different initial concentrations, as shown in Figure 2a. The time to reach equilibrium was only 15 min. Adsorption is initially rapid, and then constant, possibly due to a greater abundance of adsorption sites available for adsorption during the initial stage. Various kinetic models have been suggested for describing adsorption processes. Among these, Lagergren's pseudo-first-order kinetics (PFO) and pseudo second order kinetics (PSO) are those commonly employed to investigate adsorption onto zeolites. These models are expressed in Eqs. (1) and (2) as shown below:

$$q = q_e[1 - \exp(k_1 t)] \tag{1}$$

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{2}$$

where q is the amount of solute per unit mass of adsorbent at time t, q_e is the equilibrium value of q, k_1 and k_2 are the PFO and PSO rate constant, respectively. According to the theoretical analysis proposed by Azizian [34], PFO model better describes adsorption from a solution with a high initial solute concentration, while for initial solute concentrations which are not too high, a sorption PSO fit is generally better. It has also been demonstrated that for systems which are characterized using the PFO model, the observed rate constant is a linear function of the initial solute concentration;

whereas the observed rate constant is a complex function of initial solute concentration for PSO kinetics systems. Table 1, reports correlation coefficients (R^2), kinetic parameters (k_1, k_2) and calculated $qe_{,cal}$ values obtained by non-linear regression. R^2 comparison, obtained for PFO and PSO, suggests that TOL adsorption onto ZSM-5 takes place according to the pseudo-second-order kinetic model (Figure 2b). Moreover, TOL uptake fit on ZSM-5 at 25 °C for different initial TOL concentrations (see Figure 2a) in an aqueous solution revealed that the PSO dependence rate constant on the equilibrium concentration follows a complex trend (see Figure 2a). Thus, the PSO model was confirmed [34, 35].

In addition, the intraparticle diffusion model was applied in order to identify the adsorption steps:

$$q = k_{i,d} t^{1/2} + c_i \qquad (3)$$

where $k_{i,d}$ is the intraparticle diffusion rate constant and c_i is a constant for the i-th step.

As shown in Figure 2c, the two-phase plot suggests that the adsorption process proceeds by surface adsorption and TOL intraparticle diffusion into the zeolite micropores for an initial TOL concentration of 45 mg L^{-1}. By comparing the slopes of the two lines, it can be observed that $k_{1,d}$ is larger than $k_{2,d}$ (see Table 8 SI) for all the investigated concentrations, indicating that film diffusion is a more rapid process than intraparticle diffusion [36].

The intercept (c_i value) is significantly different from zero, confirming that the studied zeolites have a high level of initial adsorption.

3.2 Adsorption isotherm

The equilibrium adsorption isotherm provides the relationship between the concentration of organic contaminant in solution and how much is adsorbed on the solid phase when the two-phase system is in equilibrium. The experimental data reported in Figure 3a, show the Langmuirian shape and consequently the data were fitted to Langmuir and a bi-Langmuir models, which were

employed to describe the adsorption of different organic compounds on ZSM-5 [37]. These two models are expressed by Eqs. (4) and (5),

$$q = \frac{q_s b C_e}{1 + b C_e} \tag{4}$$

$$q = \frac{q_1 b_1 C_e}{1 + b_1 C_e} + \frac{q_2 b_2 C_e}{1 + b_2 C_e} \tag{5}$$

where q_s is the saturation capacity of the adsorbent material, C_e the equilibrium concentration in the solution and b the binding constant, the subscripts refer to the type of adsorption sites.

The estimated parameters from non-linear fitting are shown in Table 9SI. The determination coefficients (R^2) of the Langmuir isotherm (0.9565) are not significantly different from the Langmuir isotherm (0.9865) obtained for adsorption data at 22.5 °C. Since the difference in goodness of fitting parameters for the two isotherm models is not significant, the simplest model (i.e. Langmuir isotherm) can be employed to describe TOL adsorption onto ZSM-5. Moreover, the monolayer adsorption capacity determined using the Langmuir isotherm is about 82 mg/g which approaches experimental data (81.6 mg/g). Finally, the equilibrium parameter R_L [38] was given by:

$$R_L = \frac{1}{1 + b C_0} \tag{6}$$

where C_0 is the initial concentration R_L values are in the 0.009-0.45 range, indicating that TOL adsorption onto ZMS-5 is favourable ($0 < R_L < 1$).

3.4 ZSM-5-TOL structure refinement at room temperature

The ZSM-5 framework is characterized by two interconnected channel systems: sinusoidal 10-membered ring (ZZ ring A and ZZ ring B, respectively) channels along the [100] direction and straight 10-membered channels parallel to the [010] direction (SC ring A and SC ring B, respectively). A tortuous pore path runs along the [001] direction.

The ZSM-5 topological symmetry is orthorhombic *Pnma*, but its real symmetry strongly depends on temperature changes, mechanical stress, synthesis and post synthesis treatment, SiO_2/Al_2O_3 ratio, structural defects and the nature and amount of guest organic molecules [21-26]. The crystal system is monoclinic *P2₁/n* after small guest molecules adsorption . The same space group was also reported for the same highly siliceous ZSM-5 zeolite used in this work in its as-synthesized form (Pasti et al. [7] ; Ardit et al. [31]), as well as after adsorption of other fuel-based pollutants (Martucci et al. [9-11, 39].

In our study, the presence of peak doublets such as 131/13-1, 311/31-1, 133/13-3, and 313/31-3 (Figure 1) in the ZSM-5-TOL pattern at room temperature clearly indicated monoclinic *P2₁/n* symmetry. The difference Fourier map, generated using the GSAS package, indicated TOL molecules distribution over two crystallographic independent sites (TOL 1 = C1, C2, C3, C4, C5,C6,C7 sites; TOL 2 = C8, C9, C10, C11, C12, C13, C14 sites) (Figure 4a, Table 3SI). TOL1 is located in the straight channel, while TOL2 molecules are located at the intersection between straight and sinusoidal channels. The final difference Fourier map showed two other peaks which were attributed to co-adsorbed water molecules (W1 and W2 sites, respectively). Both the toluene and water sites are partially occupied: TOL1 and TOL2 sites in 85% and 65% of cases, whereas W1 and W2 were occupied (Table 3 SI) in 85% and 55% of cases, respectively in 85% and 55%. On the whole, 6 toluene molecules (which correspond to about 8.55 % in weight) and approximately 2 water molecules (which correspond to approximately 2.0 % in weight) were localised inside the ZSM-5 channel system. Therefore, structure refinement gave toluene content levels in very good agreement with the adsorption capacity (81.6 mg/g).

The O atom refined distances for the water molecules from themselves (W2-W2 3.24(1) Å) and the toluene atoms (C1-w1 =3.02(1) Å, C2-w2 =2.46(1) Å, C5-w2 = 2.96 (1) Å,C11-w1=2.68(1) Å, C8-w1=2.34(1) Å, w1-C11=2.68(2) Å, w2-C5= 2.96 (3) Å,) suggest the presence of water-toluene oligomers (TOL1-W1, TOL1-W2, TOL2-W1, TOL1-W2-W2) interacting with framework oxygens (C8-O18=3.15(4)Å,C9-O18=3.00(3)Å,C10-O17=3.04(4)Å,C10-O23=2.74(3)Å,   C10-

O43=2.67(3)Å)). At the same time, toluene and W1 water molecules are connected to each other to form TOL1-W1-TOL2 molecular oligomer parallel to the **b** direction which are bonded to framework oxygen atoms. Water-organic complexes interacting with the framework were also detected by XRPD in ZSM-5 after dichloroethane [7] and methyl *tert* buthyl ether [39] adsorption.

3.5 In situ XRD data refinements: temperature-dependent structural modifications

The evolution of the powder diffraction patterns as a function of temperature (Figure 1) indicated that ZSM-5 maintains its crystallinity up to the highest investigated temperature. T-dependent variations in unit cell parameters in the 30°–600 °C T-range are reported in Figure 5a. Cell parameter values defined as $V(T)/V_0$, $a(T)/a_0$, $b(T)/b_0$, and $c(T)/c_0$, are normalised compared to the reference values refined at T=30°C.

In situ synchrotron XRD data revealed a rapid increase in cell volume (Figures 5a) in the 30°<T <75°C T range. The linear expansion coefficients along *a*, *b* and *c* directions were α_a=3.269 x 10^{-5}, α_b = -2.810 x 10^{-5} and α_c= 1,771 x 10^{-5}, respectively. The volume thermal expansion coefficient is α_V=2.325 x 10^{-5}. 131 and 13-1 peak overlapping is still incomplete at 50°C, and broadening in the 2θ region is observed in the ZSM-5 pattern. This suggests that conversion to the orthorhombic symmetry is still occurring. Complete overlapping for this group of peaks is reached at about 70 ± 5°C (*Tc*), as a result of a complete monoclinic $P2_1/n$ to orthorhombic $P2_12_12_1$ phase transition. The latter space group was also adopted in the single-crystal XRD study by Nishi et al. [30] for an all-silica MFI material which was highly-loaded with toluene. Nishi et al. [30] reported three kinds of toluene molecules in the unit cell: two of these were located at the intersection of between the straight sinusoidal channels, the third one in the sinusoidal channel.

Our Rietveld refinement highlighted that $P2_1/n$- $P2_12_12_1$ phase transition is accompanied by clear discontinuity in $V(T)/V_0$, $a(T)/a_0$, $b(T)/b_0$, and $c(T)/c_0$ curves (Figure 5a). Initial cell expansion occurred even if toluene removal was only partially started, as demonstrated by the evolution of toluene content as a function of temperature (Figure 5b). After phase transition, toluene molecules

remained confined within the straight channel (TOL1 site) as well as at the intersection between straight and sinusoidal channels (TOL2 site), (Figure 4b). Difference Fourier maps also showed the occurrence of a clear weak maximum which is attributed to co-adsorbed water hosted in a fully occupied site (site W in Table 5SI). At the same time, the simultaneous presence of small diffused maxima indicates that a few other water molecules are spread over a number of low occupied positions, which remained unlocalized by Rietveld structure refinement. The refined distances of toluene and water molecules oligomers (W-C5=2.55Å; W-C11=2.76Å) confirm their interaction with framework oxygens (W-O27= 2.60Å; W-O28= 2.61Å; C12-O44 2.80Å) . The refined occupancies indicate that the toluene release is only partially started from the TOL2 site. This process is accompanied by an increase in the opening of the zeolite framework pore system and consequently, in the Crystallographic Free Areas (C.F.A.) (Figure 1SI). This result also jjustifies the volume expansion in this stage of the experiment (Figure 5a). The same cell volume increase was also reported on the same ZSM-5 sample after dichloroethane adsorption upon heating at T_c close to $70 \pm 5°C$ [19]. Structure refinements of the occupancies show that the toluene removal starts in the $75°C< T < 200°C$ temperature range. The linear expansion coefficients along a, b and c directions at 200°C are α_a=-1.846 x 10^{-7}, α_b = 3.922 x 10^{-6} and α_c= -5.969 x 10^{-9}, respectively. TOL1 content was reduced by about 50% as indicated by the decrease in toluene molecules per unit cell $vs.$ temperature (Figure 5b). At the same time, the TOL2 molecules are almost completely decomposed.

A T-dependent distortion mechanism in the framework takes place in correspondence with guest organic molecule release. Adsorbate diffusion led to significant internal pressure and caused a corresponding transient expansion (α_V=3,740 x 10^{-6}) in the 10-ring channels.

This trend suddenly changes between 200°C and 400°C as a result of structural modifications induced by complete toluene removal, in good agreement with the evolution of refined organic occupancy fractions (Figure 5b). In this T range, all the cell parameters decrease, the linear expansion coefficients along a, b and c directions at 400°C being α_a= -2.267 x 10^{-6}, α_b = -3.916 x

10^{-6} and $\alpha_c= -2.443 \times 10^{-6}$. The negative volume expansion associated with organics removal is $\alpha V= -8.620 \times 10^{-6}$. Apertures sterical features indicated that the straight channel along the *b* axis is the more viable direction for toluene decomposition product. The unit cell parameter variations and the change in the cell volume slope *vs*. T dependence suggested a new displacive phase transition from orthorhombic $P2_12_12_1$ to *Pnma* at around 400°C. The quality of the Rietveld refinement based on this crystal structure model was appreciably better, as testified by lower R_{wp} and R_p parameters (see Table 1 SI). The structure maintained this symmetry up to the highest investigated temperatures. The axial and volume thermal expansion coefficients in the 400°–600°C T-range are $\alpha_a= -2.896 \times 10^{-6}$, $\alpha_b = -3.512 \times 10^{-6}$ and $\alpha_c= -3.534 \times 10^{-6}$, $\alpha_V=-9.941 \times 10^{-6}$, respectively. Volume contraction in this T-range is true negative thermal expansion (NTE) since it occurs without any mass loss. This mechanism, which has been clearly documented in MFI-materials such as ZSM-5-loaded with dichloroethane [19], silicalite-1 [40], titanium silicalite-1 (TS-1) [41], Fe-silicalite (Fe-MFI), TS-1 and Fe-MFI [42], as well as in other microporous materials [43-45] and zeolites (e.g. zeolite omega [46], B-levyne [47] all silica sodalite [48] and all silica-faujasite [49], can also be explained by relaxation in the framework distortions induced by water molecules passing through the zeolite tetrahedral rings during the preceding dehydration stage (e.g. analcime [50]).

When all the volatile species have been expelled, the non-equilibrium framework distortions are relaxed and the window apertures progressively decrease and become more circular, as demonstrated by the evolution in ellipticity (defined as the ratio between the smaller (O-O) and larger (O-O)"free diameters" in the 10-rings) values reported in Figure 1SI.

3.6 Regenerated adsorbent adsorption behaviour

The TOL saturated ZSM-5 was regenerated by calcination at 500 °C for 2 h, in order to completely remove the organics. After regeneration, ZSM-5 was then tested for TOL re-adsorption under a solution concentration enabling zeolite saturation. The adsorption /desorption cycle was repeated twice on the same material. Figure 3b, reports the comparison of fresh and regenerated

zeolite adsorption capacities. It is clearly shown that the saturation capacity of the regenerated sample after air calcination does not significantly differ from fresh material.

4. Conclusion

Combined *in situ* high-temperature synchrotron XRPD and chromatographic study was carried out to understand the kinetics and dynamics of the toluene adsorption/desorption process in organophilic ZSM-5 zeolite. Rietveld structure refinements of the occupancies show that toluene removal starts in the 75°C< T < 200°C temperature range. Adsorbate diffusion leads to significant internal pressure and causes corresponding transient expansion in the 10-ring channels. Our results clearly demonstrated that ZSM-5 regeneration is effective when thermally treated at about 400°C. Above this temperature, non-equilibrium distortions in the framework are relaxed and channel apertures becomes more circular. ZSM-5 shows no significant difference in saturation capacity once regenerated and reloaded with toluene, thus demonstrating that thermal regeneration under mild conditions appears to be as very promising method even over several adsorption/desorption cycles. Additionally, understanding this process can help in optimizing and the design the water remediation technologies (e.g. Permeable Reactive Barriers) and using zeolites as "molecular sieves" to remove fuels-based pollutants from water.

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Figure Captions

Figure 1. Plot of selected *in situ* time resolved XRPD patterns as a function of temperature/time for ZSM-5-TOL in (a) the 1.7 – 4.7 and (b) 4.7 – 7.1 °2θ ranges within the 30 – 600°C temperature interval.

Figure 2. Adsorption kinetics of TOL on ZSM-5. a) TOL uptake on ZSM-5 at different initial concentrations; b) Pseudo second order kinetics constant vs. TOL equilibrium concentration; c) Intraparticle diffusion plots for adsorption (C_0 45 mg L^{-1}).

Figure 3. a) Isotherm for TOL adsorption onto ZSM-5; b) Pseudo second order kinetics constant vs. TOL saturation capacity on ZSM-5 after thermal regeneration.

Figure 4. Location of toluene and water molecules in ZSM-5 along [001] and [001] directions, respectively, before (30°C) (a) and after (75°C) (b) the monoclinic to orthorhombic phase transition.

Figure 5. a) Temperature evolution of ZSM-5-TOL unit cell parameters during in situ thermal burning of the organic. All values are normalized compared to those refined at room temperature; b) variation in toluene molecules per unit cell as a function of temperature. The evolution of unit cell volume (black line) is also shown for comparison.