# ADSORPTION/DESORPTION OF 1,2-DICHLOROETHANE CONFINED WITHIN ZSM-5: A COMBINED *IN SITU* HIGH-TEMPERATURE SYNCHROTRON POWDER X-RAY DIFFRACTION AND CHROMATOGRAPHIC STUDY

A. Martucci[1], E. Rodeghero[1], L. Pasti [2] and G. Cruciani[1]

[1] Department of Physics and Earth Sciences Department, University of Ferrara, Via Saragat, 1, I-44123 44100 Ferrara, Italy

[3] Department of Chemistry, University of Ferrara, Via L. Borsari, 46, I-44123 44100 Ferrara, Italy

* Email: mrs@unife.it; psu@unife.it

**Abstract**

The adsorption/desorption behaviour of ZSM-5 loaded with 1,2-dichloroethane was studied using the 'in situ' synchrotron X-ray powder-diffraction technique in the temperature range 30°-600°C. Rietveld refinements allowed to monitor the DCE decomposition process as well as the structural modifications undergoing on ZSM-5 upon a temperature-programmed thermal treatment. These results clearly demonstrated that regeneration of ZSM-5 is effective when thermally treating the adsorbent at about 300°C thus minimising the cost of the regeneration step of the adsorption process. Once regenerated and reloaded the Rietveld refinement indicates that both DCE location and content remain substantially unchanged thus confirming ZSM-5 is able to re-adsorb DCE in amounts comparable to that adsorbed in the first cycle, in very good agreement with the chromatographic results. In conclusion, the use of this adsorbent with unchanged adsorption performances after thermal regeneration under mild conditions appears very promising also over several cycles of the adsorption/desorption process.

**Keywords:**

Zeolite thermal regeneration, 1,2-Dichloroethane adsorption, in situ synchrotron X-ray powder diffraction, thermogravimetric analysis, Adsorption isotherm.

## Introduction

Chlorinated volatile organic compounds (VOCs), such as 1,2-dichloroethane (DCE) constitute an important environmental pollutants class. VOC have been used extensively in the past for many industrial and domestic applications. Leaks, spills, and wrong disposal practices have led to widespread contamination of groundwater. Because of their diffusion in the environment, their human toxicity, and tendency to persist in ground-water [1] these contaminants are of particular concern for human health. Moreover, many VOC are mutagens and teratogens, and, furthermore, are known or suspected human carcinogens." [2]. Adsorption is a reliable alternative to eliminate these organic compounds from wastewaters because of the flexibility of the system, low energy and cheap operation costs.

Recently, high-silica zeolites characterized by a silica/alumina ratio >50, have been shown to be environmental friendly materials able to efficiently sorb from water emerging organic contaminants such VOCs more efficiently than activated carbon [1, 3-7]. Zeolite advantages concerning high organic contaminant selectivity, high specific capacity, rapid kinetics, absence of salt and humic substance interference, excellent resistance to chemical, biological, mechanical or thermal stress have been reported [8].

In particular, the mechanisms and effectiveness of high-silica zeolite adsorbents (ZSM-5, mordenite, and Y zeolites) for DCE removal from water have investigated by combing X-ray diffraction, gas-chromathography and thermal analyses (TG, DTA) [6, 9]. The presence of DCE molecules inside the zeolite pores was revealed by unit cell parameters variations and structural deformations obtained from conventional X-ray structure analyses carried out using the Rietveld method on

exhausted zeolite samples. Very interestingly, structure refinements demonstrated that these changes are strongly related to the complexation of the guest species with water molecules. Therefore, these results allowed to select the isotherm models which better explained the experimental adsorption data. In particular, zeolite ZSM-5 (MFI-type framework topology, [10]) with high $SiO_2/Al_2O_3$ ratio was found to be very effective in DCE removal from water [6].

Moreover, it has been reported that zeolites can be easily thermally regenerated at low cost without changing their initial adsorption or catalytic properties [11-13]. After adsorption, the exhausted zeolites are normally subjected to a regeneration process by operating under particularly mild conditions at temperatures ranging from 250° to 350°C, for a time ranging from 0.5 to 1.5 hours, in the presence of an air flow ranging from 1.5 to 2.5 m3/hr [11].

In this work, the *in situ* high-temperature (HT) synchrotron X-ray powder diffraction (XRPD), is used as a key to continuous monitoring of DCE decomposition process as well as the structural modifications undergoing on ZSM-5 upon a temperature-programmed thermal treatment. Understanding the transient and dynamic features of desorption processes can contribute to better design and optimize the regeneration treatment of hydrophobic zeolites. Achieving the (re)activation of the microporous adsorbents under mild conditions would expand their capabilities in environmental applications.

With this purpose, the structural rearrangements on the zeolitic framework were analysed and the adsorption capacity of ZSM-5 after thermal regeneration and were also tested in order to verify whether the reactivated material can be further used for DCE removal from wastewater.

## 2. EXPERIMENTAL

### *2.1 Diffraction methods*

The powder sample of ZSM-5 organophilic zeolite (CBV28014, Zeolyst International, $SiO_2/Al_2O_3$ ~ 280, $Na_2O$ content <0.05 wt.% , $NH_4^+$ content <0.1% w/w), Surface Area of 400 $m^2/g$) loaded

with 1,2 dichloroethane has been studied “in situ” by synchrotron radiation powder diffraction. The details of sample preparation are reported elsewhere ([6]. Time – resolved diffraction data were collected (temperature range 25° - 600°C) on the ID31 beamline at ESRF (Grenoble), using a fixed wavelength of 0.400031(1) Å. The sample diffracted X-rays were collected in parallel by means of nine Si 111 analyser crystals and scintillation detectors. Measurements of X-ray powder diffraction (XRPD) patterns at room temperature of both the calcined and reloaded ZSM-5 samples was performed on a Bruker AXS Advance D8 diffractometer equipped with Si(Li) solid state detector (Sol-X). The experimental conditions were the following: Cu Kα1,α2 radiation, 2θ range: 3–110°, step size: 0.02°, time/step: 12s, scattering, divergence, and receiving slits: 0.6, 0.6 and 0.1 mm, respectively.

*2.2 Structure refinement*

The structure refinements by full profile Rietveld analysis was carried out using the GSAS [14] package and the EXPGUI graphical interface [15] starting from the atom site positions reported by Pasti et al. [6]. Extraframework site were located by difference Fourier synthesis. The Bragg peak shape was modelled using a modified pseudo-Voigt function with 0.01% cut-off peak intensity. 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 high temperature data set. The 2θ-zero shift, scale factor and unit-cell parameters were accurately refined. Soft constraints were imposed on Si–O and O-O framework distances (1.60 and 2.60 Å, respectively) and on C-C (1.34 Å), C-Cl (1.74 and 2.76 Å) and Cl-Cl (4.34 Å) DCE distances and the weight was gradually released after the initial stages of refinement, H-atoms were not considered in the structure refinement due to their low scattering factors. In the final cycles, all positional parameters, site occupancy, and isotropic temperature factors were refined. The structural model obtained at ambient conditions was then used for the high temperature pattern analysis by adopting the same structure refinement strategies. The 2θ-zero shift and the reflection intensity were preliminary refined with Le Bail extraction method and then kept fixed at the mean value in all patterns of the

data set. No evidence was found to support a change in symmetry on the powder patterns until 75 °C: the monoclinic $P2_1/n$ space group was used at room and 50°C temperature, orthorhombic P*nma* space group was used in all the crystal structure refinements in the 75° - 600 °C temperature range. Lattice parameters and refinement details of ZSM-5-DCE at 30°C (ZSM-5-DCE-30), regenerated (ZSM-5-R), and regenerated and reloaded ZSM-5 (ZSM-5-R-DCE) are reported in Table 1. The features of unloaded material [6] were also shown for comparison. Framework atoms site positions and isotropic thermal parameters, extraframework atomic coordinates, occupancy and temperature factors of ZSM-5-DCE at 30°C (ZSM-5-DCE-30), regenerated (ZSM-5-R), and regenerated and reloaded ZSM-5 (ZSM-5-R-DCE) respectively, are provided as Supporting Information in Table1S and Table2S, respectively; the dimensions of the 10-membered rings (10MRs) together with their Crystallographic Free Area (C. F. A) and their ellipticity (ε) are reported in Table 2. Mol Files of all refined structures are also uploaded as SI.

*2.3 Thermal analysis.*

Thermogravimetric (TG) and differential thermal analysis (DTA) measurements of both the calcined and reloaded ZSM-5 samples were performed in air at up to 600°C using a Netzsch STA 409 PC LUXX® - simultaneous TG/DTA thermogravimetric analyzer operating at 5 °C/min heating rate. The thermal curves are reported in Figure 1.

*2.4. 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 the minimum headspace, a solid/solution ratio of 1:4 (mg $mL^{-1}$) was employed. After equilibration, (24 hours) at a temperature of 25.3 ± 0.5 °C under stirring, the solids were separated from the aqueous solution using centrifugation (14000 rpm for 30

min) and analysed by as reported in Pasti et. Al. 2012. To determine the adsorbed quantities (q) and the equilibrium concentrations (Ce), the DCE concentrations were determined in the solutions before and after equilibration with the regenerated zeolite.

## 3. RESULTS AND DISCUSSION

### *3.1 In situ synchrotron X-ray powder diffraction and Rietveld refinements*

ZSM-5 is a pentasil zeolite widely used as shape-selective catalysts and sorbents due to its shape selectivity, solid acidity, ion exchangeability, pore size and thermal stability. The MFI framework is characterized by two intersecting sets of tubular channels, a linear or 'straight' (SC=straight channel) one parallel to the [010] direction, (apertures opening ~5.4–5.6 Å), and a sinusoidal or zigzag, (ZZ) one parallel to the [100] direction, (apertures opening ~5.1–5.5 Å) [46] (Figure2).

The topological symmetry is orthorhombic *Pnma,* but its real symmetry strongly depends by the synthesis and post synthesis treatment, $SiO_2/Al_2O_3$ ratio, structural defects, temperature, nature and amount sorbate organic molecules [16-20]. After DCE adsorption [Pasti et al., 2012] the automatic indexing of the peaks as well as the β values confirmed the $P2_1/n$ monoclinic symmetry [6]. Rietveld refinement has revealed that different DCE molecules could be connected by means of hydrogen bonds through water, to form DCE–water complexes, thus influencing the DCE trans–gauche conformational equilibrium [6]. A similar result has been recently found in hydrophobic mordenite after DCE adsorption [9].

In this work, Rietveld structure refinement of ZSM-5-DCE using in situ synchrotron X-ray powder diffraction data was performed starting from the structural model reported at room temperature by Pasti et al. [6]. The difference Fourier map, generated using the GSAS package, confirmed the distribution of the DCE molecules over the two crystallographically independent sites (DCE1 = C1, C2, Cl1, Cl2 sites; DCE2 = C3, C4, Cl3, Cl4 sites;) (Figure 2, Table S2) localized by Pasti et al. [16]. They are located in both the straight (DCE1) and sinusoidal (DCE2) channels and lye parallel to *c* and *a, b* directions, respectively. The location of co-adsorbed water molecules (W site, ~3.0

water/u.c, corresponding to ~1.5% in weight) was also confirmed. According to the starting model, all the DCE molecules (~6.5molecules/u.c., corresponding to ~9.5% in weight) assume a trans (anti)configuration and can interact with water thus forming DCE–water molecule complexes (clusters or short chains) bridged via W to framework oxygen atoms (Figure 3a).

The gradual overlapping of groups of peaks (Figure 4) reveals that the monoclinic $P2_1/n$ to orthorhombic *Pnma* phase transition, occurs with a $T_c$ close to 70 ± 5°C. This result confirms the well-known crucial influence of the Si/Al ratio [18, 19, 21, 22] as well of the adsorbed extra-framework molecules [6, 9, 16-18, 23-26] on the monoclinic-orthorhombic phase transition undergone by this zeolite. Since no evidence was found to support another change in symmetry on the powder patterns until 600°C, the same orthorhombic *Pnma* space group was used in all the crystal structure refinements in the 70-600°C temperature range.

The complete set of lattice parameters is given in Table 3 and illustrated as a function of temperature in Figure 5. To allow a better comparison between them, we report normalised values of cell parameters defined as $V(T)/V_0$, $a(T)/a_0$, $b(T)/b_0$, and $c(T)/c_0$, being the reference values those obtained in the refinement of the first orthorhombic pattern recorded at T=30°C

Up to 70°C, the slight increase of unit cell volume ($\Delta V$~1%) can be reasonably related to the relaxation of the interactions between the DCE–water molecule complexes and framework O atoms which exert a kind of negative pressure (attractive force) on the surrounding framework. A similar framework expansion was also observed upon heating in B-ZSM-5 [27], as well as in other microporous materials such as wairakite [28], analcime [29], hydro-sodalite Na6[AlSiO4]6_8H2O [30.] and silica sodalite [31].

The refined occupancies reported in Figure 6 showed that in this temperature range the DCE1 site progressively decrease its occupancy and it is emptied at temperature (225°C) lower than that found for the organic hosted in DCE2 site (350°C), which is forced into the sinusoidal channel. This is in

agreement with the thermogravimetric analysis reported by Pasti et al., [6] according which the state of the DCE-ZSM-5 system is altered in the temperature range ~150° – 350 °C.

This finding indicated that DCE molecules preferentially diffuse through the straight channel of orthorhombic ZSM-5. At 350°C all the Cl and C sites are emptied, thus confirming the completion of the thermal degradation of DCE at this temperature. A similar behaviour was observed for site occupancy of water molecules . The parallelism in the decrease of DCE and water occupancies with temperature increase, can be explained by the disassembly of water–DCE clusters caused by the DCE thermal degradation. The serial structural refinements during the thermal ramp provide information on the way in which the occupancy of the extraframework sites affect the geometry of the framework

In Figures 8 a and b are reported the Crystallographic Free Areas (C.F.A.) and the ellipticity of the 10MR channels as a function of temperature. The opening of the zeolite framework pore system change with temperature increase due the continuous structural changes associated with the heating process (see Fig. 5a, b). Consequently, the Crystallographic Free Areas (C.F.A.) that depends on channel ellipticity also vary with temperature [10](see Figure 7a). The decrease of channel ellipticity with temperature increase reported in Figure 8b is due to the framework flexibility of ZSM-5 [33, 34]. In particular, the straight (SC) 10-ring channel become narrower and its ellipticity (ε) (defined as the ratio between the smaller (O-O) and larger (O-O)‘‘free diameters’’ of the 10-rings) decreases. A similar contraction was also observed in the sinusoidal channels which become more regular: the resulting cumulative effect explains the unit-cell contraction registered upon heating (Fig. 5b). Once all DCE and water molecules are completely decomposed, no further significant variations are registered in the dimension of the 10MR channels.

At temperarure higher then 400 °C, the host molecule decomposition and expulsion process is completed, therefore the unit cell contraction of ZSM-5 above this temperature can be described as a proper negative thermal expansion (NTE) process (Figure 3). This behaviour is similar to that observed in MFI-type materials synthesized in the presence of tetrapropylammonium as well in

their calcined forms e.g. silicalite-1 [35-37] titanium silicalite-1 (TS-1) and Fe-silicalite (Fe-MFI) [38]. In particular, in TS-1 and Fe-MFI a negative thermal expansion (NTE) was reported above the temperature which marks the end of the calcination process.

*3.2 Adsorption behaviour of regenerated adsorbent*

The regeneration of ZSM-5 loaded with DCE was conducted by high temperature calcination using the TG/DTA thermogravimetric analyzer operating at 5 °C/min heating rate from room temperature to 600°C for completely burning off the organics. After regeneration, the X-ray powder diffraction pattern (ZSM-5-r) was collected and then indexed on a monoclinic unit cell that is consistent with that also observed for the unloaded material. According to Leardini et al. [13] the splitting of (131) and (133) peaks reveals the reversibility of the orthorhombic *Pnma* to monoclinic $P2_1/n$ to phase transition. Figure 9 shows that after regeneration the diffraction peaks are very sharp, indicating that ZSM-5 retain its original crystallinity upon heating.

The regenerated ZSM-5-r was then tested again for DCE adsorption. Figure 8 shows the comparison of the adsorption performance of fresh and regenerated zeolite. The regenerated sample from air calcination produced slightly higher adsorption in the low concentration range than the fresh one. Possibly, this is due to the decomposition of the low amount of NH4 in the starting material.

The data were fitted by using a Langmuir equation (see Table 4, 2$^{nd}$ column) and the parameters found for the adsorption od DCE on regenerated material were not statistically different to those charactering the fresh material reported in Pasti et al. [6].

XRD analysis demonstrates that the regenerated and reloaded zeolite does not show any significant crystallinity loss, as well as perfectly regains the unit-cell parameters of fresh material (Figure 9). The regeneration/adsorption process also occurs without any significant deformations in the channel apertures. The refined atomic fractional coordinates obtained by the Rietveld method indicates minor differences in both the DCE location (Figure 3b). On the basis of the occupancies, Rietveld

refinement of ZSM-5-DCE-30 (Figure 3a) indicates that the organic content remains substantially unchanged thus confirming that, after regeneration, ZSM-5 is able to re-adsorb DCE in amounts comparable to that adsorbed in the first cycle [6]. The occurrence of DCE–water molecule complexes (clusters or short chains) bridged via W to framework oxygen atoms (Figure 3b) was also confirmed. On the whole, ~6.6/u.c. DCE molecules (corresponding to ~10.3% in weight) and ~5$H_2O$/u.c, (corresponding to ~1.5% in weight) were re-adsorbed in the channels systems, in very good agreement with the weight loss reported on the basis of thermal analysis (Figure 1). This results suggest that the regenerated ZSM-5 behave as an adsorbent with undiminished adsorption capacity and opens up the possibility for a re-use of such materials with clear benefits on the cost/performance ratio of the whole water treatment process. How many cycles the ZSM-5 can withstand towards DCE adsorption will be matter of future investigation.

## 4. Conclusions

The adsorption/desorption behaviour of ZSM-5 loaded with 1,2-dichloroethane was studied using the 'in situ' synchrotron X-ray powder-diffraction technique. Upon heating the relaxation of the host molecules determines a slight narrowing of both the sinusoidal and straight channels thus causing a unit-cell contraction in all temperature range investigated. Once regenerated and reloaded the ZSM-5 zeolite does not show any significant difference in the saturation capacity. Moreover, regenerated zeolite does not exhibit crystallinity loss or deformations in the channel apertures, as well as perfectly regain the unit-cell parameters of fresh material. The refined occupancies obtained by the Rietveld method indicates that both DCE location and content remain substantially unchanged thus confirming that, after regeneration, ZSM-5 is able to re-adsorb DCE in amounts comparable to that adsorbed in the first cycle . These results clearly demonstrated that regeneration of ZSM-5 is effective when thermally treating this environmentally friendly and highly efficient adsorbent at about 300°C thus minimising the cost of the regeneration step of the adsorption process. In conclusion, the use of this adsorbent with unchanged adsorption performances after thermal

regeneration under mild conditions appears very promising also over several cycles of the adsorption/desorption process.

## 5. Acknowledgements

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**Figure Caption**

Figure 1. Thermogravimetric (TG, blue line), differential thermogravimetric (DTG, dotted black line) and differential thermal (DTA, grey line) curves in ZSM-5-R-DCE dry air atmosphere.

Figure 2 Projection of the straight and sinusoidal channels along the [010] (a) and [100] directions, respectively.

Figure 3. Location of DCE and water molecules in ZSM-5 along [001] and [100] directions, in ZSM-5-DCE-30 (a) and ZSM-5-R-DCE(b), respectively.

Figure 4. Plot of ZSM-5-DCE-30 in the 1.9 – 2.4 (a) and 5.7 – 6.4 (b) °2θ ranges within the 30 – 600°C temperature interval.

Figure 5. Temperature evolution of the unit cell parameters of ZSM-5-DCE during the *in situ* thermal burning of the organic. Broken lines highlight the subtle discontinuity on the cell volume trend occurring at about 380°C.

Figure 6. Variation of DCE and water molecules per unit cell as a function of temperature. The evolution of unit cell volume is also shown for comparison.

Figure 7. (a) Evolution of Crystallographic Free Area (CFA sensu (Baerlocher et al., 2007) and (b) channel ellipticity for the 10MR channels as a function of temperature.

Figure 8. Adsorption isotherms (T=298 K) of DCE on fresh (ZSM-5) and thermally regenerated (ZSM-5-r) zeolites.

Figura 9. Powder diffraction patterns of unloaded (ZSM-5) and thermally regenerated (ZSM-5-R) zeolites , respectively (the stacked plots have been shifted for easy comparison).

**Table 1.** Lattice parameters and refinement details of unloaded ZSM-5 (ZSM-5)*, after thermal regeneration (ZSM-5-R), after DCE adsorption (ZSM-5-DCE-30), and for regenerated and reloaded sample (ZSM-5-R- DCE).

| | **ZSM-5*** | **ZSM-5-DCE-30** | **ZSM-5-R** | **ZSM-5-R-DCE** |
|---|---|---|---|---|
| Space group | *P2₁/n* | *P2₁/n* | *P2₁/n* | *P2₁/n* |
| *a* (Å) | 19.8999(5) | 19.9052(3) | 19.8935(5) | 19.8954(5) |
| *b* (Å) | 20.1174(6) | 20.1199(3) | 20.1165(5) | 20.1177(5) |
| *c* (Å) | 13.3892(4) | 13.3909(2) | 13.3818(4) | 13.3835(4) |
| *β* | 90.546(3) | 90.578(1) | 90.5598(23) | 90.5641(25) |
| *V* (Å$^3$) | 5359.9(3) | 5362.7(1) | 5354.97(25) | 5356.46(26) |
| Wavelength of incident radiation (Å) | 1.5417(1) | 0.400031(1) | 1.5417(1) | 1.5417(1) |
| Refined pattern 2θ range (°) | 3-110 | 0.7-25 | 3-110 | 3-110 |
| $R_{wp}$ (%) | 9.12 | 9.2 | 11.90 | 12.94 |
| $R_p$ (%) | 8.4 | 8.5 | 8.76 | 10.07 |
| $R_F^2$ (%) | 9.1 | 7.50 | 5.75 | 5.57 |
| $N_o$ of contributing reflections | 14142 | 12252 | 6039 | 10258 |
| $N_{obs}$ | 5601 | 7239 | 8911 | 6223 |
| $N_{var}$ | 289 | 282 | 250 | 282 |

$R_p = \sum[Y_{io}-Y_{ic}]/\sum Y_{io}$; $R_{wp} = [\sum w_i(Y_{io}-Y_{ic})^2/\sum w_i Y_{io}^2]^{0.5}$; $R_F^2 = \sum|F_o^2-F_c^2|/\sum|F_o^2|$

*Pasti et al. 2012 [6].

**Table 2.** Dimensions (Å) of the apertures of unloaded ZSM-5 (ZSM-5)*, after thermal regeneration (ZSM-5-R), after DCE adsorption (ZSM-5-DCE-30), and for regenerated and reloaded sample (ZSM-5-R- DCE) assuming an oxygen ionic radius of 1.35 Å. The ellipticity (ε= largest/shortest oxygen–oxygen distances) and C.F.A. were also reported.

| **Straight Channel (SC-A)** | **ZSM-5*** | **ZSM-5-R** | **ZSM-5-DCE-30** | **ZSM-5-R-DCE** |
|---|---|---|---|---|
| **O7-O1** | 7.98(1) | 7.96(1) | 8.21(1) | 8.40(1) |
| **O8-O2** | 8.08(1) | 8.00(1) | 8.11(1) | 7.97(1) |
| **O31-O37** | 8.20(1) | 8.00(1) | 8.28(1) | 8.01(1) |
| **O44-O46** | 8.19(1) | 8.28(1) | 8.63(1) | 8.72(1) |
| **O47-O48** | 7.93(1) | 7.80(1) | 7.96(1) | 7.95(1) |
| **C.F.A.** | 22.68 | 22.16 | 24.14 | 23.88 |
| **ε** | 1.03 | 1.06) | 1.08 | 1.10 |
| **Straight Channel (SC-A)** | **ZSM-5*[6]** | **ZSM-5-R** | **ZSM-5-DCE-30** | **ZSM-5-R-DCE** |
| **O11_O5** | 8.23(1) | 8.19(1) | 8.15(1) | 8.19(1) |
| **O20_O18** | 8.21(1) | 8.19(1) | 8.49(1) | 8.33(1) |
| **O21_O22** | 8.04(1) | 8.02(1) | 8.01(1) | 7.98(1) |
| **O27_O33** | 8.03(1) | 7.95(1) | 8.38(1) | 8.31(1) |
| **O28_O34** | 8.07(1) | 7.86(1) | 7.081(1) | 8.00(1) |
| **C.F.A.** | 22.68 | 22.45 | 23.51 | 23.47 |
| **ε** | 1.02 | 1.04 | 1.08 | 1.04 |
| **Sinosuidal Channel (ZZ-B)** | **ZSM-5*** | **ZSM-5-R** | **ZSM-5-RT** | **ZSM-5-R-DCE** |
| **O17-O18** | 7.81(1) | 7.59(1) | 7.71(1) | 7.59(1) |
| **O23-O25** | 8.20(1) | 8.11(1) | 8.49(1) | 8.54(1) |
| **O30-O5** | 8.31(1) | 8.26(1) | 8.59(1) | 8.31(1) |
| **O31-O4** | 7.91(1) | 7.63(1) | 7.64(1) | 7.69(1) |
| **O44-O43** | 8.13(1) | 8.07(1) | 8.18(1) | 8.29(1) |
| **C.F.A.** | 22.65 | 21.51 | 23.12 | 22.80 |
| **ε** | 1.06 | 1.08 | 1.12 | 1.12 |
| **Sinosuidal Channel (ZZ-A)** | **ZSM-5*** | **ZSM-5-R** | **ZSM-5-RT** | **ZSM-5-R-DCE** |
| **O20-O15** | 7.95(1) | 7.90(1) | 8.28(1) | 8.38(1) |
| **O24-O26** | 7.84(1) | 7.77(1) | 8.26(1) | 8.24(1) |
| **O27-O2** | 7.85(1) | 7.89(1) | 8.16(1) | 7.95(1) |
| **O28-O1** | 7.90(1) | 7.83(1) | 7.96(1) | 8.13(1) |
| **O41-O46** | 8.22(1) | 8.29(1) | 8.68(1) | 8.57(1) |
| **C.F.A.** | 21.65 | 21.54 | 24.37 | 24.24 |
| **ε** | 1.04 | 1.06 | 1.09 | 1.08 |

*Pasti et al. 2012 [6].

**Table 3.** High-temperature lattice parameters of ZSM-5-DCE in the temperature range 30°-600°C. Figures in parentheses represent the estimated standard-deviation.

| T(°C) | a(Å) | b(Å) | c(Å) | Volume(Å$^3$) | β(°) |
|---|---|---|---|---|---|
| 30 | 19.9052(3) | 20.1199(3) | 13.3909(2) | 5362.65(1) | 90.58(1) |
| 40 | 19.9080(3) | 20.1218(3) | 13.3938(2) | 5365.10(1) | 90.54(1) |
| 50 | 19.9118(3) | 20.1213(3) | 13.3962(2) | 5367.36(1) | 90.50(1) |
| 60 | 19.9164(3) | 20.1241(3) | 13.4006(2) | 5370.79(1) | 90.43(1) |
| 75 | 19.9336(3) | 20.1129(3) | 13.4077(9) | 5375.46(1) | 90 |
| 100 | 19.9378(6) | 20.1067(5) | 13.4076(6) | 5374.90(1) | 90 |
| 125 | 19.9394(5) | 20.1024(5) | 13.4066(2) | 5373.99(2) | 90 |
| 150 | 19.9392(4) | 20.1022(4) | 13.4054(2) | 5373.15(2) | 90 |
| 175 | 19.9373(5) | 20.1031(5) | 13.4042(3) | 5373.30(2) | 90 |
| 200 | 19.9348(4) | 20.1054(4) | 13.4034(3) | 5372.05(2) | 90 |
| 225 | 19.9339(4) | 20.1040(4) | 13.4024(3) | 5371.04(2) | 90 |
| 250 | 19.9331(4) | 20.1014(4) | 13.4014(3) | 5369.72(2) | 90 |
| 275 | 19.9321(4) | 20.0978(4) | 13.4004(3) | 5368.10(2) | 90 |
| 300 | 19.9311(4) | 20.0942(3) | 13.3996(2) | 5366.51(2) | 90 |
| 350 | 19.9290(4) | 20.0886(3) | 13.3980(2) | 5363.84(2) | 90 |
| 400 | 19.9274(4) | 20.0832(2) | 13.3969(2) | 5361.53(2) | 90 |
| 450 | 19.9254(3) | 20.0785(3) | 13.3956(2) | 5359.20(2) | 90 |
| 500 | 19.9229(3) | 20.0743(3) | 13.3941(2) | 5356.83(2) | 90 |
| 550 | 19.9203(4) | 20.0708(4) | 13.3924(2) | 5354.51(2) | 90 |
| 600 | 19.9175(4) | 20.0675(4) | 13.3906(2) | 5352.14(2) | 90 |

**Table 4:** Fitting Results of the adsorption data of DCE on regenerated zeolite (ZSM-5-r). The fitting parameters are reported together with the confidence limits calculated at 95% of probability.

| **Organic -Zeolite** | **Equation** | **Parameters** | | **$R^2$** |
|---|---|---|---|---|
| *DCE-ZSM*-5-r | $q = \frac{q_s K_L C_e}{1 + K_L C_e}$ | $K_L$ | | 0.9925 |
| | | **(L mg$^{-1}$)** | $q_s$ | |
| | | 0.20 | **(mg g$^{-1}$)** | |
| | | (0.17, 0.23) | 117 | |
| | | | (111, 123) | |

**Table 1 SI.** Atomic fractional coordinates and Uiso of framework atoms after DCE adsorption (ZSM-5-DCE-30), after thermal regeneration (ZSM-5-R) and for regenerated and reloaded ZSM-5(ZSM-5-R- DCE).

| SAMPLES | | x/a | y/b | z/c | Ui/Ue*100 |
|---|---|---|---|---|---|
| **ZSM-5-DCE-30** | **T1** | 0.0548(3) | 0.4203(3) | -0.3222(5) | 0.87(5) |
| **ZSM-5-R** | | 0.0576(11) | 0.4175(11) | -0.3153(17) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.0539(4) | 0.4236(4) | -0.3289(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T2** | 0.0316(4) | 0.3162(4) | -0.1657(5) | 0.87(5) |
| **ZSM-5-R** | | 0.0323(10) | 0.3117(13) | -0.1601(14) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.0332(4) | 0.3162(4) | -0.1692(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T3** | 0.0608(3) | 0.2809(3) | 0.0541(5) | 0.87(5) |
| **ZSM-5-R** | | 0.0598(10) | 0.2771(11) | 0.0513(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.0636(4) | 0.2823(4) | 0.0442(8) | 0.19(26) |
| **ZSM-5-DCE-30** | **T4** | 0.0615(4) | 0.1245(3) | 0.0344(5) | 0.87(5) |
| **ZSM-5-R** | | 0.0610(10) | 0.1214(12) | 0.0318(17) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.0643(4) | 0.1263(4) | 0.0333(5) | 0.19(26) |
| **ZSM-5-DCE-30** | **T5** | 0.0271(3) | 0.0775(4) | -0.1780(6) | 0.87(5) |
| **ZSM-5-R** | | 0.0310(11) | 0.0708(11) | -0.1814(16) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.02781(34) | 0.0732(4) | -0.1742(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T6** | 0.0564(4) | 0.1967(3) | -0.3138(6) | 0.87(5) |
| **ZSM-5-R** | | 0.0544(10) | 0.1923(12) | -0.3129(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.0582(4) | 0.1939(4) | -0.3083(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T7** | -0.1720(3) | 0.4255(3) | -0.3246(5) | 0.87(5) |
| **ZSM-5-R** | | -0.1748(11) | 0.4248(11) | -0.3278(16) | 0.27(9) |
| **ZSM-5-R-DCE** | | -0.17206(34) | 0.42672(33) | -0.3263(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T8** | -0.1259(3) | 0.3112(3) | -0.1776(5) | 0.87(5) |
| **ZSM-5-R** | | -0.1262(10) | 0.3125(12) | -0.1773(14) | 0.27(9) |
| **ZSM-5-R-DCE** | | -0.1251(4) | 0.3110(4) | -0.1807(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T9** | -0.1752(3) | 0.2700(4) | 0.0333(6) | 0.87(5) |
| **ZSM-5-R** | | -0.1752(11) | 0.2793(11) | 0.0413(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | -0.17594(34) | 0.2682(4) | 0.0284(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T10** | -0.1780(3) | 0.1160(4) | 0.0293(6) | 0.87(5) |
| **ZSM-5-R** | | -0.1783(11) | 0.1215(11) | 0.0460(16) | 0.27(9) |
| **ZSM-5-R-DCE** | | -0.17920(33) | 0.1128(4) | 0.0274(7) | 0.19(26) |
| **ZSM-5-DCE-30** | **T11** | -0.1308(3) | 0.0686(4) | -0.1793(6) | 0.87(5) |
| **ZSM-5-R** | | -0.1286(10) | 0.0737(11) | -0.1683(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | -0.1291(4) | 0.0653(4) | -0.1774(7) | 0.19(26) |
| **ZSM-5-DCE-30** | **T12** | -0.1650(3) | 0.1844(4) | -0.3143(6) | 0.87(5) |
| **ZSM-5-R** | | -0.1684(10) | 0.1873(11) | -0.3170(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | -0.1639(4) | 0.1866(4) | -0.3145(7) | 0.19(26) |
| **ZSM-5-DCE-30** | **T13** | 0.4415(3) | 0.4291(3) | -0.3378(5) | 0.87(5) |
| **ZSM-5-R** | | 0.4423(11) | 0.4262(11) | -0.3264(17) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.4420(4) | 0.4246(4) | -0.3352(6) | 0.19(26) |
| **ZSM-5-DCE-30** | **T14** | 0.4730(3) | 0.3124(4) | -0.1884(5) | 0.87(5) |
| **ZSM-5-R** | | 0.4685(9) | 0.3102(12) | -0.1867(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.4735(4) | 0.3115(4) | -0.1870(6) | 0.19(26) |

| | | | | | |
|---|---|---|---|---|---|
| **ZSM-5-DCE-30** | | 0.4387(4) | 0.2779(3) | 0.0279(5) | 0.87(5) |
| **ZSM-5-R** | **T15** | 0.4359(10) | 0.2770(12) | 0.0311(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.4398(4) | 0.2791(4) | 0.0339(7) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.4357(4) | 0.1256(4) | 0.0324(5) | 0.87(5) |
| **ZSM-5-R** | **T16** | 0.4344(11) | 0.1200(12) | 0.0278(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.4322(4) | 0.1218(4) | 0.0287(5) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.4750(3) | 0.0713(3) | -0.1810(6) | 0.87(5) |
| **ZSM-5-R** | **T17** | 0.4689(10) | 0.0650(11) | -0.1910(16) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.4723(4) | 0.0734(4) | -0.1882(6) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.4367(4) | 0.1862(3) | -0.3148(6) | 0.87(5) |
| **ZSM-5-R** | **T18** | 0.4389(11) | 0.1834(11) | -0.3223(16) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.4388(4) | 0.1881(4) | -0.3204(7) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.6723(3) | 0.4222(3) | -0.3156(5) | 0.87(5) |
| **ZSM-5-R** | **T19** | 0.6682(11) | 0.4249(11) | -0.3184(16) | 0.0027(9) |
| **ZSM-5-R-DCE** | | 0.67207(32) | 0.4206(4) | -0.3127(5) | 0.0061 |
| **ZSM-5-DCE-30** | | 0.6325(3) | 0.3107(4) | -0.1680(5) | 0.87(5) |
| **ZSM-5-R** | **T20** | 0.6302(9) | 0.3157(12) | -0.1666(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.6324(4) | 0.3098(4) | -0.1696(6) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.6678(3) | 0.2715(4) | 0.0444(6) | 0.87(5) |
| **ZSM-5-R** | **T21** | 0.6724(10) | 0.2784(11) | 0.0550(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.6682(4) | 0.2712(4) | 0.0480(6) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.6687(3) | 0.1180(4) | 0.0333(6) | 0.87(5) |
| **ZSM-5-R** | **T22** | 0.6739(12) | 0.1206(12) | 0.0466(15) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.6691(4) | 0.1160(4) | 0.0337(6) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.6316(4) | 0.0714(4) | -0.1856(6) | 0.87(5) |
| **ZSM-5-R** | **T23** | 0.6314(10) | 0.0715(12) | -0.1810(16) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.6295(4) | 0.0732(4) | -0.1876(6) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.6810(3) | 0.1929(4) | -0.2982(6) | 0.87(5) |
| **ZSM-5-R** | **T24** | 0.6789(10) | 0.1929(11) | -0.3082(14) | 0.27(9) |
| **ZSM-5-R-DCE** | | 0.6806(4) | 0.1921(4) | -0.3043(6) | 0.19(26) |
| **ZSM-5-DCE-30** | | 0.0659(5) | 0.3772(5) | -0.2229(8) | 1.09(13) |
| **ZSM-5-R** | **O1** | 0.0626(18) | 0.3765(16) | -0.2140(23) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.0643(6) | 0.3743(5) | -0.2363(9) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.0632(6) | 0.3128(6) | -0.0553(5) | 1.09(13) |
| **ZSM-5-R** | **O2** | 0.0694(16) | 0.3126(19) | -0.0551(16) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.0659(6) | 0.3214(6) | -0.0598(6) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.0473(6) | 0.2027(3) | 0.0439(3) | 1.09(13) |
| **ZSM-5-R** | **O3** | 0.0490(17) | 0.2009(11) | 0.0271(28) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.0520(7) | 0.20476(34) | 0.0236(15) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.0665(5) | 0.1038(8) | -0.0809(6) | 1.09(13) |
| **ZSM-5-R** | **O4** | 0.0695(17) | 0.0956(19) | -0.0827(18) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.0694(5) | 0.0944(9) | -0.0761(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.0445(6) | 0.1231(4) | -0.2724(7) | 1.09(13) |
| **ZSM-5-R** | **O5** | 0.0465(20) | 0.1191(14) | -0.2696(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.0468(7) | 0.1205(4) | -0.2657(10) | 0.42(5) |
| **ZSM-5-DCE-30** | **O6** | 0.0471(7) | 0.2887(5) | -0.2245(9) | 1.09(13) |
| **ZSM-5-R** | | 0.0521(21) | 0.2465(16) | -0.2240(24) | 0.84(17) |

| | | | | | |
|---|---|---|---|---|---|
| **ZSM-5-R-DCE** | | 0.0514(8) | 0.2460(5) | -0.2185(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1601(6) | 0.3703(5) | -0.2401(9) | 1.09(13) |
| **ZSM-5-R** | **O7** | -0.1560(21) | 0.3779(17) | -0.2334(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1574(7) | 0.3712(5) | -0.2431(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1629(6) | 0.3050(6) | -0.0724(7) | 1.09(13) |
| **ZSM-5-R** | **O8** | -0.1637(17) | 0.3093(20) | -0.0697(16) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1627(7) | 0.3048(6) | -0.0759(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1565(7) | 0.1927(3) | 0.0253(2) | 1.09(13) |
| **ZSM-5-R** | **O9** | -0.1639(17) | 0.2004(11) | 0.0437(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1620(8) | 0.19022(34) | 0.0166(14) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1719(5) | 0.0834(7) | -0.0795(7) | 1.09(13) |
| **ZSM-5-R** | **O10** | -0.1648(18) | 0.0926(20) | -0.0647(19) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1725(5) | 0.0769(7) | -0.0788(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1563(7) | 0.1168(4) | -0.2671(9) | 1.09(13) |
| **ZSM-5-R** | **O11** | -0.1521(20) | 0.1194(15) | -0.2609(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1543(7) | 0.1154(5) | -0.2631(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1337(7) | 0.2432(5) | -0.2387(9) | 1.09(13) |
| **ZSM-5-R** | **O12** | -0.1466(22) | 0.2489(17) | -0.2453(28) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1340(8) | 0.2433(5) | -0.2427(11) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.0479(3) | 0.3273(6) | -0.1595(8) | 1.09(13) |
| **ZSM-5-R** | **O13** | -0.0472(9) | 0.3191(23) | -0.1539(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.04663(35) | 0.3247(6) | -0.1622(13) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.0522(3) | 0.0800(7) | -0.1587(8) | 1.09(13) |
| **ZSM-5-R** | **O14** | -0.0479(10) | 0.0779(22) | -0.1575(27) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.05115(32) | 0.0785(7) | -0.1532(11) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.1222(4) | 0.4188(6) | -0.3867(8) | 1.09(13) |
| **ZSM-5-R** | **O15** | 0.1298(14) | 0.4155(19) | -0.3680(25) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.1212(5) | 0.4253(6) | -0.3935(9) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.0060(5) | 0.3894(7) | -0.3867(9) | 1.09(13) |
| **ZSM-5-R** | **O16** | -0.0023(16) | 0.3974(21) | -0.3947(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.0078(5) | 0.3985(8) | -0.3966(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1342(4) | 0.4040(7) | -0.4245(8) | 1.09(13) |
| **ZSM-5-R** | **O17** | -0.1386(14) | 0.3987(21) | -0.4275(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1376(5) | 0.4055(7) | -0.4291(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.1308(4) | 0.2022(7) | -0.3574(6) | 1.09(13) |
| **ZSM-5-R** | **O18** | 0.1275(13) | 0.1873(19) | -0.3605(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.1316(4) | 0.1986(8) | -0.3561(6) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.0029(5) | 0.2116(6) | -0.4009(9) | 1.09(13) |
| **ZSM-5-R** | **O19** | -0.0053(15) | 0.2022(21) | -0.3925(23) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.0026(5) | 0.2092(7) | -0.3925(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.1268(5) | 0.1931(7) | -0.4188(7) | 1.09(13) |
| **ZSM-5-R** | **O20** | -0.1313(14) | 0.1938(21) | -0.4222(20) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1259(5) | 0.1878(8) | -0.4193(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.0499(6) | 0.0032(4) | -0.2042(8) | 1.09(13) |
| **ZSM-5-R** | **O21** | 0.0514(20) | -0.0008(11) | -0.2182(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.0465(7) | -0.0014(4) | -0.2052(7) | 0.42(5) |
| **ZSM-5-DCE-30** | **O22** | -0.1423(6) | -0.0068(4) | -0.2145(8) | 1.09(13) |

| | | | | | |
|---|---|---|---|---|---|
| **ZSM-5-R** | | -0.1485(21) | -0.0001(11) | -0.2009(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.1383(6) | -0.0096(4) | -0.2155(9) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.2509(3) | 0.4316(6) | -0.3473(8) | 1.09(13) |
| **ZSM-5-R** | **O23** | -0.2539(10) | 0.4186(20) | -0.3444(27) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.25148(31) | 0.4334(6) | -0.3439(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.2431(3) | 0.2047(6) | -0.3329(9) | 1.09(13) |
| **ZSM-5-R** | **O24** | -0.2467(9) | 0.1901(20) | -0.3511(20) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.24217(33) | 0.2007(7) | -0.3344(11) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.2527(3) | 0.2780(8) | 0.0618(9) | 1.09(13) |
| **ZSM-5-R** | **O25** | -0.2504(10) | 0.2975(16) | 0.0776(22) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.25221(34) | 0.2803(8) | 0.0609(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | -0.2541(3) | 0.1108(7) | 0.0667(8) | 1.09(13) |
| **ZSM-5-R** | **O26** | -0.2515(11) | 0.1039(17) | 0.0828(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | -0.25435(30) | 0.1046(8) | 0.0674(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.4459(7) | 0.3773(5) | -0.2472(8) | 1.09(13) |
| **ZSM-5-R** | **O27** | 0.4406(20) | 0.3767(15) | -0.2346(25) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.4410(7) | 0.3743(5) | -0.2427(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.4500 (8) | 0.3173(5) | -0.0745(6) | 1.09(13) |
| **ZSM-5-R** | **O28** | 0.4409(18) | 0.3141(18) | -0.0746(16) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.4538(7) | 0.3139(6) | -0.0714(6) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.4293(6) | 0.2001(3) | 0.0066(9) | 1.09(13) |
| **ZSM-5-R** | **O29** | 0.4303(17) | 0.1995(12) | 0.0094(27) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.4285(7) | 0.2010(4) | 0.0184(14) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.4530(7) | 0.0825(6) | -0.0675(7) | 1.09(13) |
| **ZSM-5-R** | **O30** | 0.4424(19) | 0.0866(20) | -0.0821(19) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.4450(8) | 0.0893(9) | -0.0787(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.4313(4) | 0.1180(5) | -0.2535(9) | 1.09(13) |
| **ZSM-5-R** | **O31** | 0.4314(17) | 0.1139(15) | -0.2650(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.4315(6) | 0.1169(4) | -0.2685(11) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.4427(7) | 0.2474(5) | -0.2386(10) | 1.09(13) |
| **ZSM-5-R** | **O32** | 0.4388(20) | 0.2459(16) | -0.2453(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.4453(7) | 0.2445(5) | -0.2364(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6674(6) | 0.3724(5) | -0.2226(8) | 1.09(13) |
| **ZSM-5-R** | **O33** | 0.6545(21) | 0.3848(15) | -0.2165(22) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6699(6) | 0.3725(6) | -0.2174(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6450(7) | 0.3154(5) | -0.0498(5) | 1.09(13) |
| **ZSM-5-R** | **O34** | 0.6531(18) | 0.3154(18) | -0.0503(16) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6432(7) | 0.3092(6) | -0.0508(5) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6488(7) | 0.1950(3) | 0.0258(10) | 1.09(13) |
| **ZSM-5-R** | **O35** | 0.6624(17) | 0.2000(11) | 0.0423(27) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6511(8) | 0.1935(4) | 0.0393(14) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6582(7) | 0.0838(7) | -0.0739(6) | 1.09(13) |
| **ZSM-5-R** | **O36** | 0.6560(20) | 0.0947(20) | -0.0683(19) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6584(7) | 0.0900(9) | -0.0784(6) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6722(6) | 0.1177(4) | -0.2614(8) | 1.09(13) |
| **ZSM-5-R** | **O37** | 0.6636(20) | 0.1201(15) | -0.2649(25) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6681(7) | 0.1172(4) | -0.2687(9) | 0.42(5) |

| | | | | | |
|---|---|---|---|---|---|
| **ZSM-5-DCE-30** | | 0.6441(8) | 0.2427(5) | -0.2086(8) | 1.09(13) |
| **ZSM-5-R** | **O38** | 0.6646(20) | 0.2528(17) | -0.2275(25) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6627(8) | 0.2429(5) | -0.2162(9) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.5534(3) | 0.3113(9) | -0.1918(11) | 1.09(13) |
| **ZSM-5-R** | **O39** | 0.5490(9) | 0.3130(24) | -0.1771(29) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.5537(4) | 0.3140(9) | -0.1958(11) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.5531(3) | 0.0887(5) | -0.1924(12) | 1.09(13) |
| **ZSM-5-R** | **O40** | 0.5497(9) | 0.0721(21) | -0.1934(30) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.5509(4) | 0.0902(6) | -0.1931(13) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.3703(4) | 0.4225(6) | -0.3936(8) | 1.09(13) |
| **ZSM-5-R** | **O41** | 0.3677(14) | 0.4175(18) | -0.3734(26) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.3718(4) | 0.4209(7) | -0.3944(9) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.5007(5) | 0.4151(6) | -0.4153(9) | 1.09(13) |
| **ZSM-5-R** | **O42** | 0.4973(15) | 0.4075(20) | -0.4082(27) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.5020(5) | 0.4057(9) | -0.4089(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6303(4) | 0.3931(6) | -0.4086(7) | 1.09(13) |
| **ZSM-5-R** | **O43** | 0.6317(14) | 0.3962(20) | -0.4164(23) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6320(5) | 0.3875(7) | -0.4044(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.3708(5) | 0.1950(6) | -0.3822(9) | 1.09(13) |
| **ZSM-5-R** | **O44** | 0.3713(14) | 0.1765(16) | -0.3872(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.3734(6) | 0.2018(7) | -0.3879(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.5020(5) | 0.1846(6) | -0.3838(8) | 1.09(13) |
| **ZSM-5-R** | **O45** | 0.5041(14) | 0.1842(18) | -0.3891(24) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.5042(5) | 0.1887(8) | -0.3889(10) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6314(4) | 0.2069(7) | -0.3907(7) | 1.09(13) |
| **ZSM-5-R** | **O46** | 0.6329(13) | 0.2108(19) | -0.4027(21) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6342(4) | 0.2077(7) | -0.3996(8) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.4625(6) | -0.0050(3) | -0.2101(8) | 1.09(13) |
| **ZSM-5-R** | **O47** | 0.4504(20) | -0.0077(10) | -0.2287(25) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.4614(6) | -0.0036(4) | -0.2134(9) | 0.42(5) |
| **ZSM-5-DCE-30** | | 0.6431(6) | -0.0050(3) | -0.2148(8) | 1.09(13) |
| **ZSM-5-R** | **O48** | 0.6572(21) | -0.0017(11) | -0.2092(28) | 0.84(17) |
| **ZSM-5-R-DCE** | | 0.6414(6) | -0.0039(4) | -0.2111(10) | 0.42(5) |

**Table 2 SI.** Atomic fractional coordinates, Uiso, and site occupancy fraction of ZSM-5 extraframework after DCE adsorption (ZSM-5-DCE-30), after thermal regeneration (ZSM-5-R) and for regenerated and reloaded ZSM-5(ZSM-5-R- DCE).

| **ZSM-5-DCE-30** | | | | | |
|---|---|---|---|---|---|
| | **x/a** | **y/b** | **z/c** | **UISO** | **Fraction** |
| **C1** | 0.772(1) | 0.468(8) | 0.060(5) | 0.11(2) | 0.85(1) |
| **C11** | 0.686(1) | 0.470(3) | 0.069(2) | 0.11(2) | 0.85(1) |
| **Cl2** | 0.893(1) | 0.484(2) | -0.029(2) | 0.11(2) | 0.85(1) |
| **C2** | 0.807(1) | 0.487(8) | -0.020(5) | 0.11(2) | 0.85(1) |
| **C3** | 0.748(8) | 0.796(1) | 0.170(2) | 0.15(2) | 0.76(1) |
| **Cl3** | 0.739(2) | 0.720(1) | 0.115(2) | 0.15(2) | 0.76(1) |
| **C4** | 0.747(9) | 0.855(1) | 0.121(2) | 0.15(2) | 0.76(1) |
| **Cl4** | 0.75(3) | 0.931(1) | 0.177(2) | 0.15(2) | 0.76(1) |
| **W** | 0.638(5) | 0.319(4) | 0.329(6) | 4.29(2) | 0.77(5) |
| **ZSM-5-R** | | | | | |
| | **x/a** | **y/b** | **z/c** | **UISO** | **Fraction** |
| **W** | 0.135(2) | 0.460(3) | -0.039(4) | 9.73(31) | 1.0(1) |
| **ZSM-5-R-DCE** | | | | | |
| | **x/a** | **y/b** | **z/c** | **UISO** | **Fraction** |
| **C1** | 0.782(3) | 0.427(11) | 0.101(1) | 0.79(3) | 0.73(1) |
| **Cl1** | 0.697(1) | 0.423(4) | 0.079(5) | 0.79(3) | 0.73(1) |
| **C2** | 0.825(3) | 0.466(11) | 0.050(1) | 0.79(3) | 0.73(1) |
| **Cl2** | 0.908(1) | 0.477(3) | 0.081(3) | 0.79(3) | 0.73(1) |
| **C3** | 0.736(11) | 0.803(4) | 0.111(2) | 0.83(3) | 0.77(1) |
| **Cl3** | 0.707(3) | 0.722(2) | 0.107(3) | 0.83(3) | 0.77(1) |
| **C4** | 0.739(11) | 0.840(4) | 0.195(4) | 0.83(3) | 0.77(1) |
| **Cl4** | 0.770(3) | 0.922(2) | 0.195(3) | 0.83(3) | 0.77(1) |
| **W** | 0.821(5) | 0.913(5) | 0.283(6) | 0.43(3) | 0.75(2) |