Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary information

Conversion of methanol to hydrocarbons over zeolite ZSM-23 (MTT): Exceptional effects of particle size on catalyst lifetime

A. Molino,[a] K. A. Lukaszuk,[a] D. Rojo-Gama,[a] K. P. Lillerud,[a] U. Olsbye,[a] S. Bordiga,[a,c] S. Svelle,*[a] and P. Beato*[b]

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[a] Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

[b] . Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

[c] Department of Chemistry, NIS and INSTM Reference Centers, University of Turin, via Quarello 15, I-10135 Turin, Italy

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Materials and Method

Powder X-Ray diffraction (PXRD) patterns were acquired using a Bruker D8 Discover diffractometer equipped with a Cu Kα source, germanium crystal monochromator (022 plane) and a LynxEye silicon detector.

Nitrogen adsorption measurements were done volumetrically at 77K in a BELSORP-Mini II instrument. The samples were evacuated at 80 °C for 1 h and at 250 °C for 3 h before the adsorption measurement. The surface area was calculated using the BET method in the range of validity for microporous materials. The micropore volume was calculated using the t-plot method (see Supplementary Information).

Scanning electron microscopy (SEM) was carried out with a Hitachi SU8200 instrument with a Cold Field Emission gun source, using a voltage of 3 kV. The uncoated sample in the powder form was glued on the holder with carbon tape.

Elemental analysis of Si and Al was done by dissolving the zeolite in HF and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) with a PerkinElmer Optima 8000.

Temperature programmed desorption (TPD) of NH_3 has been carried out on a Mettler Toledo TGA in a constant flow of 75 ml/min of inert (31% He /69% Ar). The sample (50 mg) was pretreated at 500 °C (heating rate of 20 °C/min) for 2 h and then cooled to 150 °C, where the temperature was kept for 30 min while a flow of ammonia was added to the inert (2% NH_3 /29% He /69% Ar). The flow was switched to inert again for 4h and then the desorption measurement was performed from 150°C to 600°C (heating ramp of 10 °C /min).

The conversion of methanol to hydrocarbons was performed in a continuous flow U-shaped fix-bed reactor (i.d. of 10 mm). Prior to reactions, catalysts were heated from room temperature to 550 °C under a flow pure O2 and kept for 1 hour to calcine the catalysts in-situ. After the pre-treatment, the reactor was cooled down under a flow of pure He to the temperature applied for the reaction (400 °C).

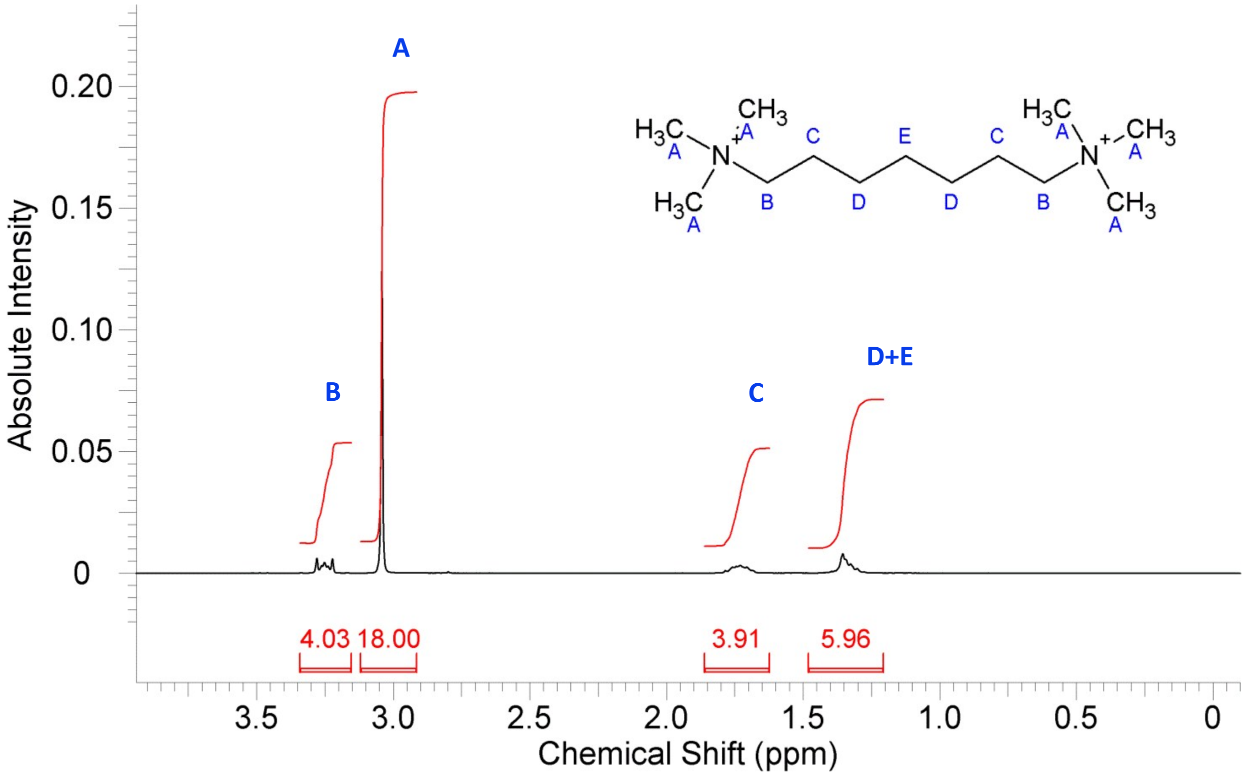
The methanol to hydrocarbon reaction was carried out at atmospheric pressure and 400 °C. 100 mg of catalyst was used (sieve fraction 250 to 420 µm). A He flow of 19.5 mL min-1 was bubbled through a saturator filled with MeOH (BDH Laboratory, purity >99.8 %) at a temperature of 20 °C, giving rise to a methanol partial pressure of 130 mbar. The resulting weight hourly space velocity (WHSV) was 2 gMeOH gcatalyst-1 h-1.

The reaction products were analyzed using an online Agilent 6890A gas chromatograph equipped with an SPB-5 capillary column (length 60 m, 0.530 mm i.d., stationary phase thickness of 5 µm) and a flame ionization detector (FID).

Methanol conversion, product selectivity and product yield were obtained by the integration of the areas from the GC-FID chromatogram. Both, methanol (MeOH) and dimethyl ether (DME) were considered to be reactants and the rest of compounds detected in the GC as products of reaction. Measured response factors were used for MeOH and DME, whereas the response was considered proportional to the number of carbon atoms in the molecule for the hydrocarbon products.

Synthesis of heptamethoniumdibromide (C7 diquat templating agent)

The SDA was prepared by refluxing 15 g dibromoheptane (DBHep) in 75 ml ethanol with 27.71 g 33 wt-% trimethylamine (TMA, 31-35 % solution in ethanol, Aldrich), giving a relative molar ratio of 2.5 : 1 of TMA/DBHep. The solution was let under reflux overnight, and then cooled in ice to start the crystallization. to the white precipitate was then filtered, washed several times with cold acetone and dried at 70 °C prior to use. The purity was checked by H-NMR.



S1. H-NMR spectrum of the synthesized C7 diquaternary templating agent.

Synthesis and basic characterization of ZSM-23 using the C7 diquaternary templating agent (heptamethoniumdibromide)

-In a Teflon liner 1.60 g of NaOH 50% w/w are mixed with 0.74g of $Al(NO_3)_3 \cdot 18H_2O$ and 30 g of water under stirring until complete dissolution.

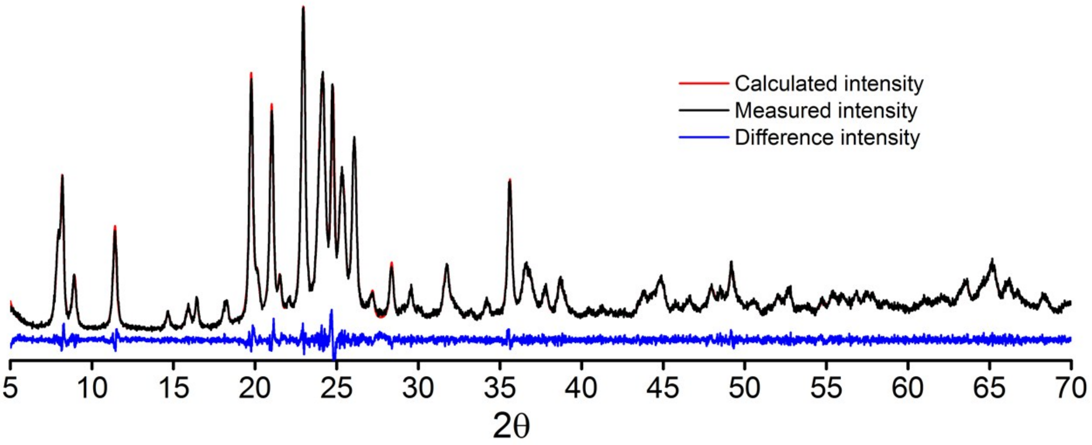
-3.24 g of the C7 diquaternary templating agent were added to the solution under stirring.

-3.45 g of fumed silica (Aldrich) was added under stirring until the formation of a dense gel.

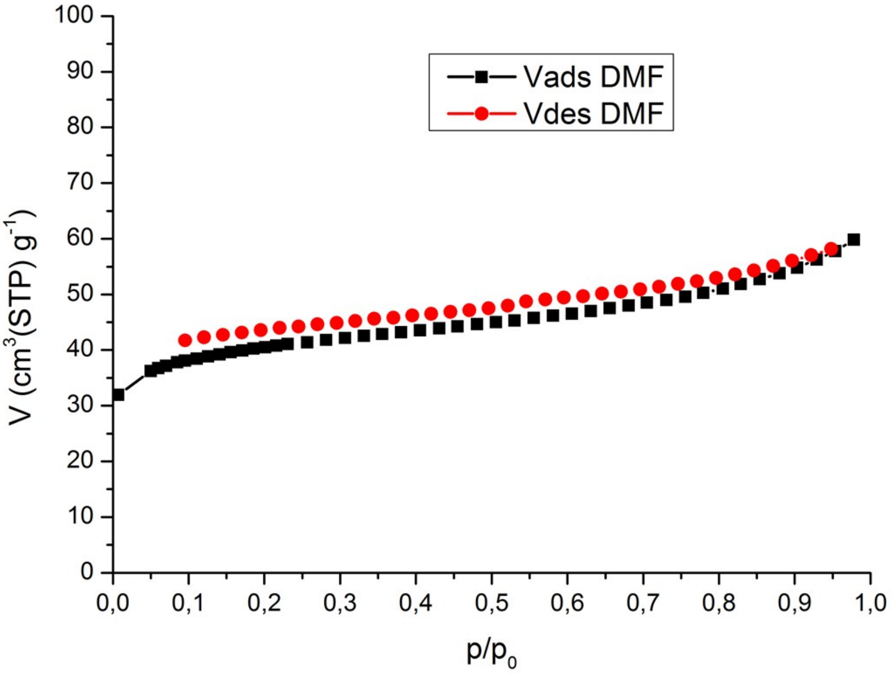
-The remaining 10 g of water were added to the gel.

The gel mixture was the let under magnetic stirring for 3h and then the Teflon liner was put in a stainless steel autoclave. The synthesis was performed in a tumbling oven (rotation speed 30 rpm) preheated at the temperature of 160°C. After 14 days the autoclave was quenched in cold water and the product was collected by filtration and washed several times with distilled water.

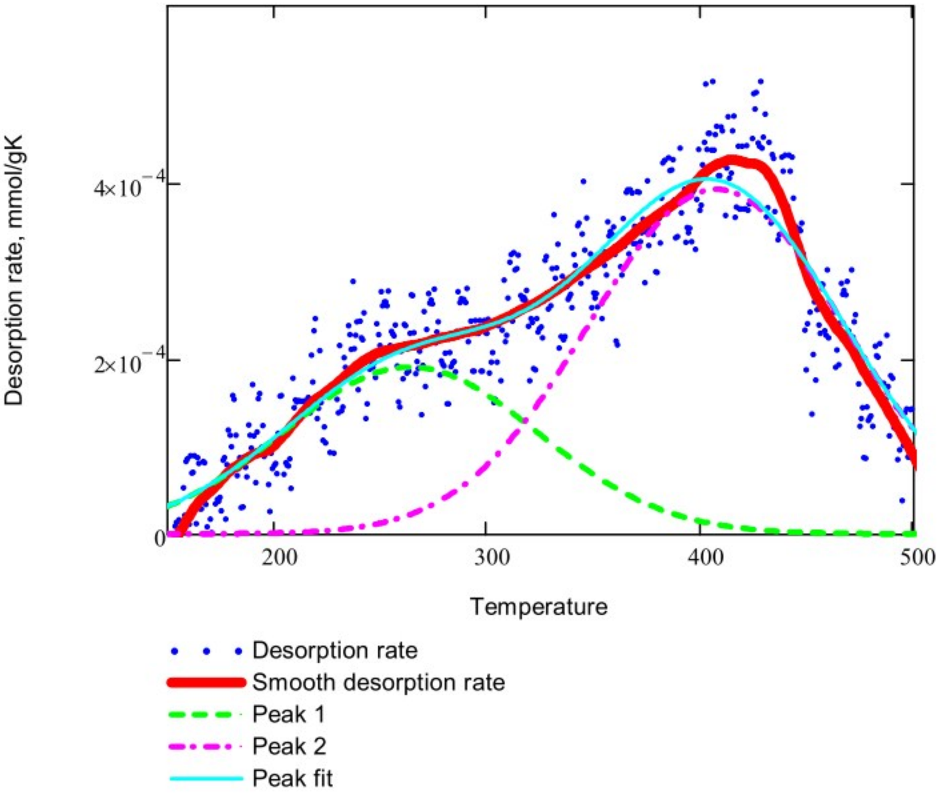
The powder was then dried overnight at 80°C and calcined in a muffle with at ramp of 6h from RT to 550°C and then for 8h while keeping the temperature constant to remove all the organic compounds trapped into the pores. The sample was then ion exchanged 3 times with a solution of NH_4NO_3 1M at 80C for 3-5 hr. The sample in the ammonium form was then calcined again with the same condition as before.



S2. Powder XRD of the H-ZSM-23 diquaternary.



S3 N_2 isotherm of adsorption (red circles) and desorption (black squares) of the H-ZSM-23 C7 diquaternary.



S4. NH_3-TPD of the H-ZSM-23 C7 diquaternary.

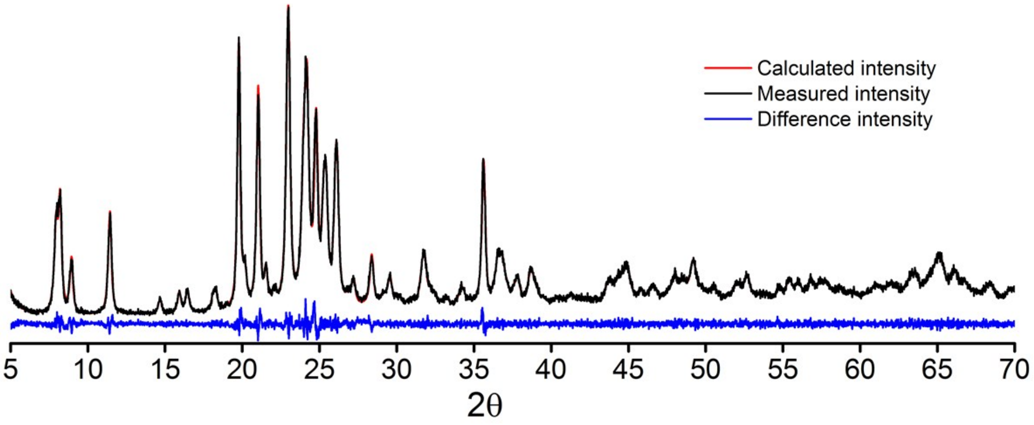
Synthesis and basic characterization of ZSM-23 using the mixed templating agent HTMP/TMPD (HTMP40/60TMPD molar ratio)

-In a Teflon liner 0.125 ml of NaOH 50% w/w are mixed with 0.13g of $NaAlO_2$ and 15 g of water under stirring until complete dissolution.

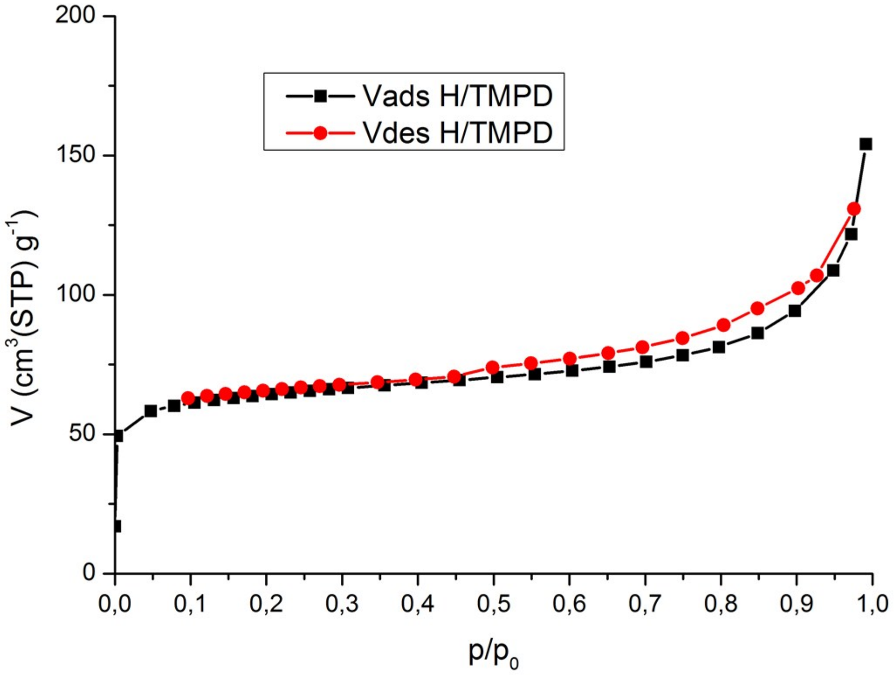
-3.80 ml of TMPD and 2.14 ml of HMPD were added to the solution under stirring.

-8.82 g of 40% colloidal silica in water (Ludox AS-40, Aldrich).

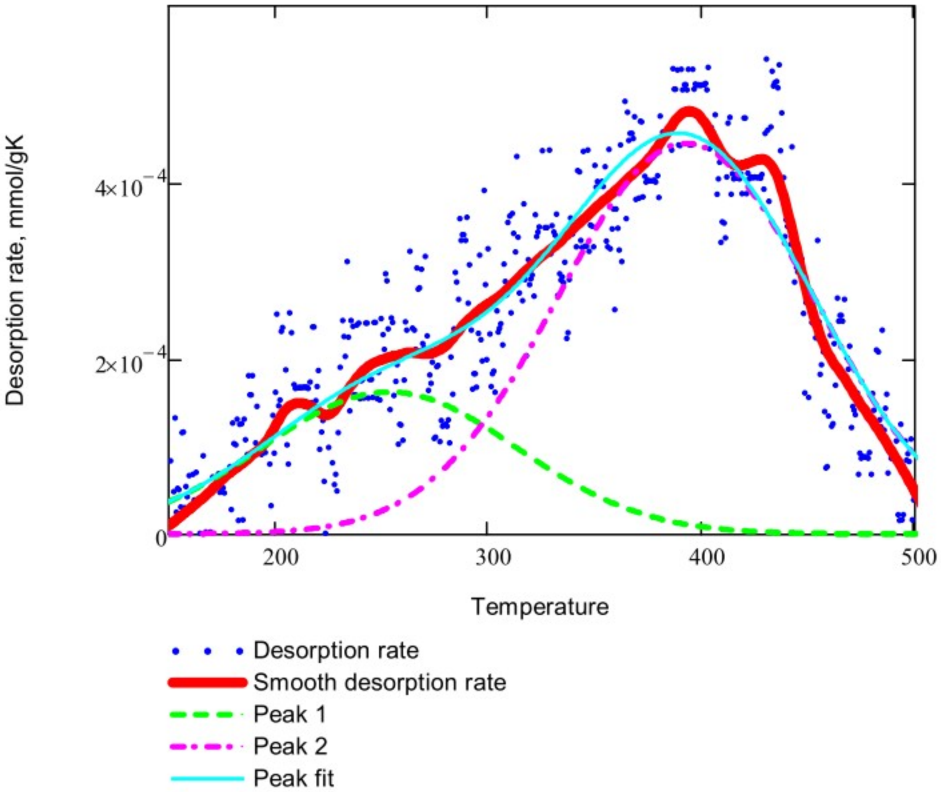
The gel mixture was the let under magnetic stirring for 4h and then the Teflon liner was put in a stainless steel autoclave. The synthesis was performed with the same conditions as before but for 6 days.



S5. Powder XRD of the H-ZSM-23 H/TMPD mixed.



S6. N_2 isotherm of adsorption (red circles) and desorption (black squares) of the H-ZSM-23 H/TMPD mixed.



S7. NH_3-TPD of the H-ZSM-23 H/TMPD mixed.

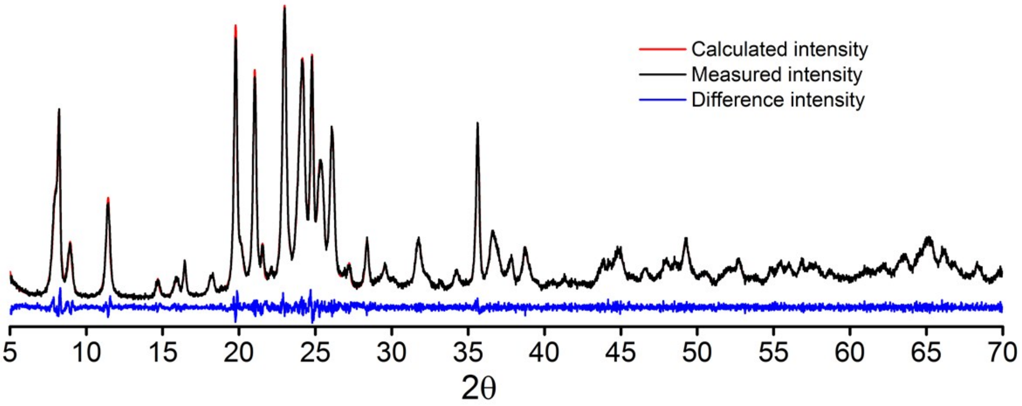
Synthesis and basic characterization of ZSM-23 using isopropylamine (iPA)

-In a Teflon liner 0.093 g of NaOH (Aldrich, pellet) and 0.064 g of $NaAlO_2$ were dissolved in 16 g of water.

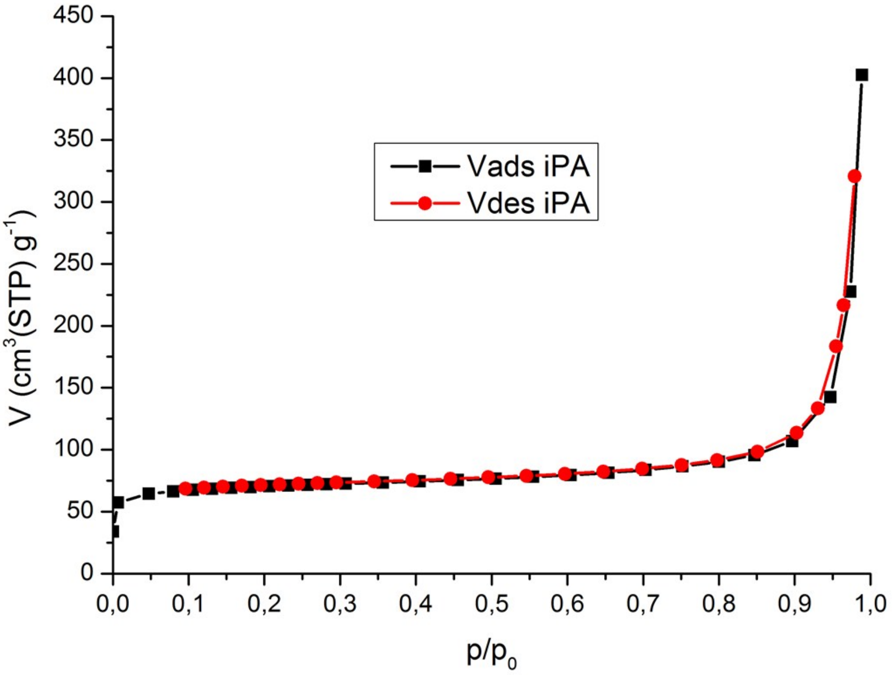
-2g of fumed silica were added under stirring until a dense gel is formed.

-5.6 ml of isopropylamine were added to the solution that become less viscous.

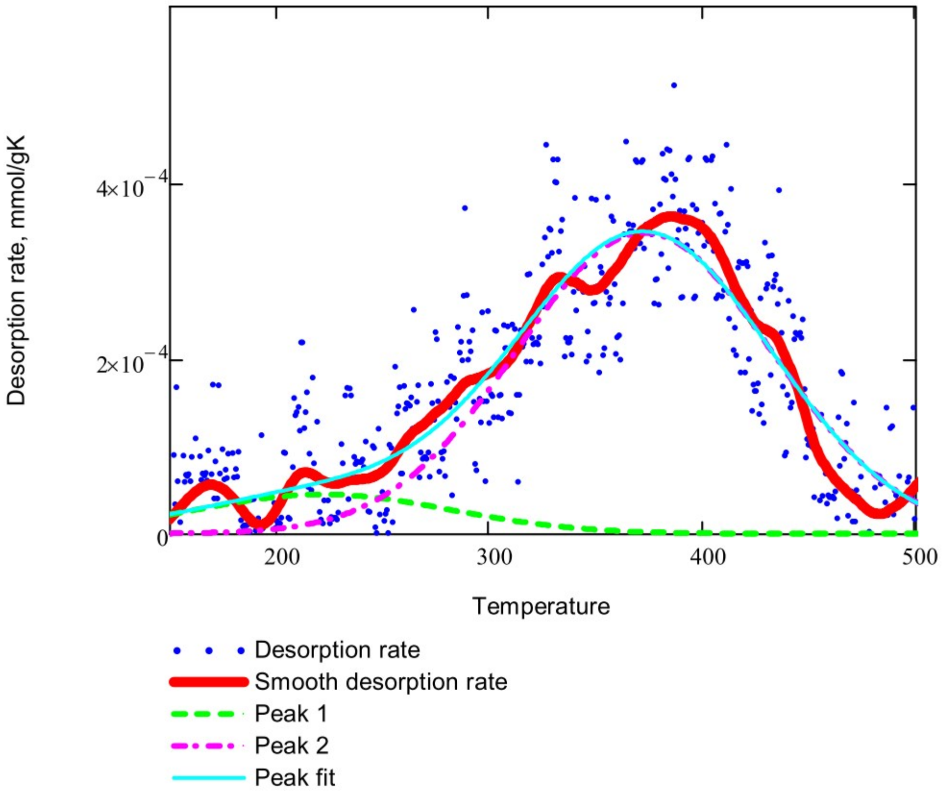
The gel mixture was the let under magnetic stirring for 3h and then the Teflon liner was put in a stainless steel autoclave. The synthesis was performed with the same conditions as before but for 4 days.



S8. Powder XRD of the H-ZSM-23 isopropylamine.



S9. N_2 isotherm of adsorption (red circles) and desorption (black squares) of the H-ZSM-23 isopropylamine.



S10. NH_3-TPD of the H-ZSM-23 isopropylamine.

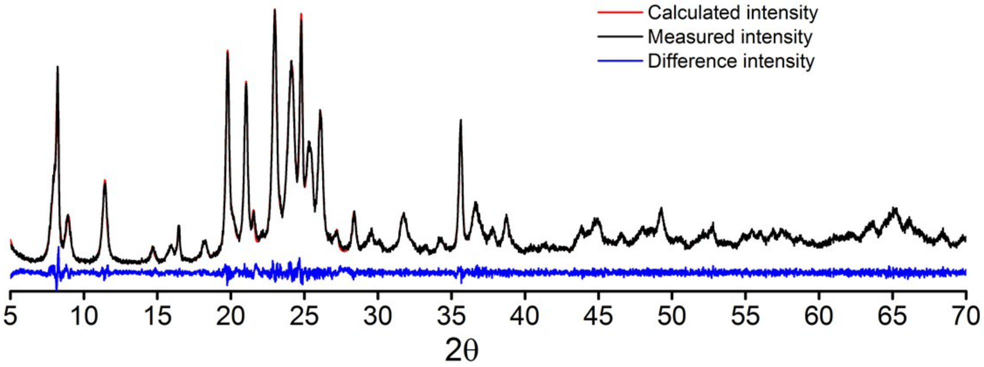
Synthesis and basic characterization of ZSM-23 using pyrrolidine (Pyrr)

-In a Teflon liner 0.036 g of NaOH (Aldrich, pellet) and were dissolved in 14 g of water.

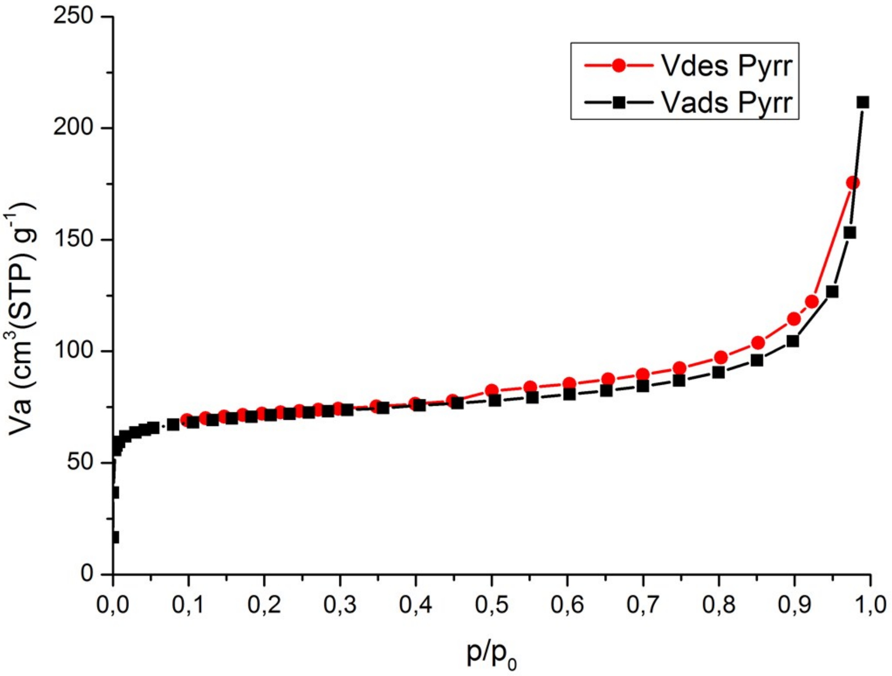
-A solution of 0.28 g of $Al(NO_3)_3 \cdot 18H_2O$ in 4g of water was added to the silica suspension.

-0.8 ml of pyrrolidine was added to the gel, followed by 0.19 ml of sulfuric acid (98%) to adjust the pH and also has the effect to reduce the viscosity of the gel.

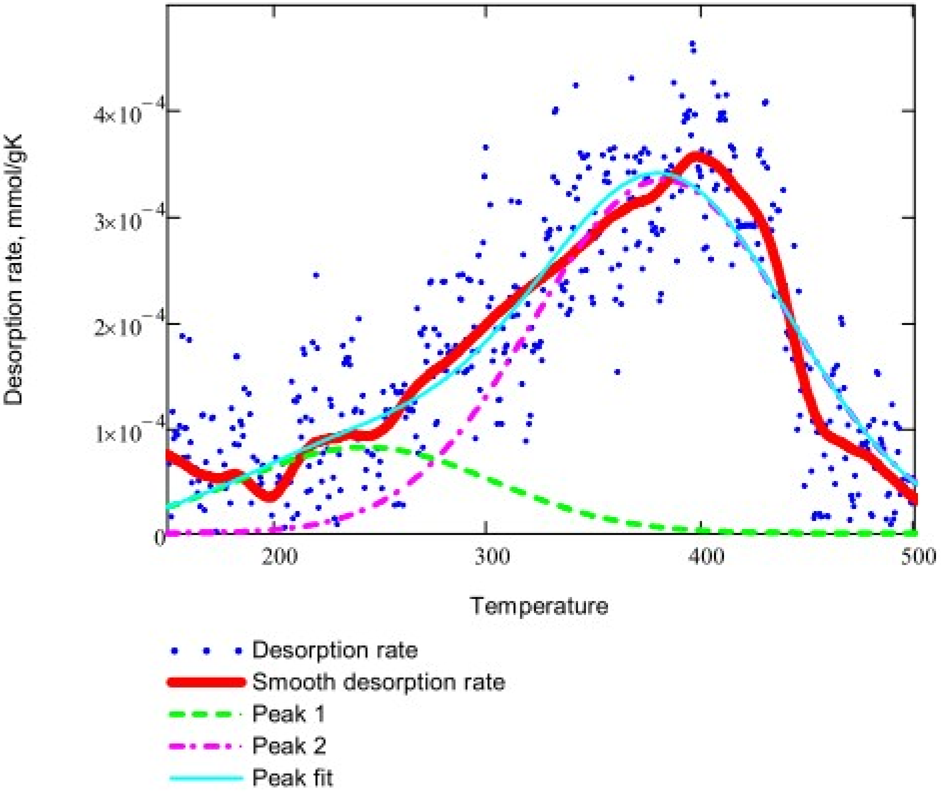
The gel mixture was the let under magnetic stirring for 3h and then the Teflon liner was put in a stainless steel autoclave. The synthesis was performed with the same conditions as before but for 3 days at 180°C.



S11. Powder XRD of the H-ZSM-23 pyrrolidine.



S12. N_2 isotherm of adsorption (red circles) and desorption (black squares) of the H-ZSM-23 pyrrolidine.



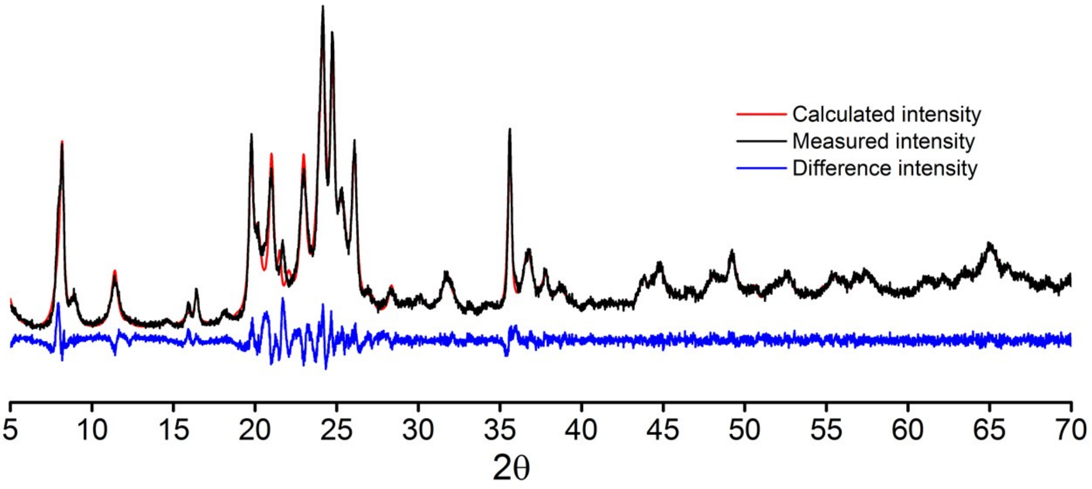
S13. NH_3-TPD of the H-ZSM-23 pyrrolidine.

Synthesis and basic characterization of ZSM-23 using N,N-Dimethylformamide (DMF)

- 0.8 g of $Al_2(SO_4)_3 \cdot 18H_2O$ and 4g of DMF were dissolved in 3.6 g of water under stirring for 6h

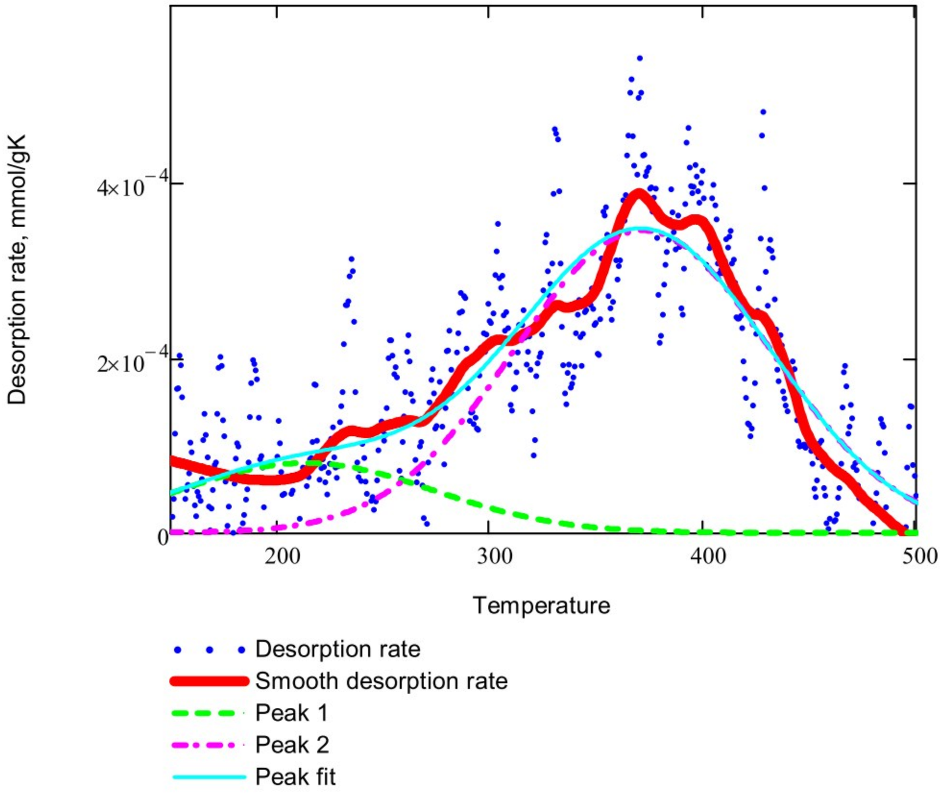
-The solution was added to the mixture of 2.4 g of NaOH, 37g of H_2O and 16.3 g of 30% colloidal silica in water (Ludox AM-30, Aldrich)

The mixture was split into two Teflon liners and stirred overnight and then the Teflon liners were put in a stainless steel autoclave. The synthesis was performed with the same conditions as before but for 4 days at the temperature of 185°C.



S14. Powder XRD of the H-ZSM-23 DMF.

S15. N_2 isotherm of adsorption (red circles) and desorption (black squares) of the H-ZSM-23 DMF.



S16. NH_3-TPD of the H-ZSM-23 DMF.