Supporting information for:

Influence of organic structure directing agent isomer distribution on the synthesis of SSZ-39

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CONTENT

Figure S1. Reported SDAs in literature for SSZ-39[2]

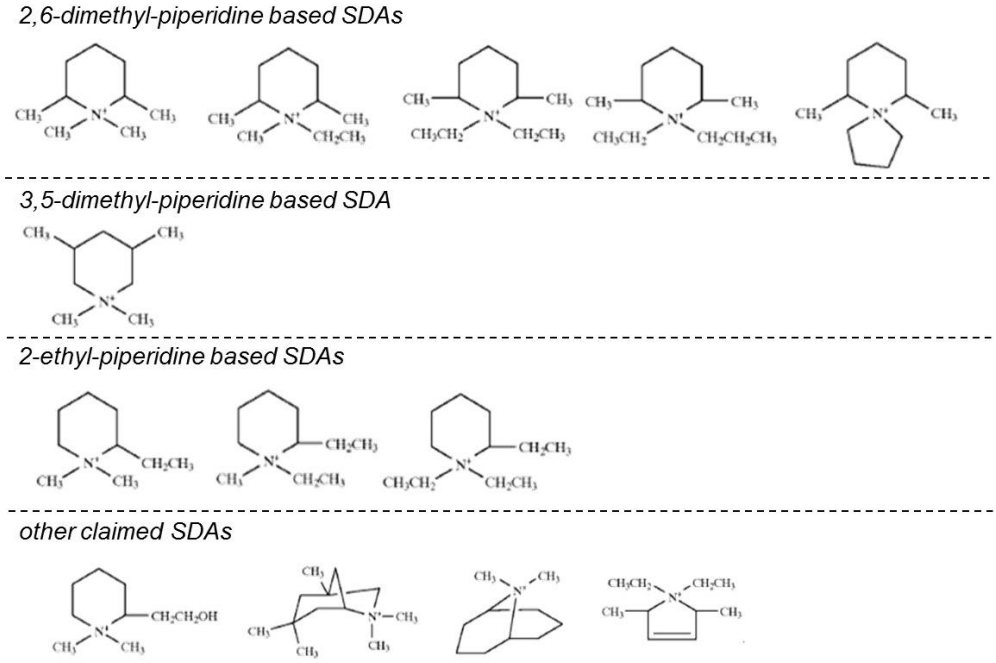
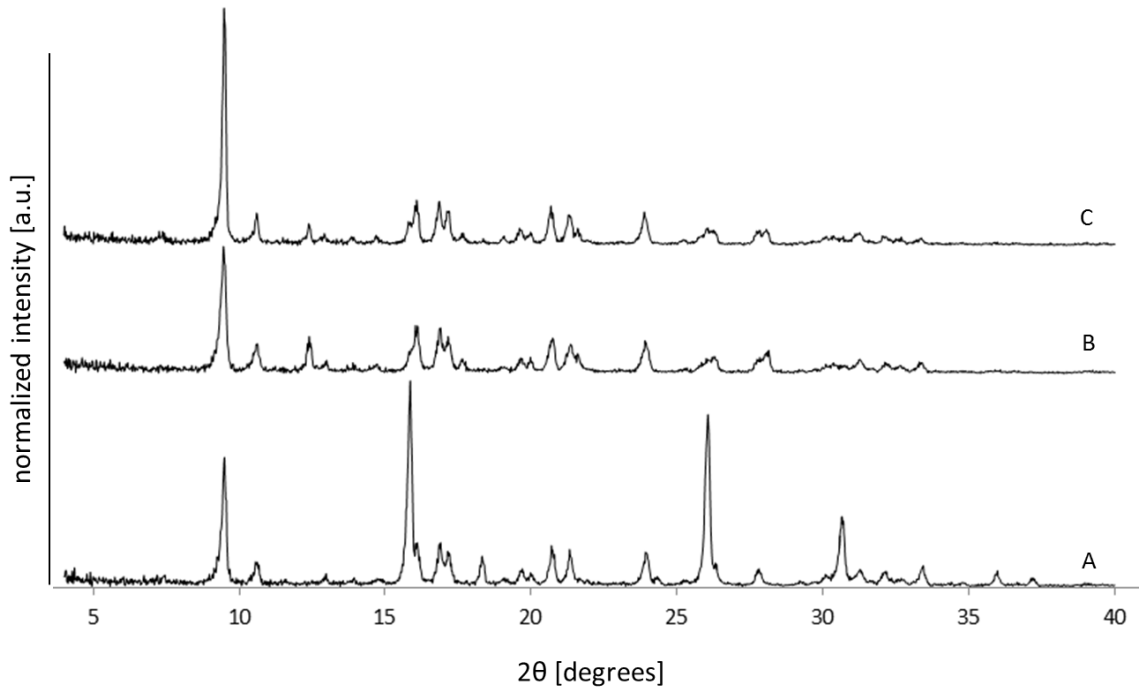


Table S1: Screening approach to an SSZ-39 recipe assessed with the N,N-dimethyl-*cis*-3,5-lupetidine SDA

Si source	Al source	Si/Al	time	T	Outcome
LUDOX	NH_4-Y (FAU)	30	18d	140(160)	MFI/MTW + SSZ36
LUDOX	NH_4-Y	15	12d	140 (160)	RTH/ITE = SSZ-36
Cabosil	Reheiss	15	12 d	140 °C	/
Sodium Silicate	NH_4-Y (FAU)	15	12d	140 °C	**AEI = SSZ-39** (FAU)
LUDOX	Na-aluminate	15	12 d	140 °C	/
Cabosil	Reheiss	15	12 d	160 °C	/
Cabosil	Reheiss	30	12 d	160 °C	/
LUDOX	Na-aluminate	15	12 d	160 °C	/
LUDOX	Na-aluminate	30	12 d	160 °C	/ + MFI
Cabosil	LZY-52	20	6d - 9d	160 °C	/ + FAU
Cabosil	NH_4-CBV712	35	6d - 9d	175 °C	MFI/TW
Cabosil	Reheiss	50	5d - 8d	175 °C	MFI/MEL
TOSOH-390 HUA		150	6d only	160 °C	MFI (silicalite)

/ = Amorphous. In-house NH_4-FAU has Si/Al 2.6. Syntheses similar to Wagner, P.; Nakagawa, Y.; Lee, G. S.; Davis, M. E.; Elomari, S.; Medrud, R. C.; Zones, S. I. J. Am. Chem. Soc. 1999, 122, 263

Fig. S2: SSZ-39 synthesis with different silica sources and FAU as alumina source

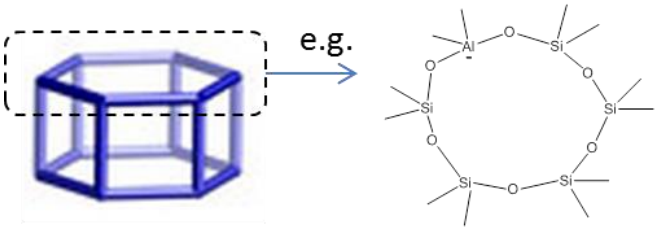


A) colloidal silica Ludox AS-40, B) tetraethylorthosilicate (TEOS) and C) sodium silicate.

Used SDA: N,N-dimethyl-*cis*-3,5-lupetidine SDA. Rotating oven at 140 °C, 6-7 days.
Gel composition of A) *Si:0.067Al:0.17SDA:0.71OH*$^-$*:0.54Na:20*H_2O. B) *Si:0.067Al:0.14SDA:0.65OH*$^-$*:0.51Na:28*H_2O. C) *Si:0.067Al:0.14SDA:0.65OH*$^-$*:0.51Na:28*H_2O. 6

The large impurity at 2.theta 16 and 26 values in pattern A is indicative of major analcime (ANA topology, dense phase) side-product formation.

Fig. S3 double six ring composite zeolite building unit (d6r)[1]



Each corner of the blue structure on the left represents a T-atom. The oxygen atoms are omitted for clarity on the left, but can be seen on the right. Both FAU and AEI can be built up by only translating and linking this composite d6r building blocks. Other molecular sieves that can be exclusively built with d6r are found within e.g. CHA, KFI, AFX and GME topologies.

Fig S4. PXRD analysis of SSZ-39 made in conditions of Table I. entries 3, 4 and 5 and II.6.

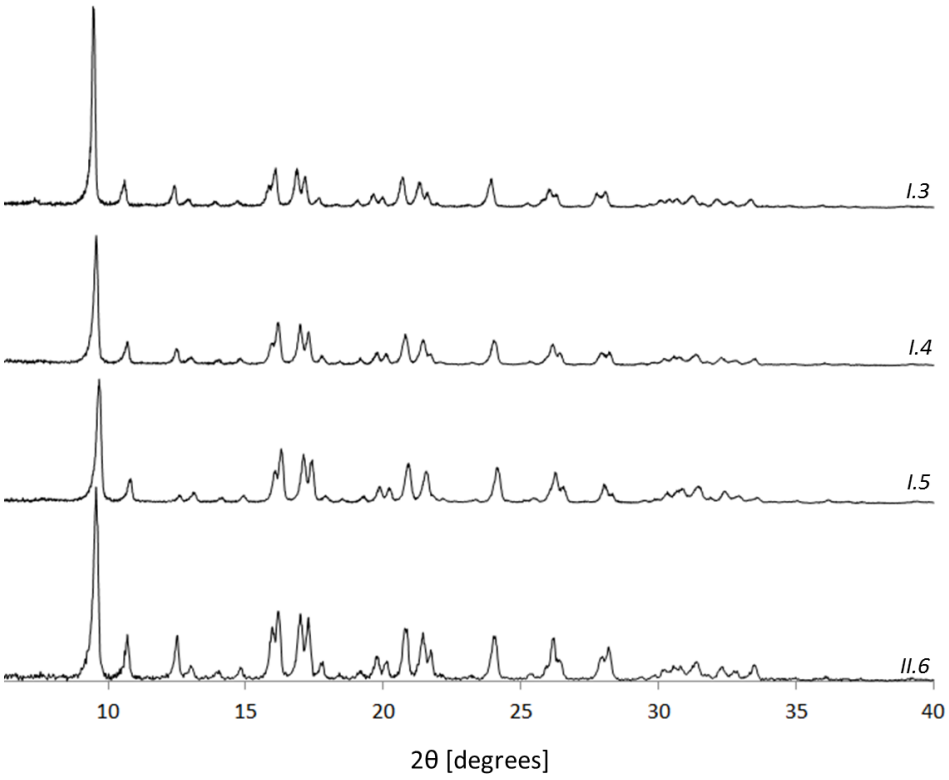
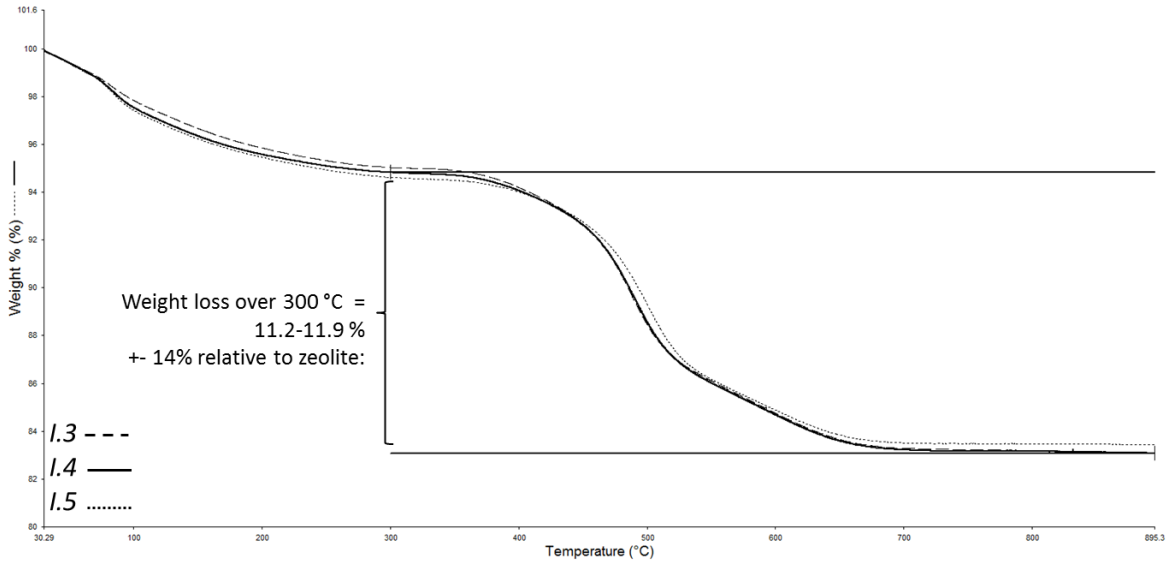


Fig S5. TGA analysis of SSZ-39 made in conditions of Table I entry 3, 4 and 5.



The weight loss of the organic (300°C - 900°C) with respect to the input 'wet' zeolite is about 11-12%. Normalized on the amount of dry, pure solid recovered at 900 °C (83.5 % of the input weight), the amount of included OSDA per zeolite is about 14%.

Fig S6. SEM analysis of SSZ-39s made in identical conditions as those in Table 1 entries 3, 4 and 5. (repeat experiments, yielding same products, same PXRD.)

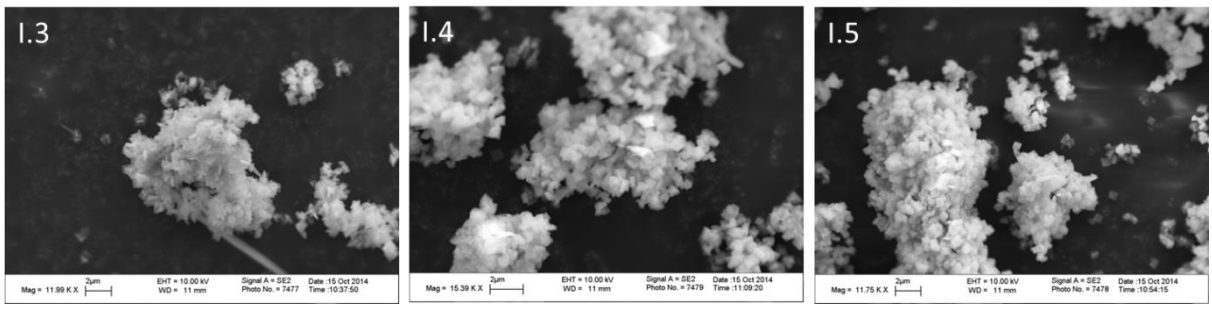
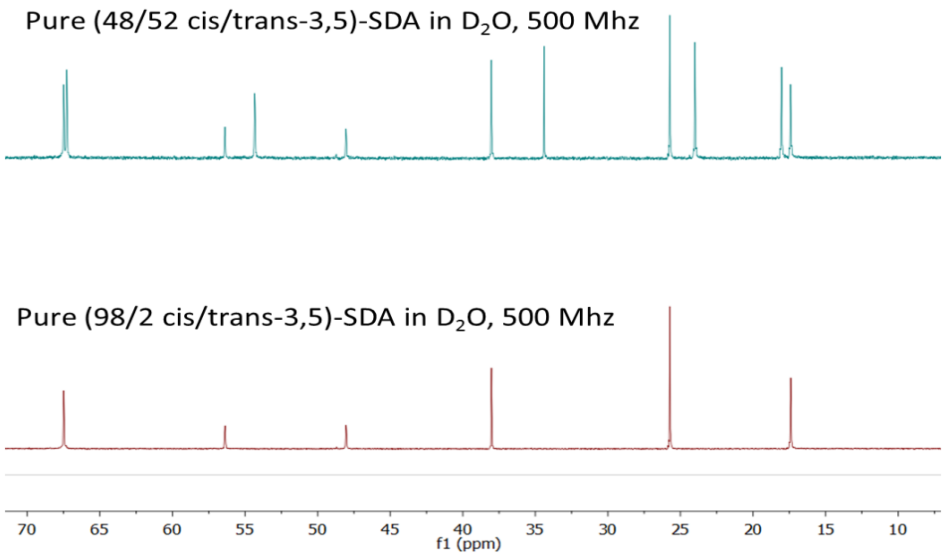


Fig S7. ^{13}C NMR (liquid phase) analysis of pure *cis* and 48/52 *cis*/trans-3,5-lupetidine based SDAs



Assignments, see Main manuscript, Figure 3.

Fig S8. ^{1}H-^{13}C-HSQC liquid phase NMR analysis of pure *cis*-2,6-lupetidine based SDA

The 3,5-isomers were also assessed likewise (not shown).

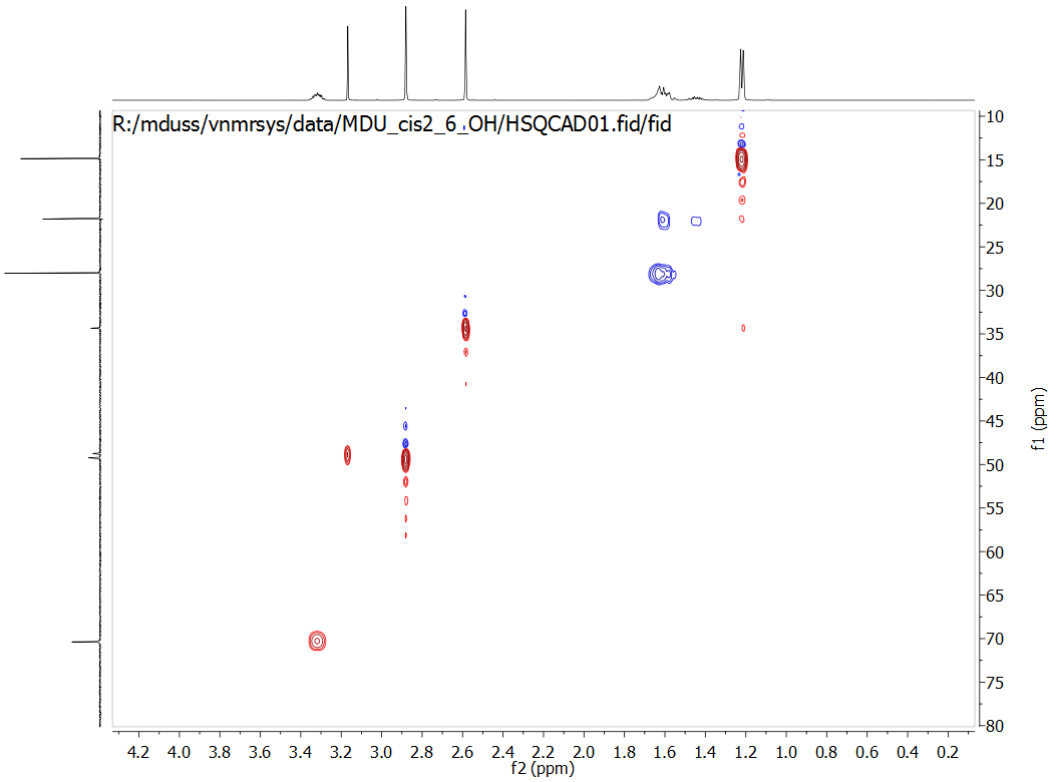


Fig S9. Additional PXRD pattern of as synthesized SSZ-39 made from table II. Made with different grades of *cis*-3,5/*cis*-2,6. The numbers correspond to Table II entries. II.9) 0/100 ratio; II.10) 50/50; II.11) 100/0.

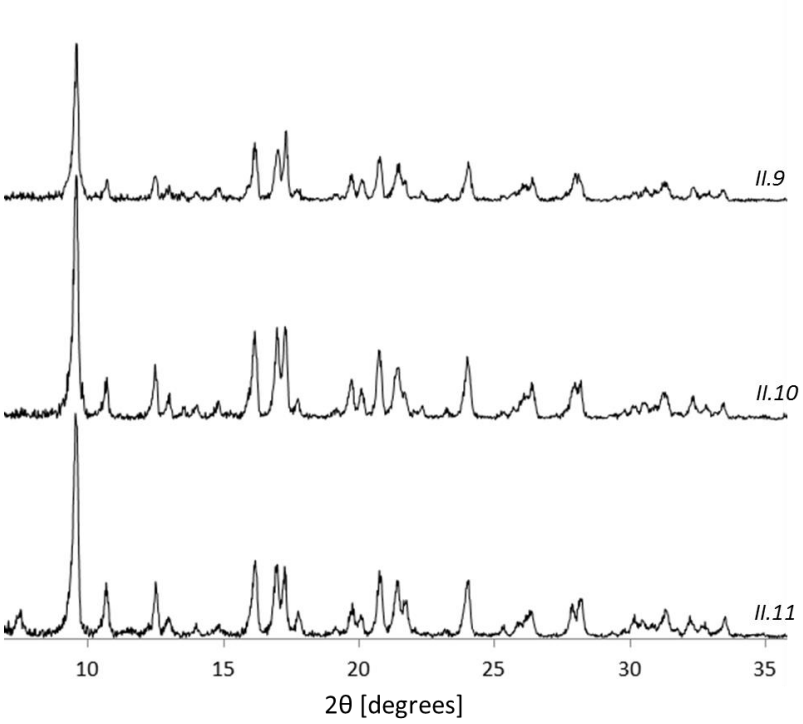


Fig S10 Additional PXRD analysis of synthesis in Table II. Entries 13 (*cis*-2,6); 14 (51/49 *cis*-3,5/*cis*-2,6); 12 (*cis*-3,5); 15 (24/26/50 *cis*-3,5/trans-3,5/*cis*-2,6).

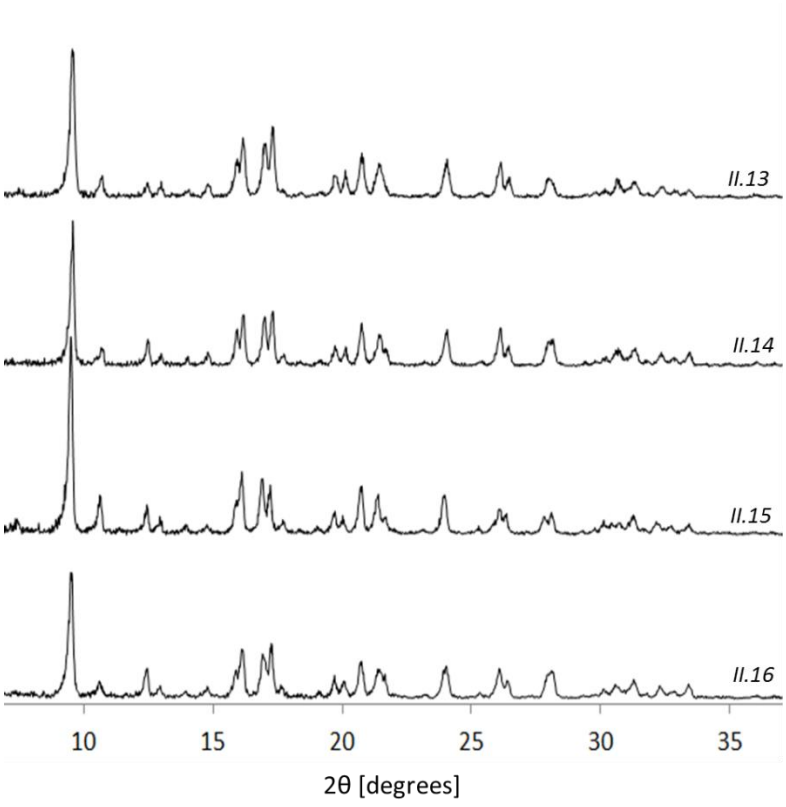


Fig S11. Additional SEM images of zeolites from synthesis in Table II, Entries 13 and 14.

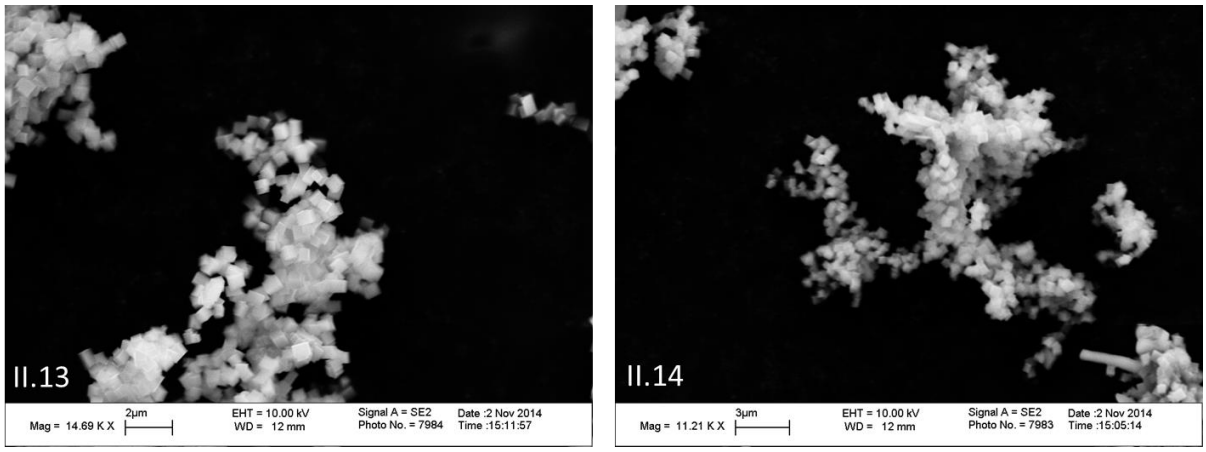
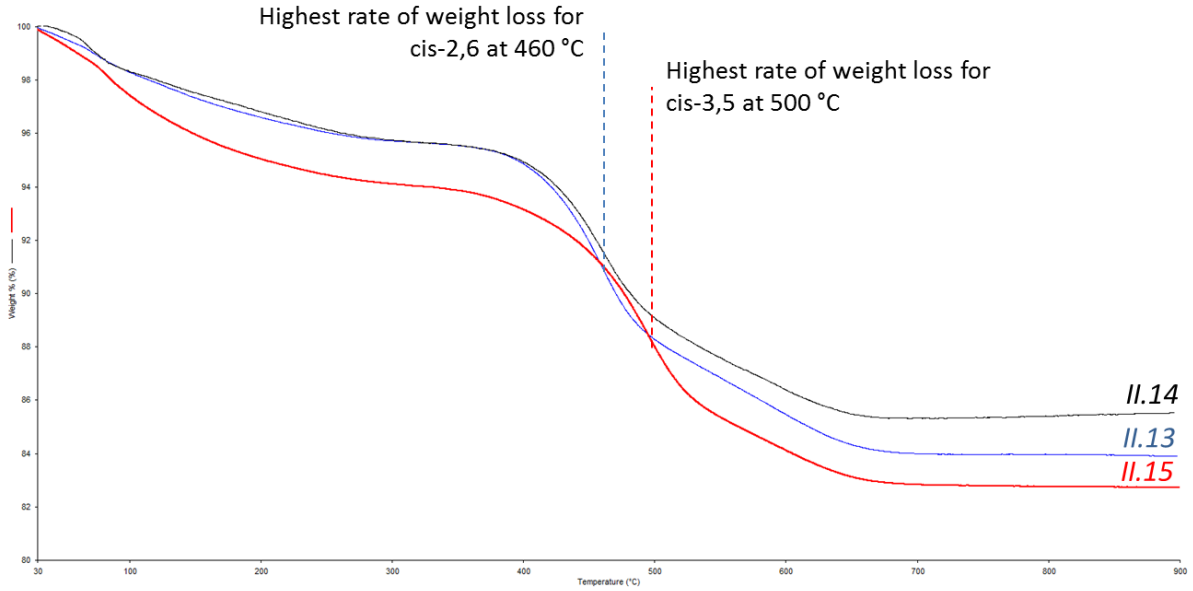
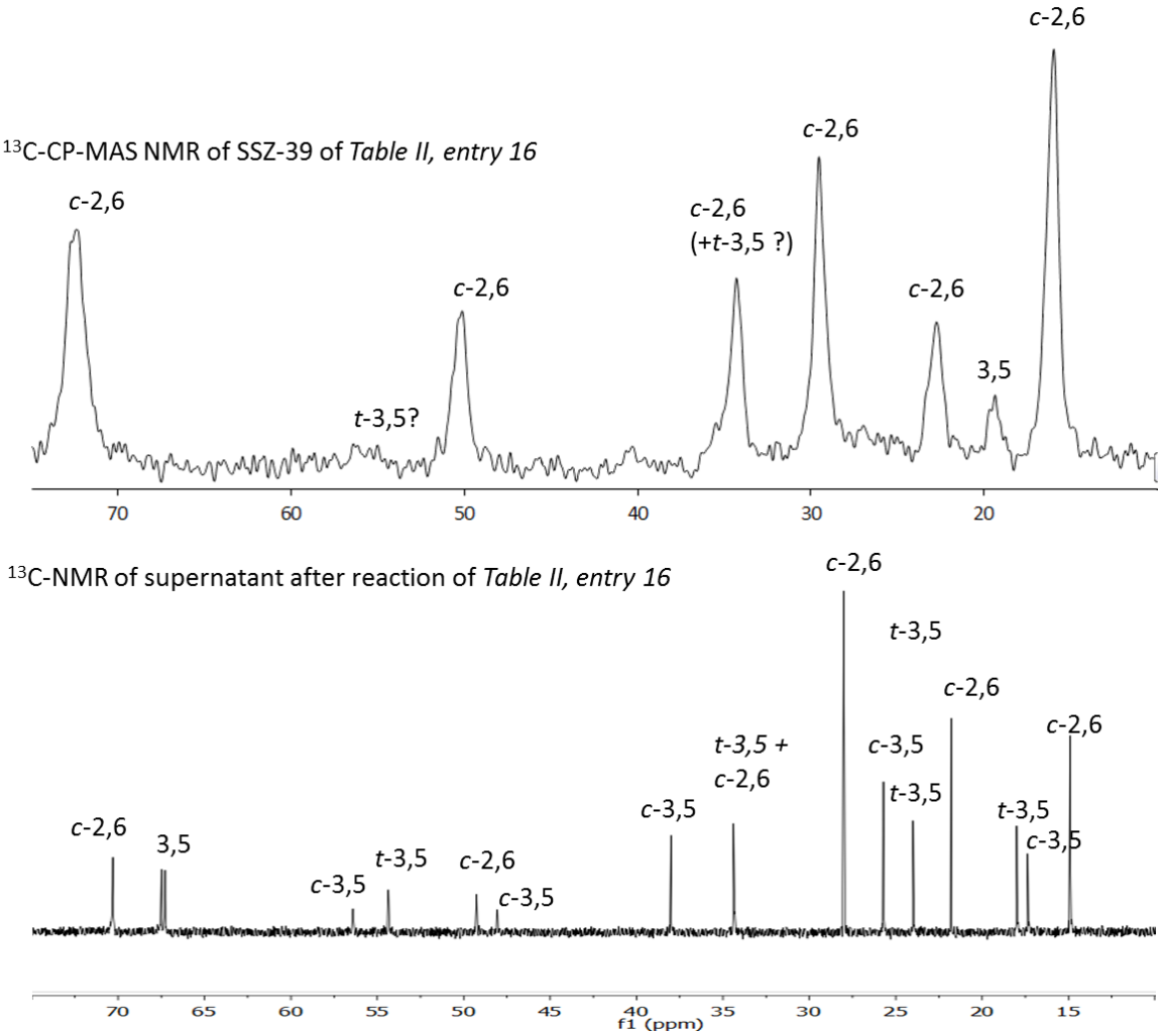


Fig S12. Additional TGA analysis of synthesis in Table II. Entries 13, 14 and 15.



Note how the weight loss of the zeolite made with the 50/50 *cis*/*cis* gel (II.14) displays a similar weight loss profile as the zeolite made with pure *cis*-2,6 (II.13), with maximum weight loss at 460 °C. The *cis*-3,5 isomer leads to a profile with maximum weight loss at 500 °C (II.15). TGA thus corroborates the MAS NMR data that showed that zeolites made in 50/50 mixtures preferentially incorporate *cis*-2,6. The end point of the TGA analysis is dependent on the total organic and moisture weight loss.

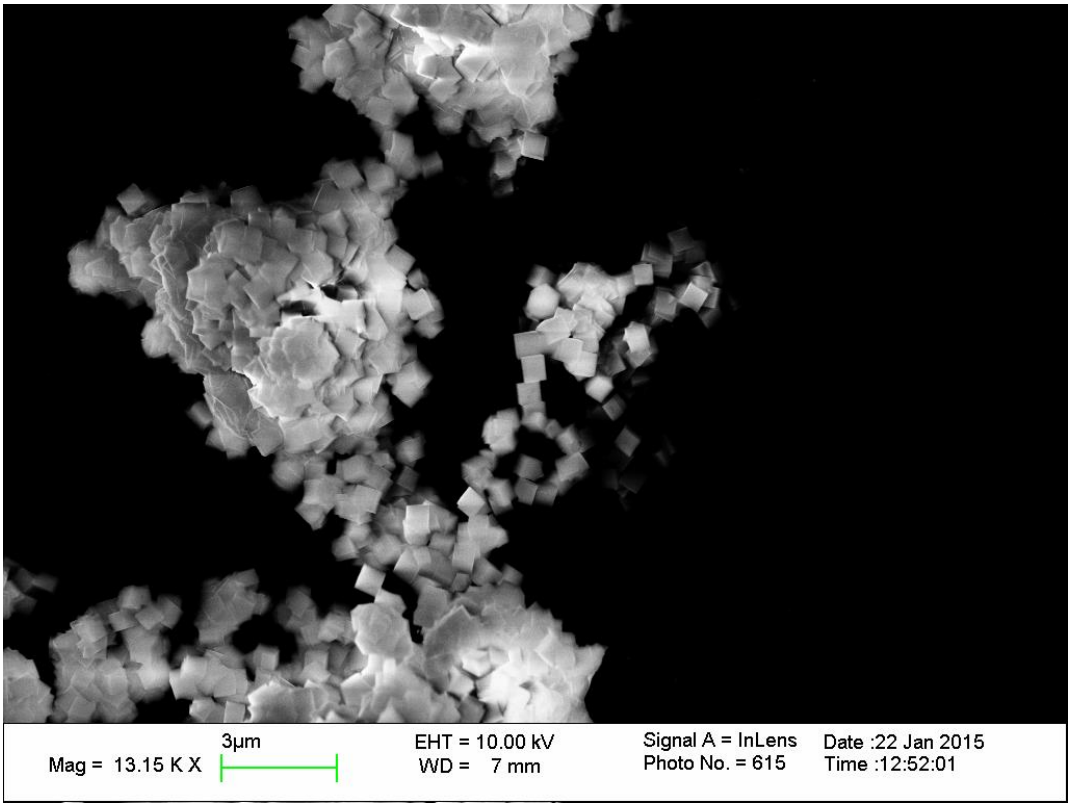
Fig S13. Supernatant liquid phase NMR and zeolite MAS NMR study for the synthesis of Table II.16



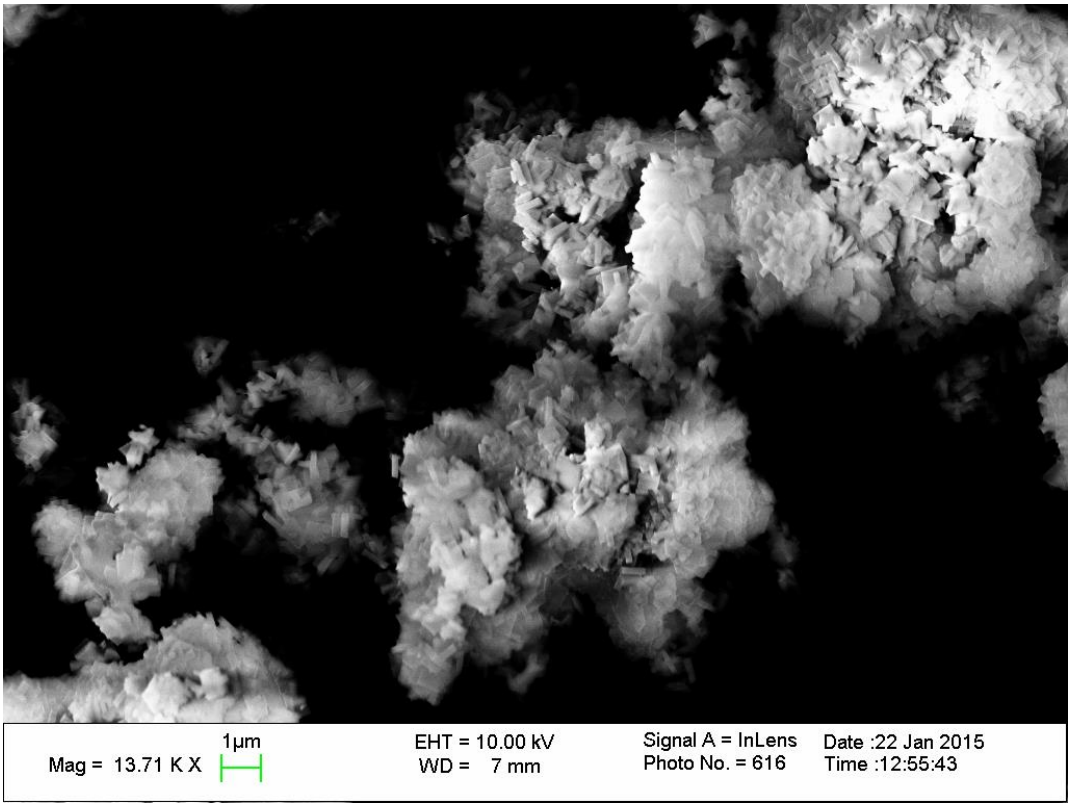
Reaction carried out as seen in main manuscript Table II, entry 16. This reaction started with a 24/26/50 *cis*-3,5/trans-3,5/*cis*-2,6 ratio. After reaction, the ^{1}H-NMR of the supernatant pointed to a distribution of 28.3/28.3/43.3. Based on the total amount of OSDA taken up in the SSZ-39 as analyzed by TGA (14.1%), the stereospecific uptake in the zeolite could be calculated and pointed to an 3.9/15.8/80.8 distribution. The CP-MAS NMR spectra in Fig S8 confirms that the *cis*-2,6 is again taken up in excess. Some signals belonging to the 3,5 isomer could be picked up. Interestingly, the zeolite should have taken up more *trans*- than *cis*-3,5 according to the calculation. In the non-quantitative CP MAS NMR this is hard to verify. Therefore, the SSZ-39 was dissolved in 50 wt% HF according to the procedure outlined in the main manuscript. After drying, the organic content was extracted in $CDCl_3$ and analyzed by ^{1}H-NMR. The analysis rendered a 12/24/64 distribution, indeed confirming the preferential incorporation of the 2,6 over the 3,5-isomer and that the *trans*- over the *cis*-3,5 isomer and in the same order as in the calculated distribution based on supernatant and TGA.

Fig S14 Additional SEM images of SSZ-39s in main manuscript Fig 6.:

II.2



II.3



I.5 HCl washed

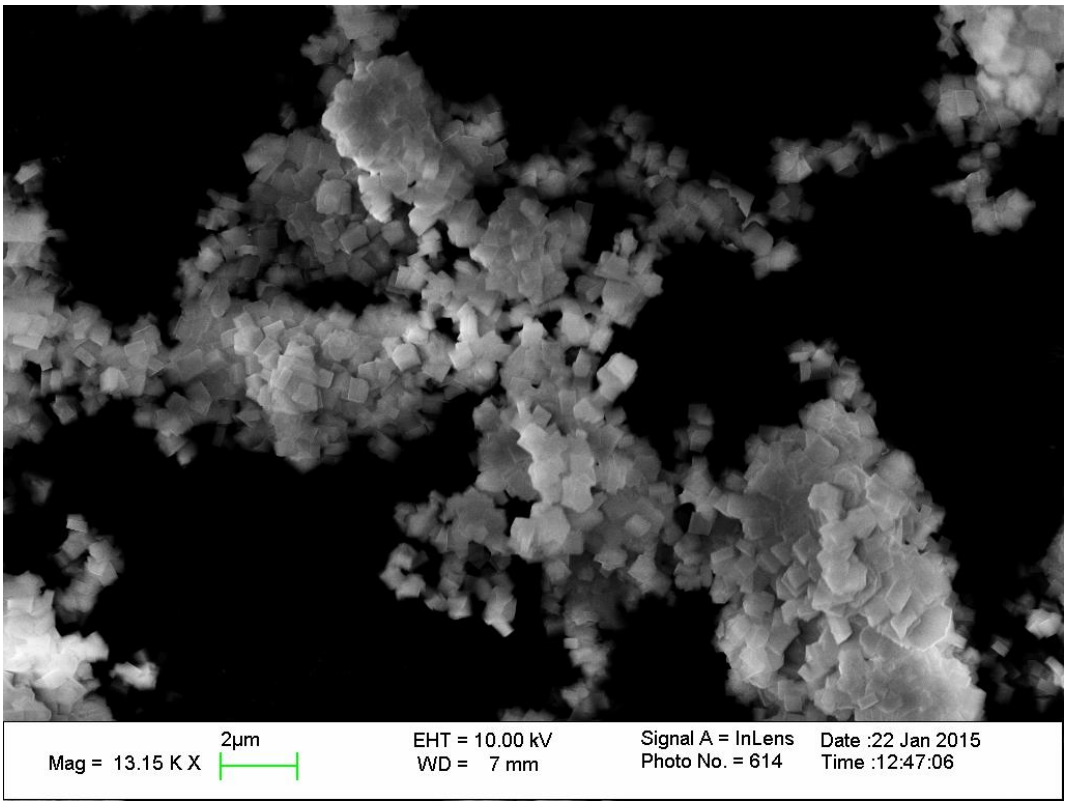
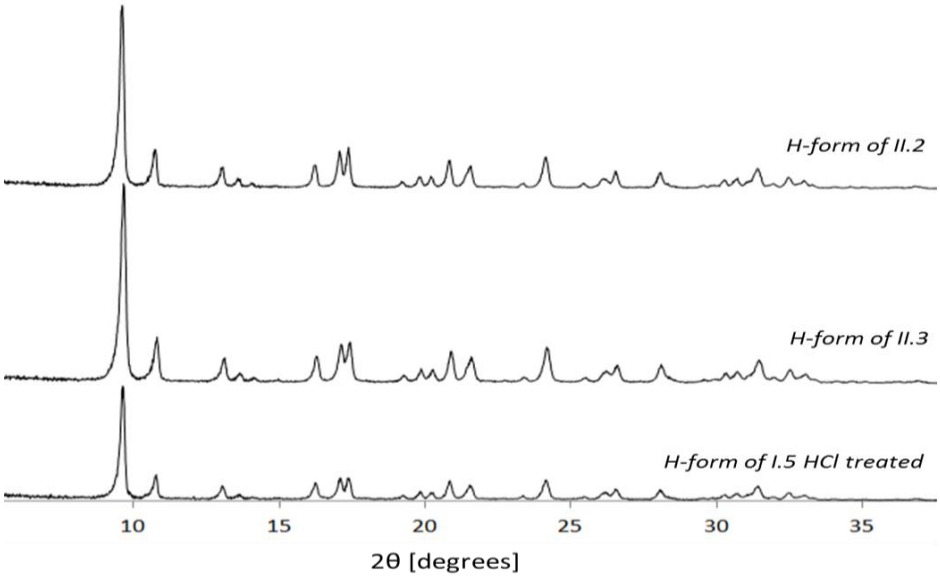


Fig S15 PXRD analysis of H^+-SSZ-39s of Fig. 6 (Table II.2 and 3 and Tabel I.5 HCl treated)

These SSZ-39s are the ones on which the pore volume physisorption experiments have been run. They have been calcined, exchanged trifold with 1M NH4NO3 solutions (1g/100mL, 2h at 90 °C) and calcined again.



These PXRD profiles contain all the reflections matching calcined SSZ-39 as reported by Moliner[3] and Zones et al.[2a]

Annex: Synthesis procedures and analysis of the OSDAs as provided by SACHEM Inc.

Preparation of *cis*-1,2,6-Trimethylpiperidine (fw=127.23).

2516 g Reagent-grade, 37% aqueous formaldehyde (31.00 mole, fw=30.03, ~2308 mL, formalin - with some methanol as stabilizer, d=1.09) is added to a 12 L, 4-neck, round-bottom flask that is equipped with a heating mantle, mechanical stirrer, 2 L addition funnel with a pressure-equalizing side-arm, reflux condenser and teflon-coated thermocouple. The liquid in the cooling coils of the condenser is maintained at about 1°C. An oil-bubbler is placed on the exit of the condenser in order to observe the rate of gas evolution. The reaction is carried out under a nitrogen atmosphere with a *slow* N_2 purge. Using the 2 L addition funnel, 2604 g purified *cis*-2,6-dimethylpiperidine (23.0 mole, fw=113.20, ~3119 mL, d=0.835) is carefully added in two batches (~1800 mL/~1319 mL) to the reaction mixture over a period of about 3 hours. An obvious exotherm is observed, and the rate of addition is adjusted so that the reaction temperature is maintained in the range 45-50°C. If needed, external cooling can be used. Then, 2542 g reagent-grade 96% formic acid (53.00 mole, fw=46.03, ~2083 mL, d=1.22) is placed in a clean 2 L addition funnel in two portions (~1800mL/~283 mL). The addition of formic acid to the reaction mixture is a strongly exothermic reaction with vigorous gas evolution (CO_2). The addition rate of formic acid is carefully controlled in order to maintain the temperature of the stirring mixture at 65-75°C. Under these conditions, addition time of formic acid is about 3-4 hours. When CO_2 evolution is evident, the N_2 purging is stopped. The end of the reaction is easily observed after 2.0-2.1 equivalents (~1772 mL) of formic acid is added; the reaction temperature rapidly drops, and the rate of CO_2 evolution rapidly decreases. The entire amount of formic acid is added while the reaction temperature is maintained at about 80°C using external heating. The reaction mixture is stirred at this temperature for about 6-12 hours in order to insure complete reaction, and then the reaction mixture is allowed to cool to ambient temperature.

With stirring, KOH pellets or flakes (~1750 g, fw=56.11) are added portionwise to the stirring mixture until the pH is about 13. When the neutralization is complete, the mixture is allowed to stand for two hours at room temperature without stirring in order to allow for phase separation. The upper product layer is decanted off and divided into two equal portions. The lower layer is discarded. To each portion in a 6 L separatory funnel is added 3.5 L n-pentane. After standing at room temperature for about 2 hours, more lower layer forms; it is also discarded. The other portion of the upper product layer is likewise processed, and the two upper pentane layers are combined. To this product-containing pentane layer is added a good excess of anhydrous $MgSO_4$. The mixture is vigorously stirred for about 2 hours. This mixture is filtered through fine-porosity, sintered glass. In a portionwise manner, the clear solution is placed in a rotary evaporator while most of the n-pentane solvent is removed. This process is carried out in three stages: (1) a bath temperature at 35°C at a working pressure of 455 torr; (2) a bath temperature at 40°C at a working pressure of 380 torr; a bath temperature at 45°C at a working pressure of 305 torr. The product fractions are combined and allowed to stand at room temperature overnight, Finally, the product, *cis*-1,2,6-trimethylpiperidine, is filtered through a 0.2 µm nylon filter before use in order to remove magnesium particulates and other solids.

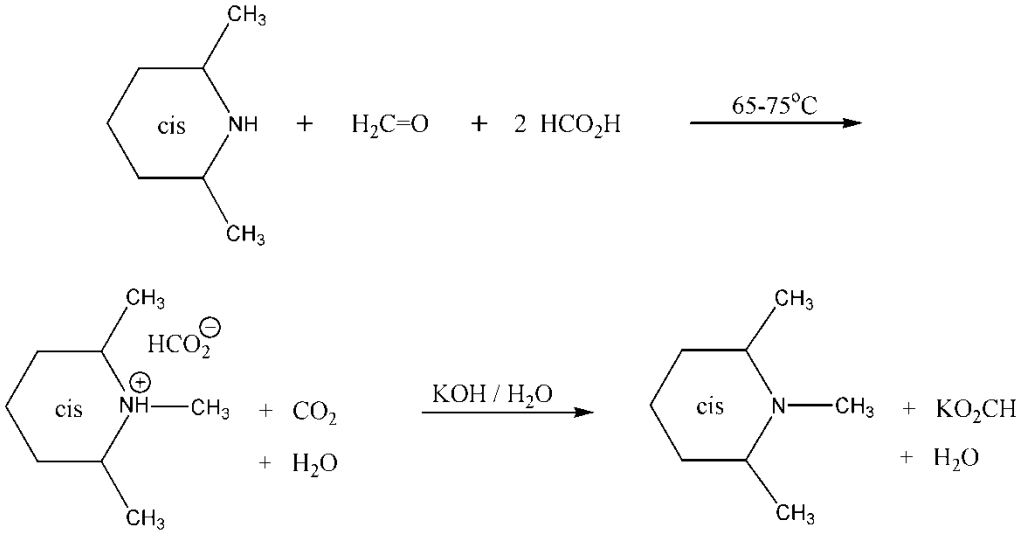
Notes:

- The addition of anhydrous magnesium sulfate to an amine/n-pentane mixture (33/67 v/v) leads to a 2-4% yield loss, but it cleans up the amine without distillation. Low boiling petroleum ether can be used instead of pentane.

$MgSO_4$ (solid) + 7 H_2O -> $MgSO_4 \cdot H_2O / MgSO_4 \cdot 7H_2O$ (solid)

$MgSO_4$ (solid) + 2 KOH -> K_2SO_4 (solid) + $Mg(OH)_2$ (solid)

- During the removal of pentane from the product using a rotary evaporator, small amounts of water comes over with the pentane owing to azeotropic distillation.
- The product can be purified by distillation at atmospheric pressure (b.p. ~136°C). Note that the boiling point of the starting *cis*-2,6-dimethylpiperidine is similar (128°C).



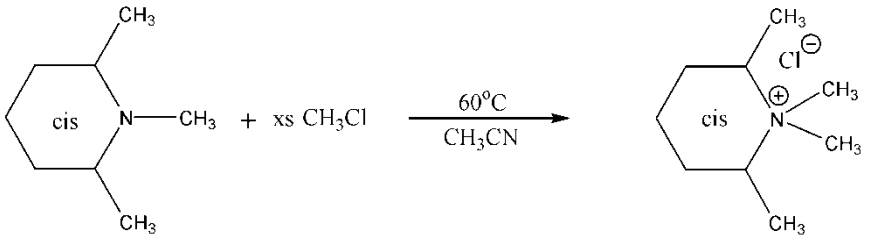
Preparation of *cis*-1,1,2,6-Tetramethylpiperidinium Chloride (fw=177.72).

A four-necked, 12 Liter round-bottom flask is equipped with an overhead stirrer, Dry Ice condenser, gas inlet connector with dual gas inputs, heating mantle and a temperature sensor. The gas inlet connector is attached to sources of N_2 (purge gas) and methyl chloride (reactant). The flask is charged with 2545 g *cis*-1,2,6-trimethylpiperidine (20.00 mole, fw=127.23, ~3030 mL, d=0.84), and 4.2 L of reagent-grade acetonitrile. Vigorous mechanical stirring is important in order to disperse the crystalline product that is produced in the reaction mixture during the methylation reaction. The stirred mixture is gently heated to 60°C, and then gaseous methyl chloride (fw=50.49, d=0.92 [liquified gas]) is carefully distilled from a pressurized container containing liquified methyl chloride, and then it is carefully bubbled through the gas inlet tube into the stirring reaction mixture. Initially a minor reaction exotherm (~2°C) is observed that subsides within 30-60 minutes. After the exotherm, the reaction temperature is maintained at 60°C using external heating. The rate of addition of methyl chloride is adjusted so that there is *slow* refluxing (~1 drop per second) of the methyl chloride from the Dry Ice condenser. Early in the course of the reaction, beautiful white crystals of the product begin to crystallize from solution. The progress of the reaction is determined by periodically (every 3 hours) monitoring the reaction mixture using HPLC. The reaction is essentially complete after a period of about 21-30 hours (99+% conversion of the starting amine). An excess of methyl chloride is used during the course of the reaction in order to insure completeness. After the reaction is essentially complete, the reaction flask is briefly purged with N_2 in order to remove part of the excess, unreacted methyl chloride; methyl chloride is very soluble in acetonitrile. The hot reaction mixture is allowed to cool to ambient temperature over a period of about 2-3 hours, and then it is allowed to stand at 4°C overnight in a refrigerator (4°C). Under a dry nitrogen atmosphere, the cold mixture is then filtered

through medium porosity sintered glass in order to obtain the main part of the product (nice white crystals, Crop1). The product is hygroscopic in laboratory air. The product is washed with a minimum amount MTBE and then allowed to partially dry by passing dry N_2 through the filter cake. The crystals are dried in a vacuum oven overnight (80°C, 20 torr) yielding 3234g (91%, Crop1). In a melting point apparatus, the product does not melt but decomposes at 255-260°C (dec). MTBE is added to the filtrate and more white microcrystals come out of solution. This material is recovered by filtration (Crop2) and washed, and 142g (4%, Crop2) of a white crystalline solids are produced. For Crop1, typical purity is 99.6-99.8% (HPLC). For Crop2, typical purity is 98.2-99.2% (HPLC) depending on the purity of the starting amine.

Notes:

- The methylation reaction in acetonitrile allows it to proceed at a reasonable rate at atmospheric pressure at 60°C. Reaction rates in other solvents are slower.
- This reaction will probably proceed faster when methyl bromide or methyl iodide is used instead of methyl chloride.
- Because the product is very soluble in water, the *cis*-1,2,6-trimethylpiperidine must be dry and contain minimal amounts of water left over from the previous reaction.
- Crop1 is usually not recrystallized, but it may crystallized using the method below. Crop2 may be discarded, recycled or recrystallized depending on its purity. Method: dissolve the product in a minimum amount (~3.5 mL solvent/g product) of hot (near boiling) 85/15 MeCN/IPA (v/v). Allow to slowly cool to room temperature, and then stand at this temperature about 2 hours. Then allow the mixture to stand at 4°C for 6-12 hours and finally filter through sintered glass under dry N_2. Wash with MTBE and dry.



HPLC Method

Analyses were carried out using Waters Corp. (Milford, MA) gradient HPLC equipped with a Waters 996 PDA detector in tandem with a Dionex/ESA Biosciences (Chelmsford, MA) Corona Plus CAD detector and (1) a SIELC Technolgies Primesep 200, 5 □m, 100 Å, 4.6 x 150 mm SS, mixed-mode surface coating over porous silica, reversed-phase/cation-exchange chromatography column with 4.6 x 50 guard column (Prospect Heights, IL) or (2) a Waters Xbridge BEH 130, 5 □m, 130 Å, 4.6 x 250 mm SS column (C_{18} reversed-phase surface-coating over porous silica) without guard column (Milford, MA). Same buffers and gradient method used for both columns. Sample Injection: 10 µL of a sample solution in 80/20 (v/v) water/acetonitrile w/0.1% HTFA. Flow-Rate: 1.0 mL/min.
A buffer: HPLC-grade water + 1% (v/v) HPLC-grade acetonitrile + 0.1% (v/v) trifluoroacetic acid
B buffer: HPLC-grade acetonitrile + 1% (v/v) HPLC-grade water + 0.1% (v/v) trifluoroacetic acid

Gradient Method:	100% A	0-1 min
	100% A to 100% B	1-61 min
	100% B	61-70 min

Peak Identification: A = *cis*-2,6-dimethylpiperidine**;** B = *cis*-1,2,6-trimethylpiperidine – conformer 1; C = *cis*-1,2,6-trimethylpiperidine – conformer 2; D = *cis*-1,1,2,6-tetramethylpiperidinium chloride
I = injection peak

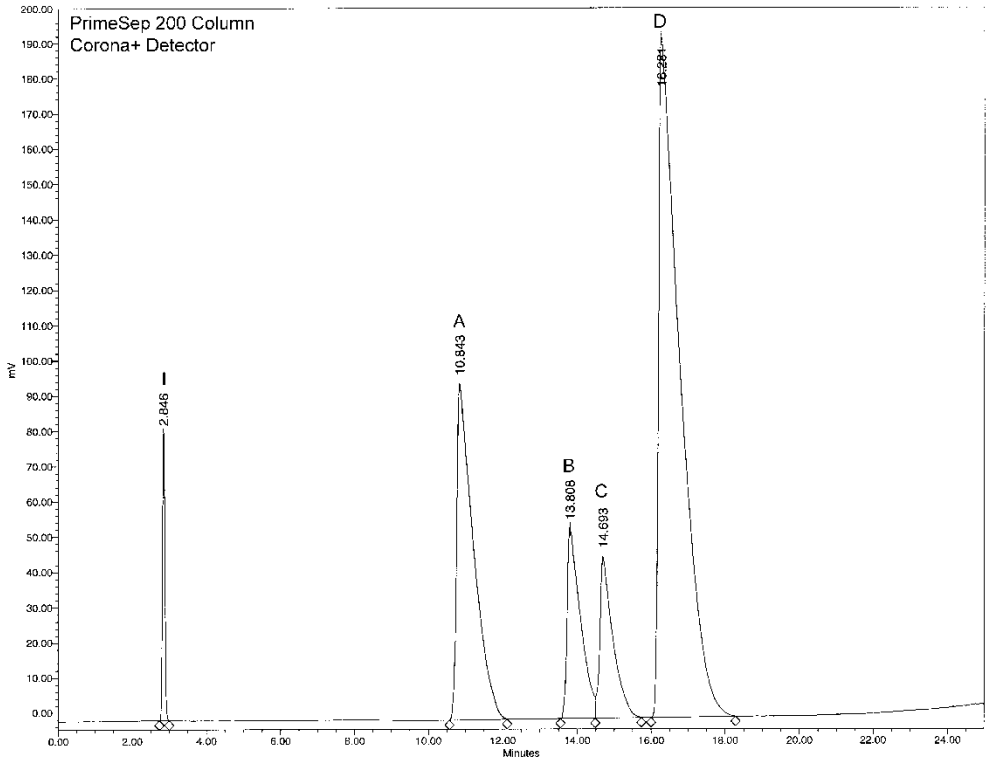


Figure 1: Chromatogram of a mixture of methylated piperidines: *cis*-2,6-Me_2Piperidine (A: 0.6 mg/mL), *cis*-1,2,6-Me_3Piperidine (B, C: 0.6 mg/mL), *cis*-1,1,2,6-Me_4Piperidinium Chloride (D: 0.6 mg/mL).

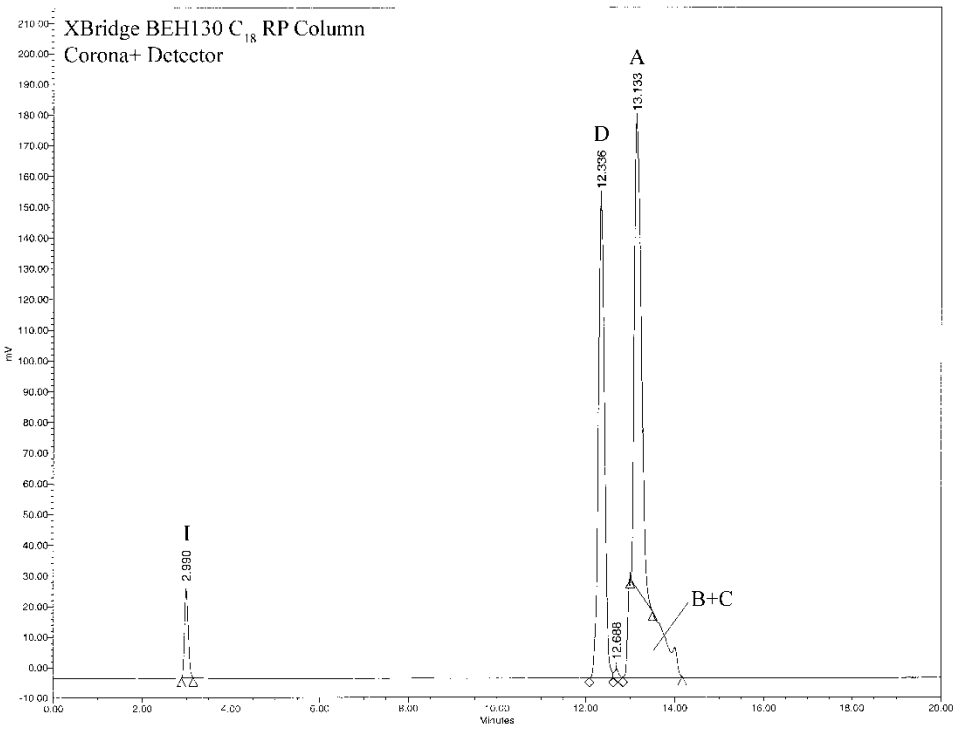


Figure 2: Reversed-Phase chromatogram of a mixture of methylated piperidines: *cis*-2,6-Me_2Piperidine (A: 0.9 mg/mL), *cis*-1,2,6-Me_3Piperidine (B, C: 0.9 mg/mL), *cis*-1,1,2,6-Me_4Piperidinium Chloride (D: 0.9 mg/mL).

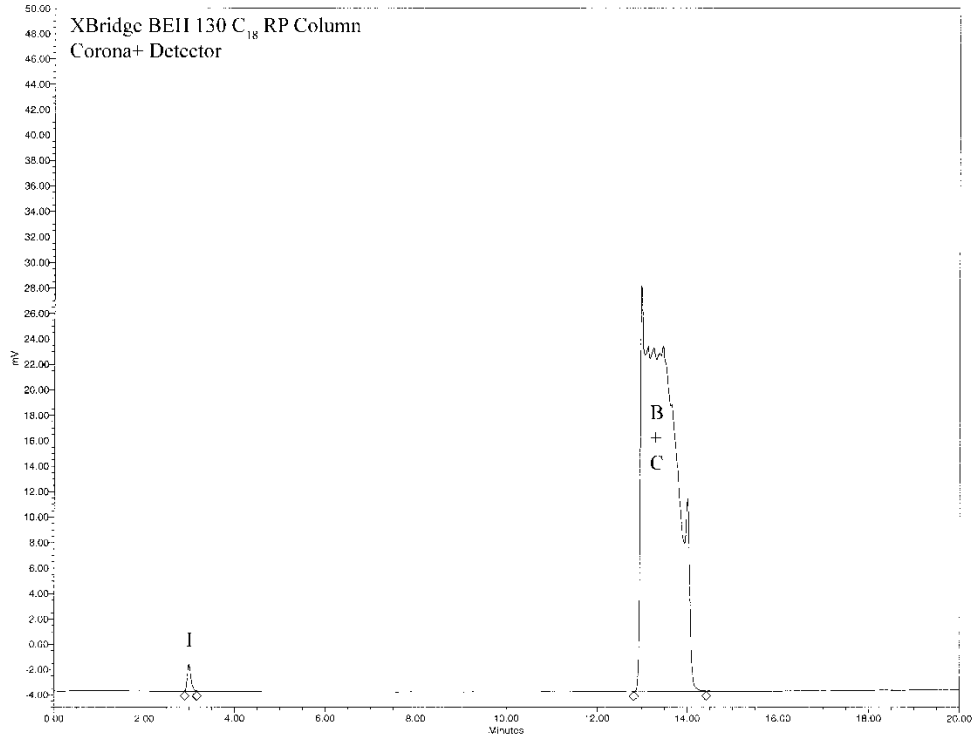


Figure 3: Reversed-Phase chromatogram of pure *cis*-1,2,6-Me_3Piperidine (B, C) – mixture of conformers.

1. IZA-Structure-Commission, *Database of Zeolite Structures http://izasc.biw.kuleuven.be/fmi/xsl/IZA-SC/ft.xsl, Accessed 23rd Jan. 2015*.
2. (a) Zones, S. I.; Nakagawa, Y.; Evans, S. T.; Lee, G. S. Zeolite SSZ-39. US 5,958,370, 1999; (b) Cao, G.; Strohmaier, K. G.; Li, H.; Guram, A. S.; Saxton, R. J.; Muraoka, M. T.; Yoder, J. C.; Yaccatu, K. Synthesis of AEI-type zeolites and their use in the conversion of oxygenates to olefins. WO2005063624A1, 2005.
3. Moliner, M.; Franch, C.; Palomares, E.; Grill, M.; Corma, A., Cu-SSZ-39, an active and hydrothermally stable catalyst for the selective catalytic reduction of NOx. *Chem. Commun.* **2012,** *48* (66), 8264-8266.