

Supplementary Information

IZM-7: A new stable aluminosilicogermanate with a promising catalytic activity

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Preparation of the organic structure directing agent

The organic structure directing agent (OSDA) used for the synthesis of IM-12 zeolite, is the (6R,10S)-6,10-dimethyl-5-azoniaspiro [4,5] decane hydroxide. To prepare this OSDA, 420 mL of distilled water, 17.04 g of sodium hydroxide (Sigma Aldrich, >97%) and 91.98 g of 1,4-dibromobutane (Sigma Aldrich, 99%) were mixed in a flask. Then, 48.21g of (2R,6S)-2,6-dimethylpiperidine (TCI, 99%) were added drop by drop over a period of 30 min under reflux. The mixture was refluxed for 12 hours then cooled with ice bath. 210 mL of ice-cooled sodium hydroxide solution (40 wt.%) was added. The mixture was placed in a freezer for 12 hours. The produced solid was then filtered and extracted three times using 600 mL of chloroform (Sigma Aldrich, 99%). After that, 60 g of anhydrous magnesium sulfate (Sigma Aldrich, 99.5%) were added. The mixture was then filtered and washed with 150 mL of chloroform. The organic fractions were evaporated at 40°C until reaching a volume of 300 mL using a rotary evaporator. The ammonium salt was precipitated and washed with ethyl ether (Sigma Aldrich, 99%). The yield of the reaction was 80%. The obtained OSDA is in its bromide form,

thus it was exchanged before its use in zeolites synthesis to its hydroxide form. This procedure was performed on ion exchange resin (Dowex Mariathon OH⁻ Anion exchange Resin) or using silver oxide (Sigma Aldrich, 99.9%).

Synthesis and post-treatment of the materials

A gel with the following molar composition: 0.7 SiO₂: 0.3 GeO₂: 0.25 ROH: 25 H₂O was prepared by dissolving 32.622 g of amorphous germanium oxide (ABCR, 99.9%) in 300.534 g of a 16.02 wt.% (6R,10S)-6,10-dimethyl-5-azoniaspiro[4,5]decane hydroxide (ROH) solution. Then, 153.090 g of the silicon source (tetraethyl orthosilicate, TEOS, Sigma Aldrich, 99%) and 213.755 mL of distilled water were added to the solution. The mixture was stirred at room temperature until complete hydrolysis of TEOS. The resulting fluid gel was charged into a reactor and heated at 170°C for 18 days under stirring (100 rpm). The solid was recovered by filtration, washed with distilled water and dried overnight at 100°C. 3 g of the as prepared IM-12 silicogermanate were then loaded into the tubular-bed reactor then were calcined under dry air at 550°C for 6 hours, before silicon tetrachloride treatment. The nitrogen flow saturated with SiCl₄ at ambient temperature (vapor pressure of SiCl₄ = 0.32 bar) entered then the reactor containing the IM-12 at 550°C with a flow rate of 0.2 NL/h/g of zeolite. After 5 hours to reach full evaporation of SiCl₄ (the amount of the SiCl₄ was 3 times higher, in moles, than the quantity of germanium present in the treated silicogermanate), the reactor was left for 1 hour under a nitrogen flow of 1.5 NL/h/g at the temperature of the treatment before cooling down. The alumination of IM-12 using aqueous solution of polyaluminum chloride (PAC, Pluspac 1340, 7% Al) was then carried out with a solid: liquid ratio of 1:50. Thus 150 mL of PAC solution were added to 3 g of SiCl₄ treated IM-12. The mixture was stirred in a round-bottom flask under reflux at 80°C for 6 hours. The obtained sample was filtered and washed 3 times with distilled water. The sample was then left for drying overnight at 100°C. After the PAC

treatment, a treatment with an aqueous solution of HCl (0.1 M) at room temperature under stirring for 3 hours with a solid: liquid ratio of 1:30 was made in order to reduce the amounts of extra framework aluminum. Typically, 2 g of zeolite treated with PAC were mixed with 60 mL of HCl (0.1 M). After the treatment, the sample was thoroughly washed with distilled water and dried at 100°C overnight. This two-step procedure was further repeated 2 times. The obtained material was then calcined under air at 550°C for 6 hours. The new material obtained is called IZM-7.

Characterization of the materials

Powder samples are compacted in a sample carrier. X-ray diffractions were collected on a Bruker D4 Endeavor diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a Bragg-Brentano geometry.

The overall Si/Al and Si/Ge ratios of the zeolites were obtained by X-ray fluorescence (XRF) using an ARL PERFORM'X sequential X-ray fluorescence spectrometer from ThermoFisher Scientific. The glass disks were prepared by mixing 1 g of dry sample (after loss of ignition) with 9 g of the eutectic flux 66:34 (Tetraborate de lithium 66% / Metaborate de lithium 34%). The mixture is then heated to 1000°C in a platinum crucible. The sample is dissolved in the flux, then is cast into a mold.

The N₂ physisorption was used to determine the microporous volume following the t-plot method, the total volume and the surface area S_{BET} of the studied zeolites. The samples were pre-treated at 200°C for 2 hours then at 550°C for 6 hours under vacuum. Measurements were done with a Micromeritics ASAP 2420 equipment.

SEM was used to study the morphology of zeolites. The samples were diluted in ethanol under ultrasound. A drop of the suspension was then deposited on an aluminum pad previously polished with SiC granulo paper of 2500 then 4000, then left to dry. The samples were observed

in topographic contrast mode (secondary electrons) using the SE2 detector at 2kV and with a beam size of 20 μm .

Chemical mapping using energy dispersive X-ray spectroscopy (EDS) in annular dark-field scanning transmission electron microscopy (ADF-STEM) were performed with a probe-corrected transmission electron microscope (ARM200F cold-FEG, JEOL) operated at an acceleration voltage of 200 kV. The samples were prepared by dispersing the powder in ethanol and placing few drops of the solution onto the copper TEM grids covered with carbon.

The average particle size determined via STEM can be used to estimate the Pt dispersion using the following equation [1]: $d_{\text{Pt}} = 101.64 \times D_{\text{Pt}}^{-1}$

where D_{Pt} is the average size of the platinum particle in nm and d_{Pt} is the dispersion (in %).

^{27}Al MAS NMR measurements were performed in a Bruker 500 MHz Avance III spectrometer equipped with a 4 mm H/X/Y triple resonance probe. Samples were filled in a 4 mm ZrO_2 rotor and subjected to magic angle spinning (MAS) at 15 kHz. ^{27}Al spectra were acquired with 170 kHz radio frequency (RF) pulse (solid, CT), relaxation delay of 1s and 73728 transients with spinal64 ^1H decoupling (50 kHz RF) [2]. ^{27}Al spectra were referenced to 0.1M $\text{Al}(\text{NO}_3)_3$ in D_2O solution and were acquired on hydrated samples. Hydration was done by equilibrating a packed 4 mm rotor in an atmosphere with controlled 77% relative humidity for 48 hours. Al quantification was performed using an external reference (LTA with Si/Al=1). To ensure an identical instrumental response between different samples, the procedure described by Houllberghs et al. [3] was implemented: ensuring the same coil filling factor (sample volume) and the tuning of the probe to obtain same quality-factors (Q-factor). Once these conditions are assured, the amount of Al and the Si/Al ratios in the catalysts can be deduced by comparing the areas of the measured samples to those of the Na-LTA (Si/Al = 1) reference sample. The ATR-IR measurements and the *In situ* transmission IR monitoring of adsorption / thermodesorption of pyridine were performed on a Nexus spectrometer (ThermoOptek Nicolet)

with a resolution of 4 cm^{-1} , 64 scans and a DTGS detector. For ATR-IR, the samples were measured without any preparation (powder). For *In situ* FTIR monitoring of adsorption / thermodesorption of pyridine, the samples were pelletized before contact with pyridine (disc of 16 mm in diameter and mass of about 20 mg) then pretreated under secondary vacuum for 10 hours at 450°C . After activation, a first spectrum is recorded. Pyridine was then put in contact with the sample (ca. 20 mbar equilibrium) at room temperature for 10 min then diffused at 150°C for 10 min. Once the adsorption equilibrium was reached (followed by IR), spectra after different thermodesorption temperature were measured: after 2 hours at 150°C , 1 hour at 250 , 350°C and 450°C . By subtracting the spectrum of the activated sample from the thermodesorption spectra, the concentrations of Brønsted (pyridinium concentration from the contribution at ca. 1545 cm^{-1}) and Lewis acid sites interacting with pyridine (from the contribution at ca. 1455 cm^{-1}) were quantified. The molar extinction coefficients of IZM-7 and of pyridine adsorbed on the IZM-7 are not defined, thus we used the coefficients from the literature assuming that they are independent of the catalyst or the strength of the acid site [4]. The concentrations in $\mu\text{mol.g}^{-1}$ of silanols (around 3740 cm^{-1}) were calculated using the molar extinction coefficient determined by Gallas et al. on silica equal to $3\text{ cm}.\mu\text{mol}^{-1}$ [5] while those of Brønsted and Lewis acid sites were calculated using the coefficients determined by Emeis for Si/Al-based catalysts equal to 1.67 and $2.22\text{ cm}.\mu\text{mol}^{-1}$ respectively [4].

Preparation of the bifunctional catalyst

100 mg of IZM-7 aluminosilicogermanate zeolite were impregnated with 0.1 mL of an aqueous solution containing 0.052 g of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2.\text{H}_2\text{O}$ (Alfa Aesar) in the aim of obtaining a catalyst with a platinum loading of 0.3% wt. The suspension was then dried for 24 hours at 60°C . The powder obtained was pelletized, crushed and sieved between 125 and $250\text{ }\mu\text{m}$.

Hydroisomerization of n-decane

n-decane hydroconversion was performed in a custom-made high throughput 16 parallel tube reactors with online reaction product analysis as described in literature [6]. 50 mg of catalyst pellets with a size between 125 and 250 μm were loaded in each reactor. After one hour at 400°C under oxygen (ramp: 5°C/min with an oxygen flow of 4.7 mL/min per microreactor), the microreactors were flushed with nitrogen for approximately 10 minutes at the same flow. Then the catalysts were reduced under hydrogen for one hour at 400°C with a hydrogen flow of 12.5 mL/min. Finally, the reactors were cooled down to the reaction temperature. The reactor unit was operated at a total pressure of 0.45 MPa and at hydrogen to *n*-decane molar ratio of 214. The weight hour space velocity (WHSV) was 0.37 g/g.h. The temperature was then increased by 5°C with a ramp of 5°C/min. Several temperatures were then tested, for each new one, a stabilization time of 1 hour was required before starting the product analyses. Product analysis was performed using on-line GC and a CP Sil-5 capillary column (Chrompack).

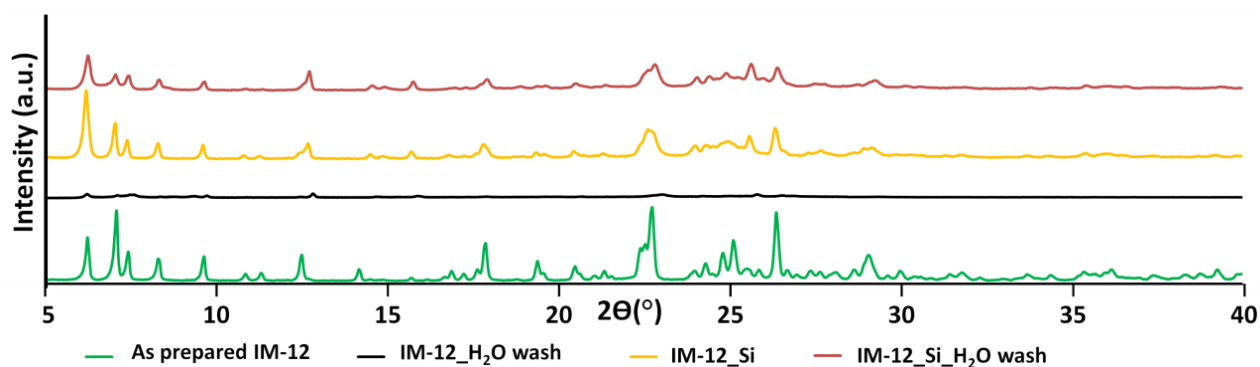


Figure S1: XRD patterns of as prepared IM-12, calcined IM-12 then washed with water (IM-12_H₂O wash), calcined IM-12 then treated with SiCl₄ (IM-12_Si), and calcined IM-12 then treated with SiCl₄ then washed with water (IM-12_Si_H₂O wash).

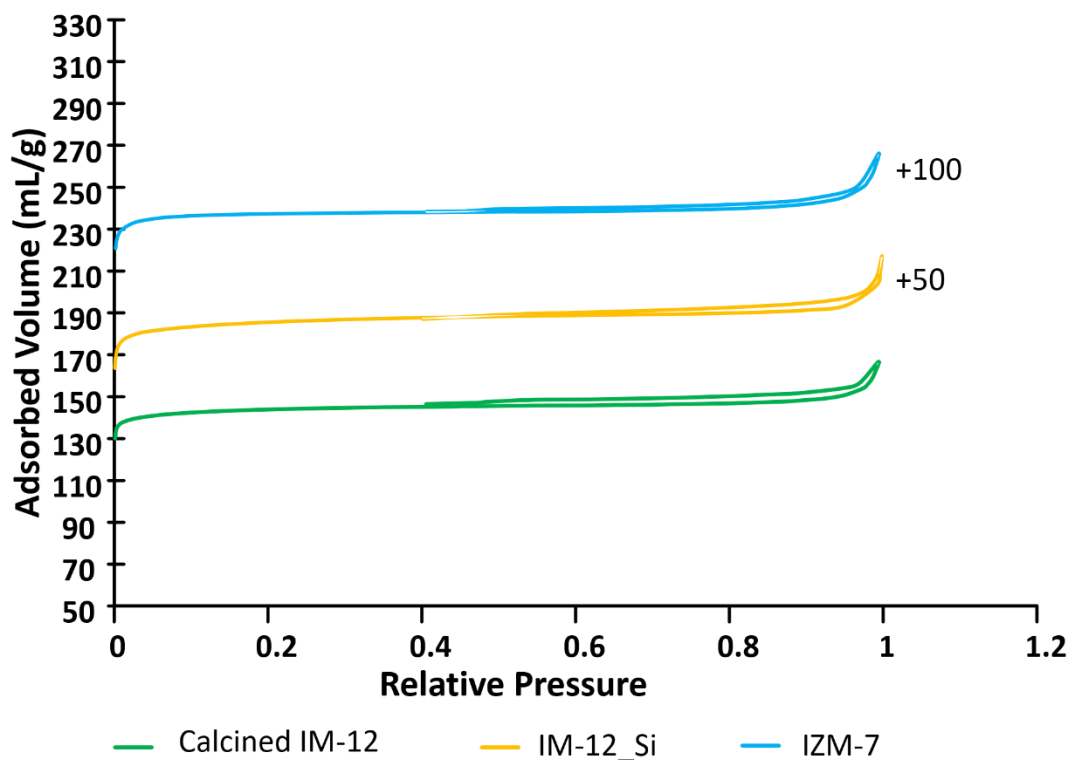


Figure S2: N₂ physisorption isotherms of calcined IM-12, IM-12 treated with SiCl₄ (IM-12_Si) and of IZM-7.

Table S1: Surface and volume features measured by N₂ physisorption, XRF results and wavenumber at maximum absorbance in ATR-IR of as prepared/calcined IM-12, IM-12 treated with SiCl₄ (IM-12_Si), and of IZM-7.

Sample	N ₂ physisorption				XRF			ATR-IR	
	BET Surface (m ² /g)	External Surface (m ² /g)	Volume at P/P0=0.99 (mL/g)	Microporous Volume (mL/g)	Si/Ge (mol)	(Si+Ge)/Al (mol)	Si/Al (mol)	$\nu_{\text{max (SiOSi)}}$ (cm ⁻¹)	$\nu_{\text{(d4r)}}$ (cm ⁻¹)
As prepared IM-12					5	-	-	1073 / double peak at 1045	570
Calcined IM-12	592	29	0.258	0.210		-	-		
IM-12_Si	553	47	0.259	0.189	10	-	-	1054	582
IZM-7	529	17	0.243	0.191	173	28	27	1043	584

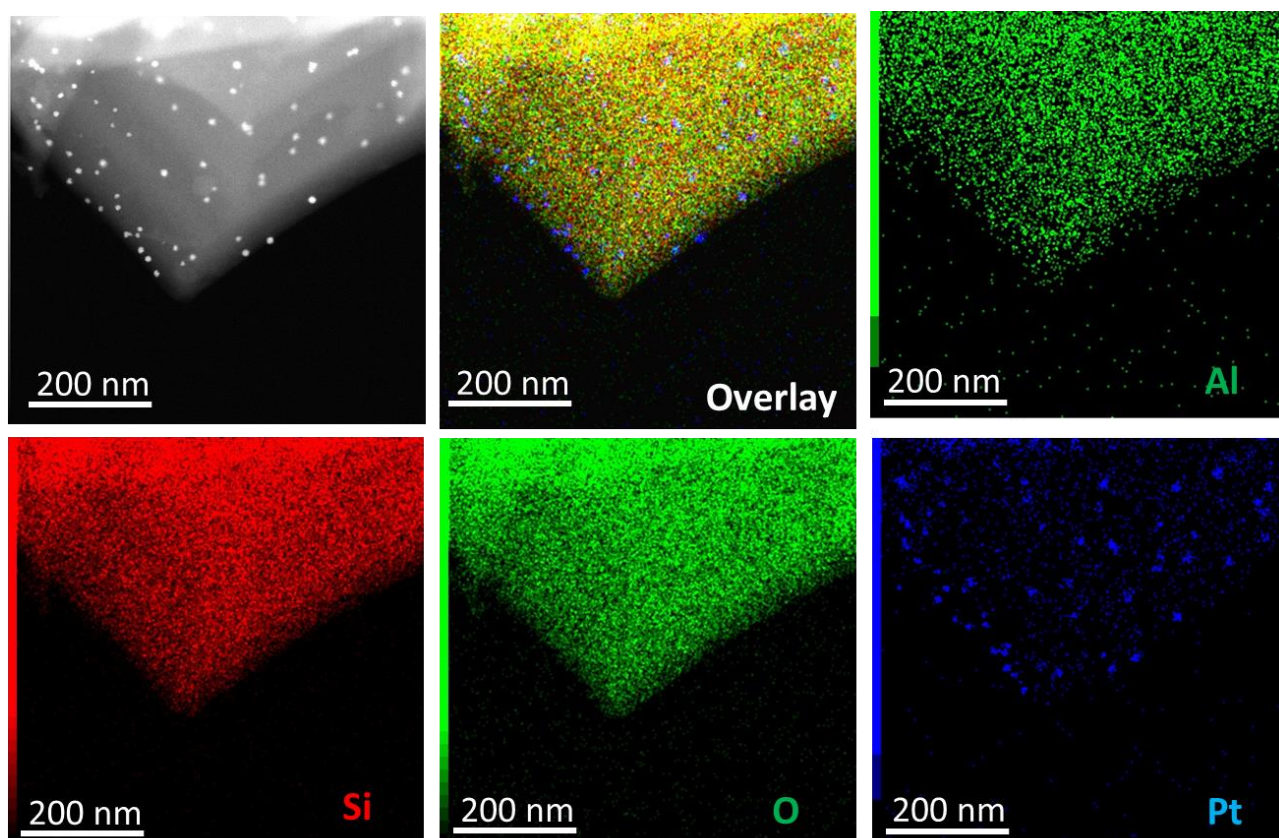


Figure S3 :ADF-STEM-EDS chemical mapping of IZM-7 sample.

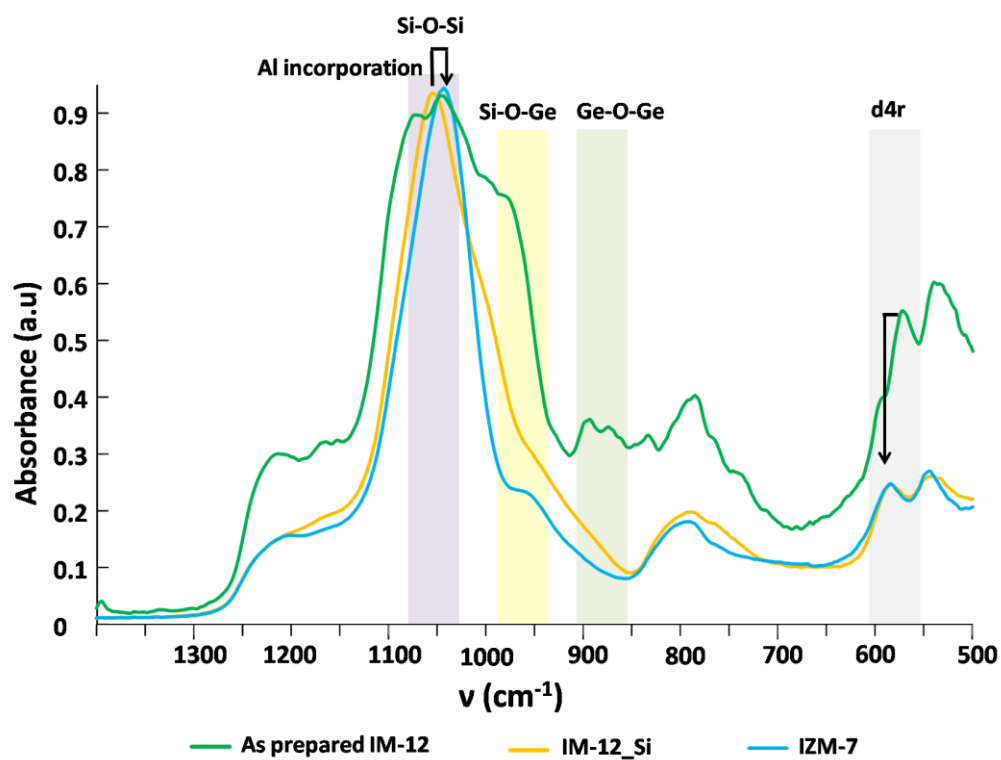


Figure S4: ATR-IR spectra of as prepared IM-12 and treated samples normalized at the maximum absorbance ($\approx 1050\text{cm}^{-1}$).

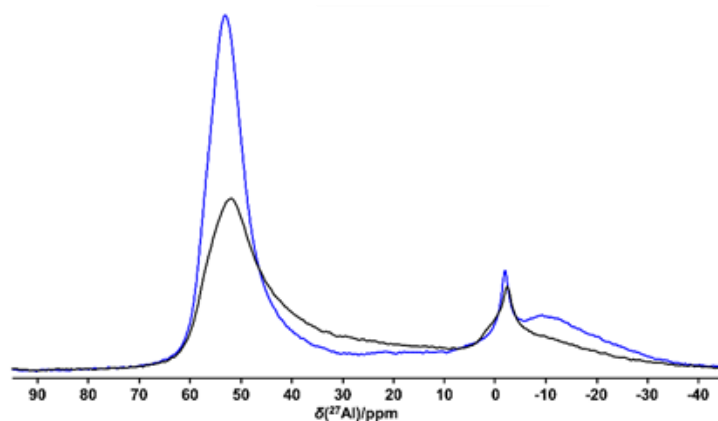


Figure S5 : ^{27}Al NMR of IZM-7 before (blue) and after (black) HCl washing.

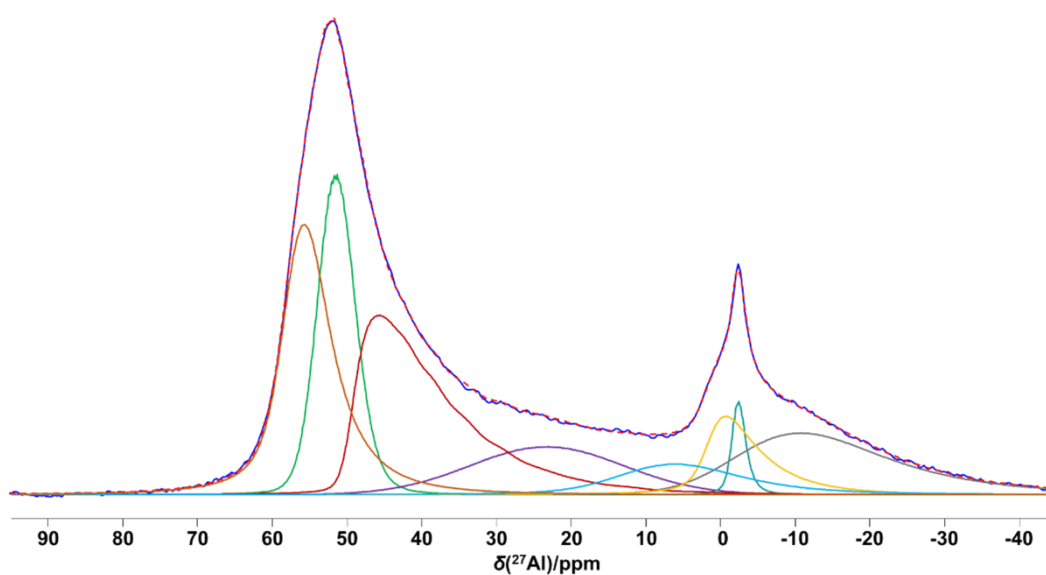


Figure S6: Deconvoluted ^{27}Al MAS NMR spectrum of IZM-7.

Table S2: Relative amounts and assignments of Al from the deconvoluted ^{27}Al MAS NMR spectrum of IZM-7.

δ ^{27}Al (ppm)	C_Q (MHz)	dCS (ppm)	Relative amounts (%)	Assignment
57.3	2.5	4.4	22.0	T1
52.6	1.7	5.1	17.0	T2
49.6	5.1	2.8	23.2	DT1
25.8	2.5	23.5	9.9	P1
10.7	4.0	13.3	5.8	H1
1.6	3.5	3.3	6.9	H2
-2.0	1.2	1.5	2.0	H3
-2.7	5.5	15.1	13.2	H4

Table S3: Al content and Si/Al ratio determination of IZM-7 based on ^{27}Al MAS NMR. Na-LTA (Si/Al 1) is used as reference for Al content determination.

	Normalized Integral	Al, wt%	Si/Al	Al, $\mu\text{mol/g}$
NaA	1.00	19.01	1	
IZM-7 (Total Al)	0.07	1.39	31.4	514
IZM-7 (T1+T2+DT1)	0.05	0.86	51.2	319
IZM-7 (T1+T2)	0.03	0.54	82.2	200
IZM-7 (T1)	0.02	0.31	146.4	113
IZM-7 (T2)	0.01	0.24	189.8	87

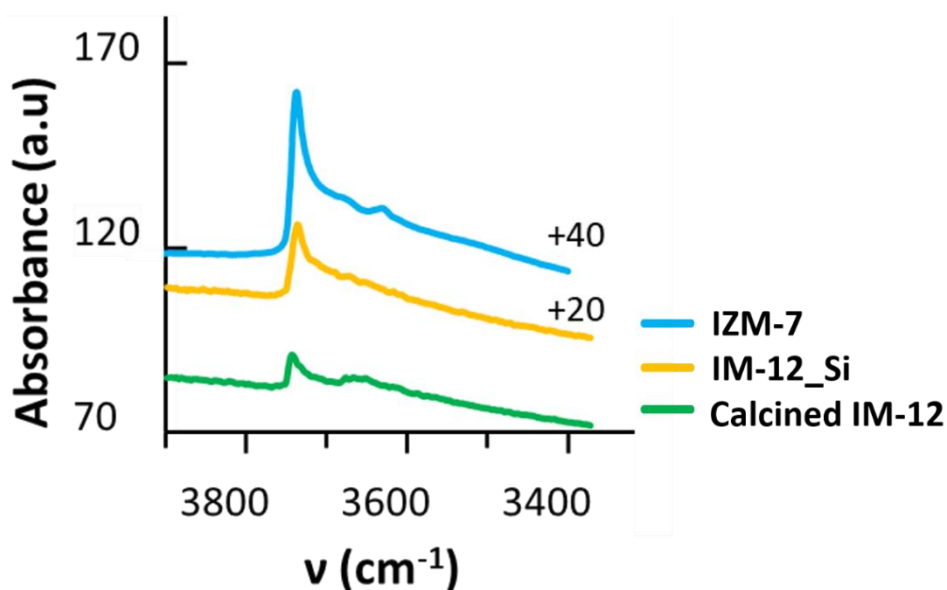


Figure S7: IR spectra of calcined IM-12, IM-12 treated with SiCl_4 (IM-12_Si) and of IZM-7, region of hydroxyl vibrations after treatment at 450°C for 10h under secondary vacuum.

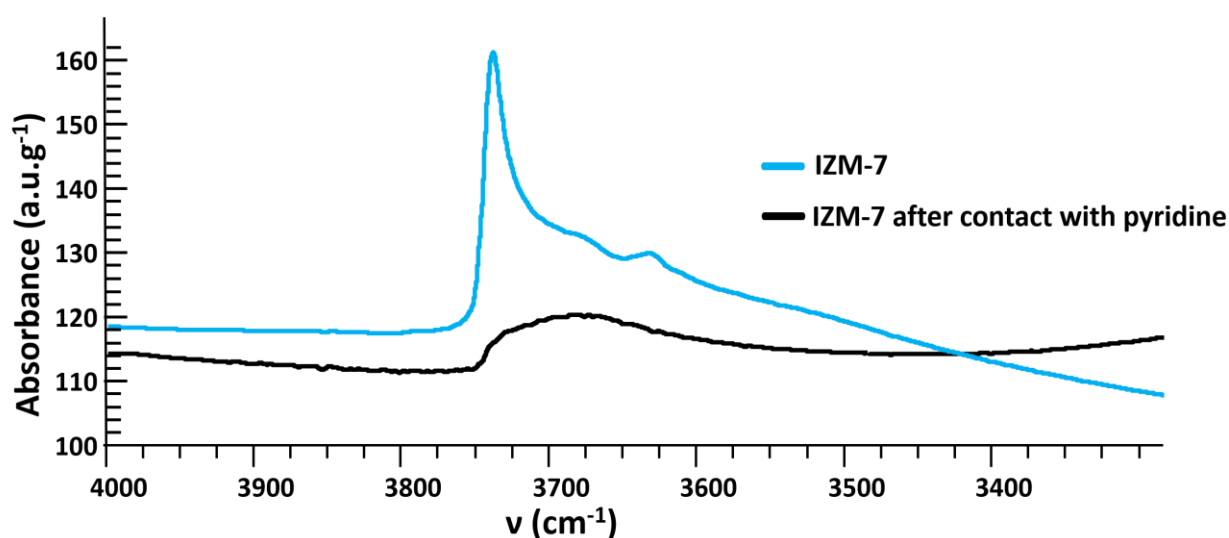


Figure S8: OH region of the spectrum of IZM-7 activated at 450°C and after contact with pyridine at ambient temperature for 10 min.

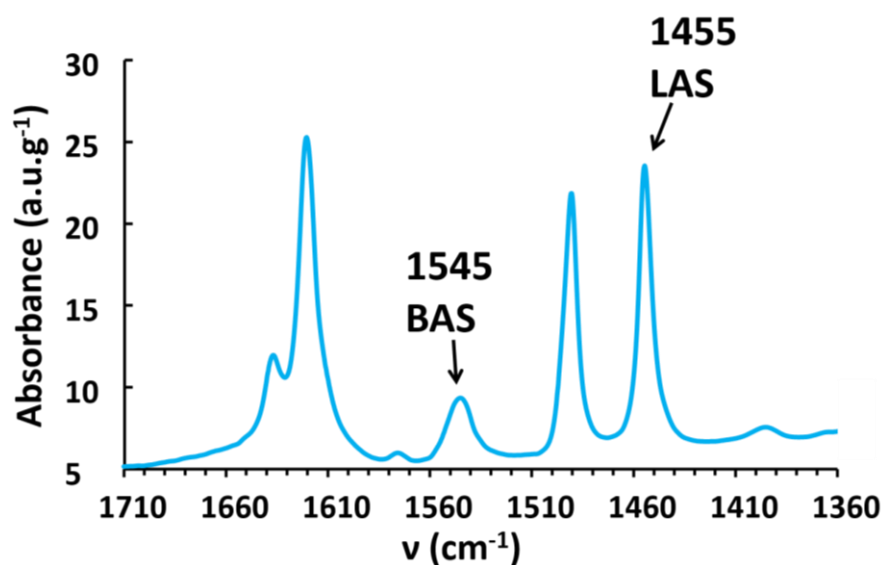


Figure S9: Pyridine ring vibration zone of the IR spectrum after subtraction of the activation spectrum and thermodesorption of pyridine at 150°C on the IZM-7 sample.

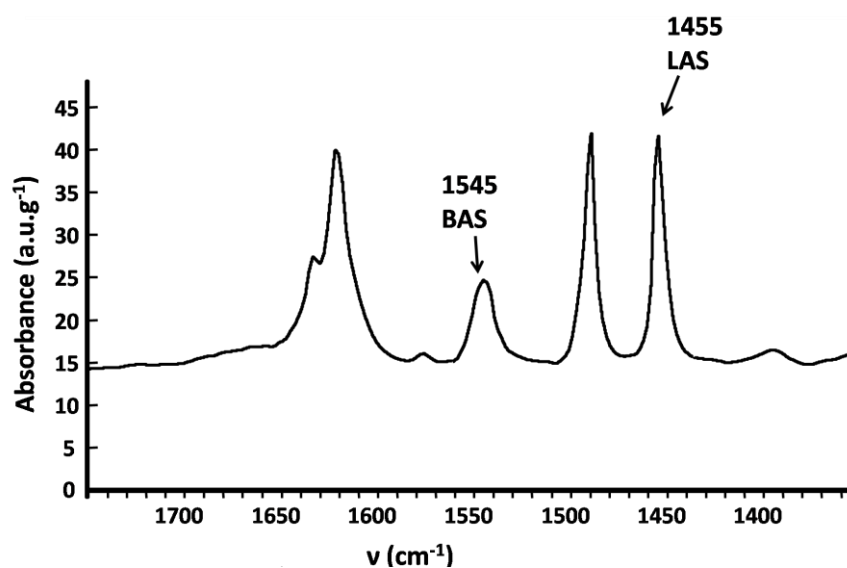


Figure S10: Pyridine ring vibration zone of the IR spectrum after subtraction of the activation spectrum and the thermodesorption of pyridine at 150°C on the USY sample (CBV-760).

Table S4 : Amount of BAS and LAS sites for IZM-7 (UTL) and CBV-760 (USY) samples at different pyridine desorption temperatures.

Temperature of Pyridine desorption (°C)	BAS ($\mu\text{mol.g}^{-1}$)		LAS ($\mu\text{mol.g}^{-1}$)	
	IZM-7 (UTL)	CBV-760 (USY)	IZM-7 (UTL)	CBV-760 (USY)
150	81	129	96	29
250	69	124	86	24
350	39	90	75	24
450	-	35	50	22

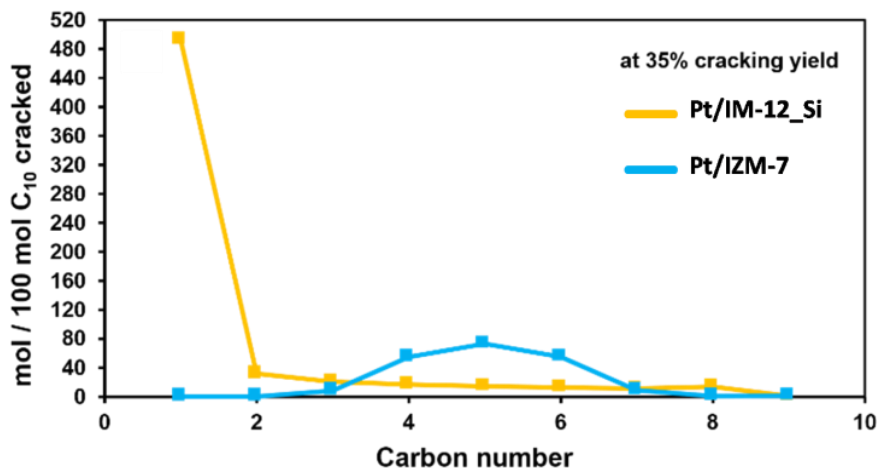


Figure S11: Molar yields of carbon number fractions per 100 mol of *n*-decane cracked at 35% *n*-decane hydrocracking in *n*-decane hydroconversion over Pt/IM-12_Si and Pt/IZM-7 catalysts.

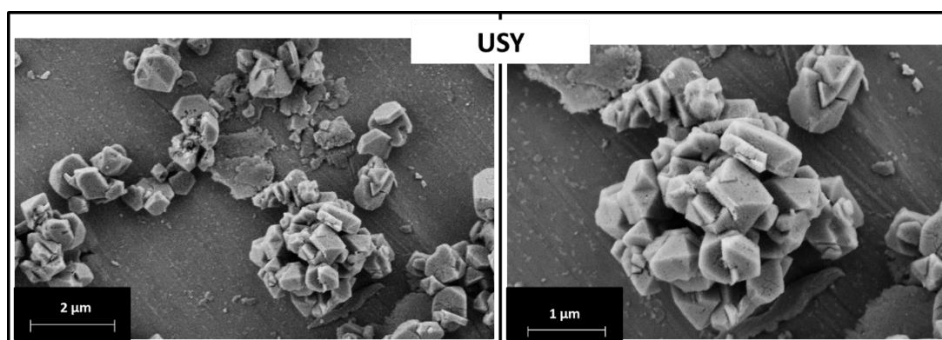


Figure S12: SEM images of USY zeolites (CBV-760).

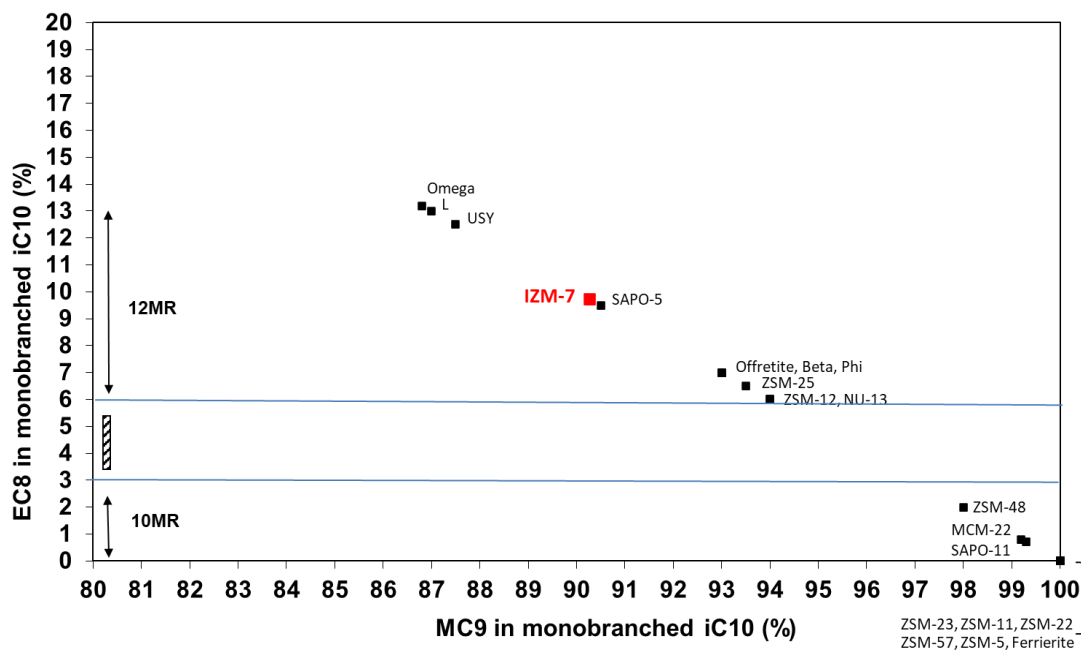


Figure S13: Plot of ethyloctanes (EC8) vs methylnonanes (MC9) in monobranched isomers at 5% conversion for IZM-7 compared to reference frameworks.

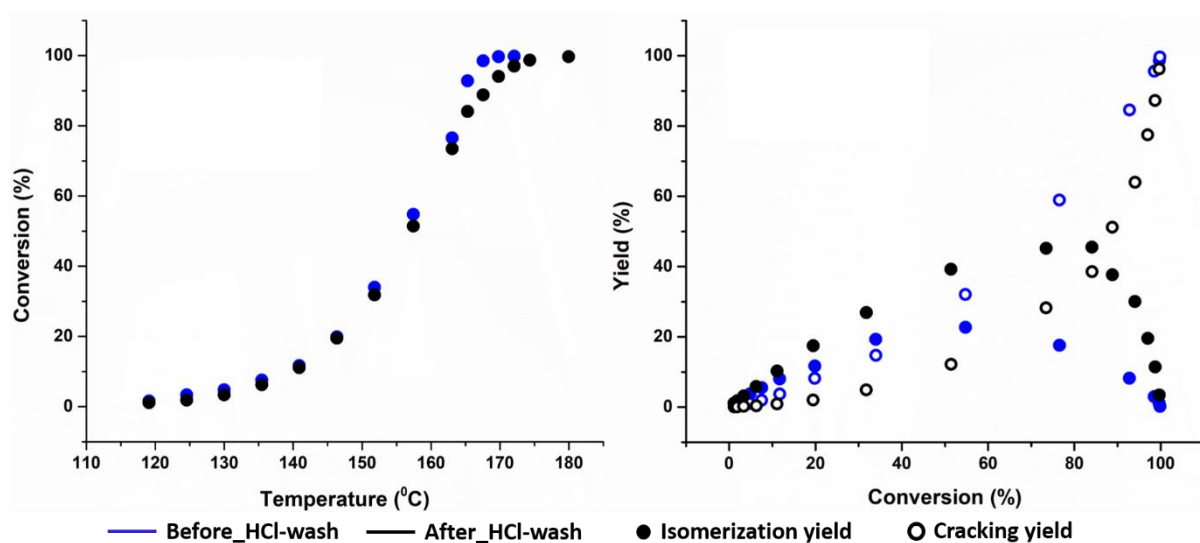


Figure S14: Left: Conversion of *n*-decane against reaction temperature; right: yield of *n*-decane skeletal isomers and cracked products against *n*-decane conversion, of the 0.3 wt.% Pt/IZM-7 before HCl wash (blue) and 0.3 wt.% Pt/IZM-7 after HCl wash (black).

References

- [1] S.P. Sree, J. Dendooven, P.C.M.M. Magusin, K. Thomas, J.-P. Gilson, F. Taulelle, C. Detavernier, J.A. Martens, *Catal. Sci. Technol.* 6 (2016) 6177–6186.
- [2] B.M. Fung, A.K. Khitrin, K. Ermolaev, *J. Magn. Reson.* 142 (2000) 97–101.
- [3] M. Houllberghs, A. Hoffmann, D. Dom, C.E.A. Kirschhock, F. Taulelle, J.A. Martens, E. Breynaert, *Anal. Chem.* 89 (2017) 6940–6943.
- [4] C.A. Emeis, *J. Catal.* 141 (1993) 347–354.
- [5] J. P. Gallas, J. C. Lavalley, A. Burneau, O. Barres, *Langmuir* 7 (1991) 1235–1240.
- [6] W. Huybrechts, J. Mijoin, P.A. Jacobs, J.A. Martens, *Appl. Catal. A Gen.* 243 (2003) 1–13.