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Properties of Desilicated ZSM-5, ZSM-12, MCM-22 and ZSM-12/MCM-41 Derivatives in Isomerization of α-Pinene

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Abstract Limited information is available on the isomerization of α-pinene proceeding on zeolites and related desilicated materials. We wish therefore to report on the title reaction proceeding over ZSM-5, ZSM-12 and MCM-22 type zeolites, parent and modified by the sodium hydroxide treatment. The NaOH solutions of various concentrations (0.05–1 M) were used as a desilicating agent. Such treatments with basic solutions were applied: (i) under atmospheric pressure, and (ii) under hydrothermal conditions. It was shown that ZSM-12 was more resistant towards the basic solutions treatment, and its structure was retained over a whole range of NaOH concentrations studied. Nitrogen sorption revealed strong influence of the desilication process on the pore structure of modified materials—the mesopores system was formed in the zeolite crystals. Finally, catalytic studies were carried out using ZSM-5, ZSM-12, MCM-22, their desilicated derivatives and a ZSM-12/MCM-41 composite material. Catalytic properties of the samples studied were affected to a large extent by the NaOH treatment.

Keywords Desilication · Pinene isomerization · 27Al NMR · ZSM-5 · ZSM-12 · MCM-22

1 Introduction

Terpenes comprise a large class of natural chemicals, which are the most abundant components of the essential oils isolated from numerous plants, animals and microorganisms. Monoterpenes are formed from two isoprene building blocks, usually arranged in a *head-to-tail* way. Among monoterpene molecules, α-pinene, camphene, limonene and *p*-cymene are of paramount importance for chemical and pharmaceutical industries. All of the compounds mentioned above can be obtained by the catalytic isomerization of α-pinene (i.e. the most abundant member of the terpene hydrocarbons). Reducing of crude oil consumption and use of biomass as a source for production of higher value added chemicals, remains one of the main goal of research today. The industrial isomerization of terpenes belongs to such processes, yielding important raw materials required for the flavour & fragrance and pharmaceutical industries [1].

Various acidic catalysts, such as oxides [2, 3], oxides treated with acids [4], zeolites [5–12], mesoporous materials [12–14], activated clays [15–19], resins [20, 21] and heteropolyacids [22], have been explored in isomerization of α-pinene. Currently, the acid-impregnated TiO_2 is used as an industrial catalyst for this purpose, but due to the low rate of the reaction, there is still a great interest in developing novel, viable contacts for the process.

In many catalytic processes, especially aimed at fine chemicals production, mild reaction conditions are needed. We also note that reacting molecules often display kinetic diameters comparable with the pore apertures of the suggested zeolitic catalysts, thus providing an opportunity to achieve conversion and selectivity not otherwise obtainable over standard catalysts with fully accessible active sites [23].

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While acidic solutions generally result in removal of (some) aluminium from tetrahedral positions of zeolites, giving dealuminated materials [5, 24, 25], treatment with alkali solutions might bring about various results, depending on the conditions used. For example, treatment with potassium aluminate realuminates the zeolite just under medium conditions, if aluminium source is available as extraframework species or added deliberately to a solution [26–29]. Otherwise, alkali solutions might extract some of silica during more severe treatment. A very limited information on using the desilicated zeolitic materials in catalytic processes is available [29, 30]. We would like therefore to apply treatment with NaOH solutions to various zeolites, to characterize the resultant materials and to screen them in liquid phase transformation of α-pinene. In particular, we wish to report on the isomerization of α-pinene over ZSM-5, ZSM-12 and MCM-22 zeolites and a zeolite/MCM-41 composite, pristine and treated with alkali solutions. Additionally, alkali treatment of ZSM-5, ZSM-12 and MCM-22 under *hydrothermal conditions* is reported here for the first time.

2 Experimental

ZSM-12 and MCM-22 zeolite were synthesized, following conditions given in [31, 32], and ZSM-5 was provided by Zeolyst. The initial Si/Al ratio of all the zeolite samples was 40. The materials were modified by applying desilication with alkali solutions under various conditions. First, desilication was carried out with 0.05, 0.1, 0.5 and 1.0 M NaOH solutions for 1 h, under atmospheric pressure. Second, treatment with NaOH was carried out in Teflon-lined autoclaves at 100 °C under autogeneous pressure.

A composite ZSM-12/MCM-41 type material was obtained under hydrothermal conditions (100 °C, 2 × 24 h), for comparison purposes, by introducing the known amount of CTABr to a mixture of zeolite and sodium hydroxide.

After modification, all the materials were transformed to ammonium forms by ion exchange with 0.5 M ammonium nitrate (4 × 2 h) and finally into the hydrogen forms by calcination at 550 °C. The parent and modified samples were characterized by ^{29}Si & ^{27}Al MAS NMR, FT IR, SEM, XRD, TPD and sorption techniques. N_2 adsorption at 77 K was performed in a Quantachrome Nova 2000 series analyzer. Before the adsorption measurements the samples were heated in vacuum at 300 °C for 20 h. The BET method was applied to calculate the total surface area, while discrimination between micro- and meso-porosity was done by the *t*-plot method.

FTIR spectra were recorded on a Nicolet 6700 FTIR spectrometer. Samples were diluted in KBr prior to analysis. Temperature programmed desorption of ammonia was performed on a homemade apparatus equipped with a Stanford Research Systems RGA 200 detector. The sample was pretreated at 100 °C for 60 min and then cooled to 50 °C at Ar flow (10 cm^3/min). Pure NH_3 was injected until saturation (30 min, 5 cm^3/min), followed by purging with Ar for 60 min (10 cm^3/min). Then temperature was rised from 50 to 650 °C at rate 5 °C/min (Ar 10 cm^3/min).

X-ray diffraction was measured in a PANanlytical X'Pert PRO diffractometer with Bragg-Brentano geometry using Cu Kα radiation, in the 2θ 5–50° range. SEM and TEM images as well as EDAX analysis were recorded on a JEOL JSM 7500F electron microscope (with TEM mode).

Solid state Magic-Angle-Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra of ^{69} Ga nuclei were measured on the APOLLO console (Tecmag) at the magnetic field of 7.05 T produced by the 300 MHz/89 mm superconducting magnet (Magnex). A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to record the ^{29}Si and ^{27}Al MAS-NMR spectra at the spinning speed of 4 and 8 kHz, respectively. ^{29}Si MAS-NMR spectra were acquired using a single 2 μs rf excitation pulse corresponding to $\pi/2$ flipping angle in the liquid, and 256 acquisitions were averaged with the acquisition delay equal to 20 s. For ^{27}Al spectra, a single 2 μs rf excitation pulse corresponded to $\pi/6$ flipping angle in the liquid, and 2,000 scans were acquired with 1 s delay. The frequency scales in ppm were referenced to TMS and to 1 M solution of $Al(NO_3)_3$, for ^{29}Si and ^{27}Al spectra, respectively.

Catalytic tests were carried out in liquid phase at 40–90 °C, using batch type reactors. The reaction products were analyzed by GC (HP 5890) equipped with a packed column and a TCD detector [33].

Scientific visualization techniques help to handle a large/complicated set of experimental data by mapping them into a more convenient graphical form. We have applied one of the algorithms, i.e. Renka–Cline, which is a built-in module in the Origin 7.0 software. It was used for interpolation of scattered desilication data: concentration of NaOH, temperature of treatment and crystallinity of a sample (which is a scalar value associated with concentration and temperature).

First, scattered experimental data points m (x_r, y_r, z_r), where x_r = concentration of NaOH solution, y_r = temperature of treatment, z_r = crystallinity of a sample, were converted into a random matrix (it must be so because NaOH concentration values were not equally spaced). Second, triangulation and partial derivatives computation took place and finally a polynomial surface was calculated. Samples labelling used is as follow: d0585—desilicated with 0.5 M NaOH at 85 °C, d01A—desilicated with 0.1 M

NaOH under hydrothermal conditions at 100 °C. Product distribution is given in mol%.

3 Results and Discussion

3.1 Desilicated Materials

X-ray diffraction patterns of the pristine ZSM-5, ZSM-12 and MCM-22 revealed the presence of reflexes characteristic for the MFI, MTW and MWW structure type (diffractograms not shown). SEM microphotographs show ZSM-5 crystals with the diameter of ca. 0.7–0.8 µm, ZSM-12 crystals with the diameter of ca. 1 µm, and MCM-22 with pellet-like crystals morphology of 1–1.5 µm diameter (Fig. 1).

Treating ZSM-12 samples with alkaline solutions caused significant changes in the morphology of the zeolite crystals and their pore structure, whereas the MTW structure was more resistant towards the treatment and its structure was preserved in whole temperature and sodium hydroxide concentration range. Even mild desilication conditions (i.e. with 0.05 M NaOH solution at 65 °C) results in increasing external surface area due to the mesopores formation. Simultaneously SSA is lowered and micropore area is greatly reduced—some silicon is dissolved and released from the framework, and pore openings are being blocked. Hydrothermal treatment with NaOH also led to lowering of the specific surface area. Simultaneously, insignificant increase of the external surface area (Table 1) was observed. Finally, prolongation of the desilication time (hydrothermal conditions) has not brought about any significant changes in the pore structure of ZSM-12.

^{29}Si NMR spectra revealed the presence of the Q3 and Q4 groupings in the two samples, whereas very intensive ^{27}Al NMR signals were associated with tetrahedral aluminium sites (the intensity of the octahedral species was negligible).

Crystallinity of the samples was determined by XRD measurements and crystallinity degree was calculated as follows:

$$\begin{aligned}&\text{Sum total of sample's intensities}/\\&\quad\text{sum total of a standard intensities} \times 100\%\\&\quad\;= \text{degree of crystallinity}(\%)\end{aligned}$$

A sample with the highest sum total of intensities was chosen as a standard for each series of materials studied.

According to these data, the maps visualizing crystallinity of desilicated materials were calculated using a Renka–Cline gridding method (Fig. 2). As seen, ZSM-5 (left), ZSM-12 (center) and MCM-22 (right) exhibited totally different behaviour in the desilication process. (Note the concentration of NaOH in Fig. 2.) ZSM-5 and ZSM-12 zeolites proved to be more resistant towards alkaline

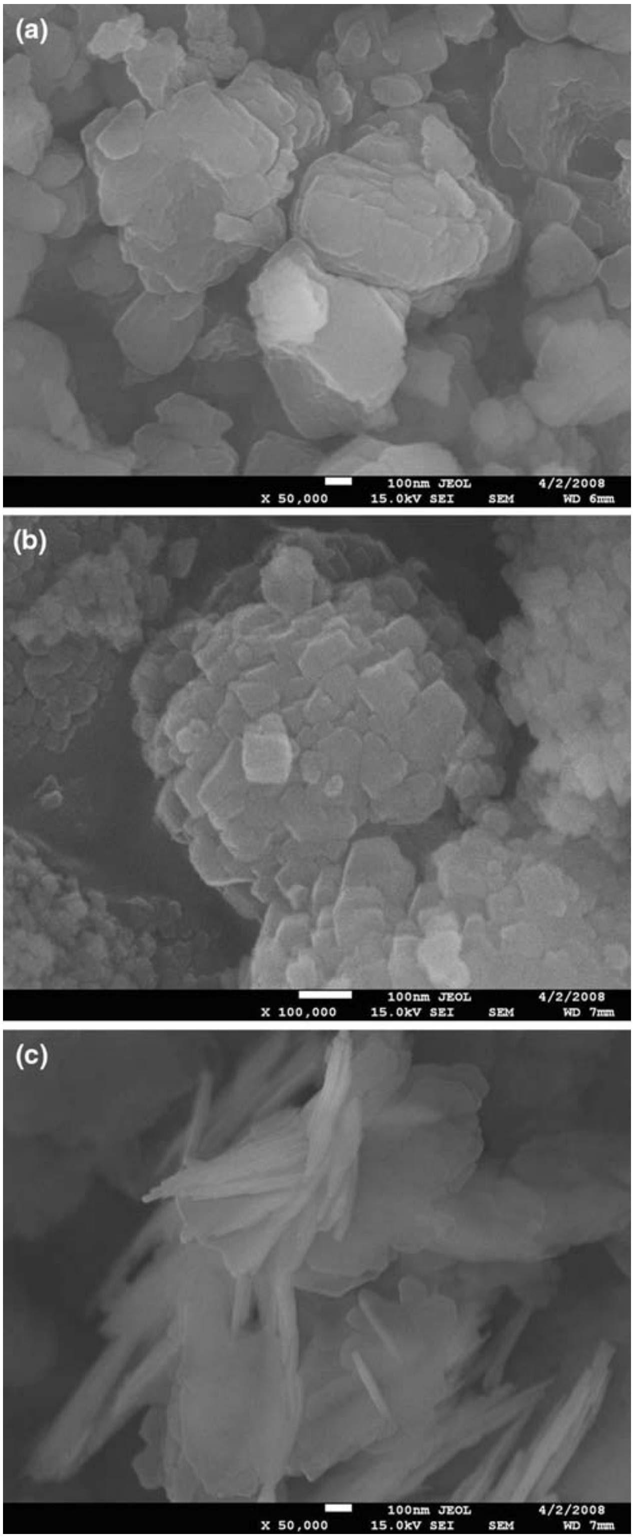

Fig. 1 SEM microphotographs of ZSM-5 (**a**), ZSM-12 (**b**) and MCM-22 (**c**) *samples*

Table 1 Nitrogen sorption data

Sample	SSA (m^2/g)	External surface area (m^2/g)	Micropores area (m^2/g)	Total pores volume (cm^3/g)	Micropores volume (cm^3/g)	Mesopores/total mesopores volume
ZSM-5	347	67	280	0.226	0.140	0.380
MCM-22	418	93	337	0.518	0.160	0.691
ZSM-12	342	103	239	0.279	0.100	0.642
d00565	276	117	159	0.244	0.075	0.692
d00585	264	116	148	0.224	0.075	0.665
d005100	258	104	154	0.234	0.076	0.675
d0185	294	125	169	0.240	0.081	0.662
d01A	268	120	148	0.250	0.076	0.696
d0565	258	154	104	0.362	0.053	0.853
d0585	306	167	139	0.421	0.072	0.829
d05100	283	147	136	0.297	0.066	0.778
d185	280	189	91	0.578	0.043	0.925
d005A	317	107	210	0.331	0.089	0.731
d005A 120 min	310	110	200	0.286	0.086	0.699
d005A 180 min	287	106	181	0.296	0.078	0.736

Samples labelling: d0585, desilicated with 0.5 M NaOH at 85 °C; d01A, desilicated with 0.1 M NaOH under hydrothermal conditions at 100 °C. Product distribution is given in mol%

treatment; their crystallinity was preserved despite the NaOH concentration (0.05–1 M) and temperatures used, even under *hydrothermal conditions* (i.e. more severe alkali treatment).

On the other hand, MCM-22 was much more sensitive to basic solutions. The MCM-22 samples modified with 0.5 M and 1 M NaOH lost their crystallinity and became amorphous. Such a behaviour was in accord with observed earlier—0.5 N NaOH solution led to collapse of the MCM-22 framework [34]. The SEM microphotographs of the desilicated ZSM-5, ZSM-12 and MCM-22 samples revealed that the alkali treatment affected morphology of crystals; the external layers of zeolite crystals were penetrated by NaOH solutions to a greater extent than the crystal core (Figs. 2, 3).

^{29}Si MAS NMR measurements revealed the presence of the Q3 (at 98 ppm) and Q4 (at 120–110 ppm) sites in each unmodified sample (Fig. 4). On the other hand, essentially one strong signal was found in the ^{27}Al MAS NMR spectra, indicating the presence of tetrahedrally coordinated aluminium in the ZSM-5 and ZSM-12 type zeolites (not shown).

On the contrary, two signals corresponding to tetrahedral and octahedral coordination of aluminium were seen in MCM-22 treated with 0.1 and 0.05 M NaOH, respectively (Fig. 4b, top traces). The presence of the octahedral Al species suggested that part of the aluminium was located outside the MCM-22 zeolite framework. The amount of octahedral aluminium in MCM-22, as well as character of the signal, both indicated that Al was not soluble by NaOH solutions under mild conditions (Fig. 4b, two upper traces). The octahedral signal disappeared completely only after hydrothermal treatment with 0.1 M solution (Fig. 4b, bottom). Aluminium species were therefore solubilized by NaOH under such conditions, and could realuminate the solid (as simultaneously the signal at 56 ppm was significantly increased).

Catalytic tests revealed different behaviour of ZSM-5, ZSM-12 and MCM-22 zeolites in liquid phase isomerization of α-pinene (Table 2). As it can be seen, the unmodified ZSM-12 sample, containing mesopores resulting from the morphology of polycrystalline aggregates, was highly active in the reaction carried out at 75 °C. Upon increasing the reaction temperature, a decrease of the α-pinene conversion was observed, probably due to formation of the heavier products affecting diffusion in the parent ZSM-12.

Desilication process led to “cleaning” [35] of the parent zeolite, by dissolving very small contaminations (if present) at the crystal facets, by partly dissolving and removing silicon from the zeolite framework (thus generating intracrystalline mesoporosity), and by destroying agglomerates of zeolite particles.

For ZSM-12 samples modified with 0.05 (results not shown) and 0.1 M NaOH solutions, suppressing of catalytic activity in comparison with the parent sample was observed—the intercrystalline mesopores were mostly diminished, while formation of intracrystalline

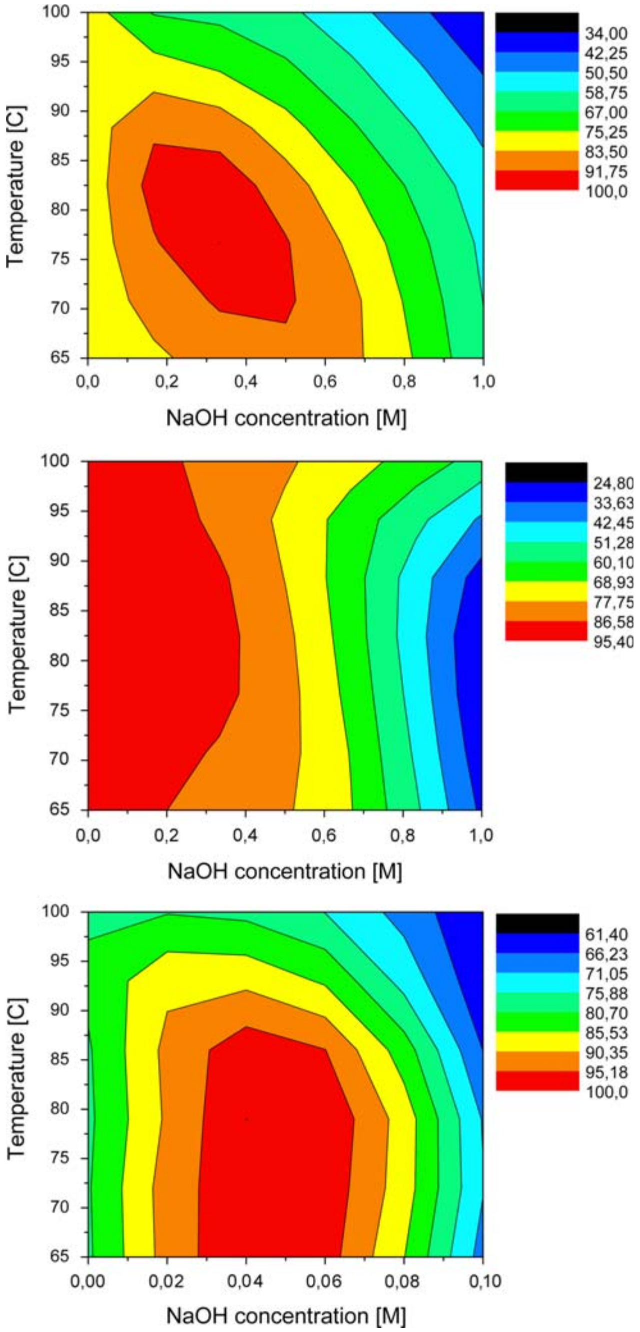

Fig. 2 Crystallinity maps obtained by a Renka–Cline method: ZSM-5 (*left*), ZSM-12 (*center*) and MCM-22 (*right*). The colour scale bars denote crystallinity: from *red* (maximum) to *black* (minimum)

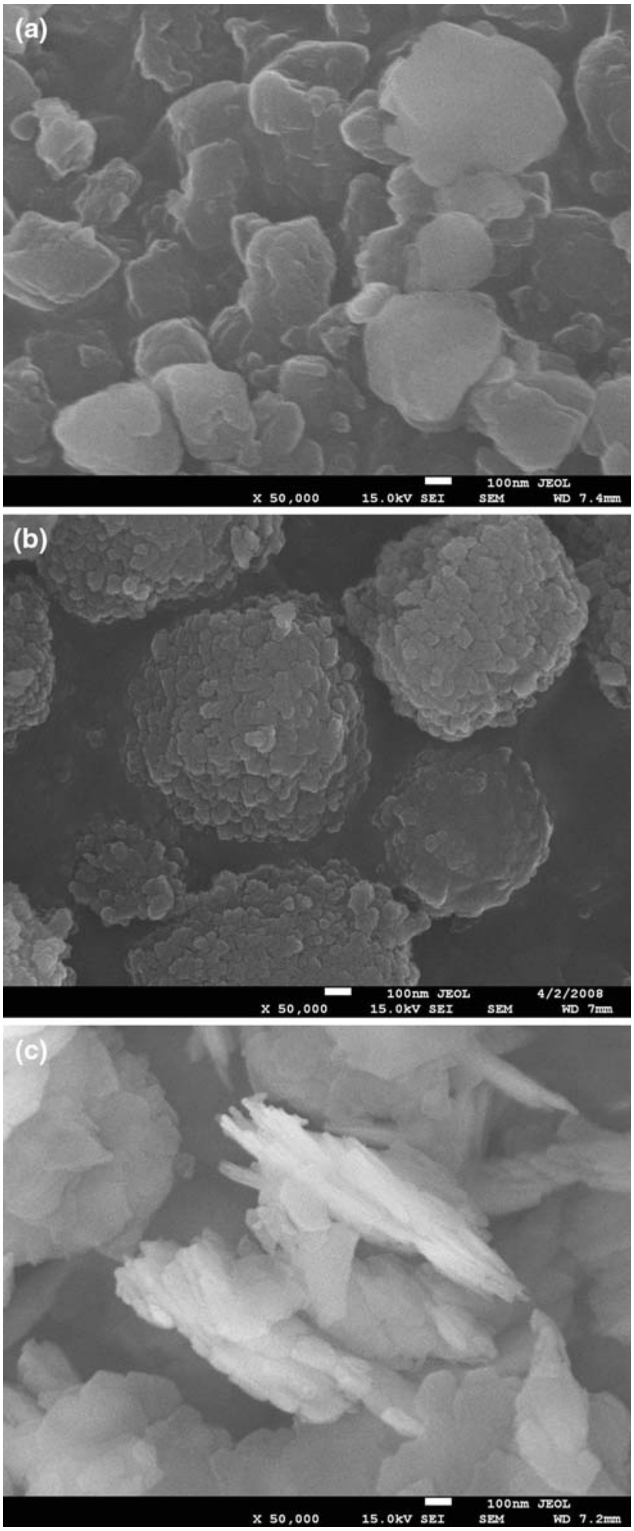

Fig. 3 SEM microphotographs of desilicated ZSM-5 (0.1 M, 85 °C) (**a**), ZSM-12 (0.1 M, 85 °C) (**b**), and MCM-22 (0.1 M, 85 °C) materials (**c**)

mesoporosity was not advanced yet. Nevertheless, the desilicated materials exhibited much higher activity (up to 6–7 times) in the reaction carried out at 90 °C in comparison to the pristine sample. Upon increasing NaOH concentration to 0.5 M the conversion was enhanced to nearly 70%, which was the best result observed for the ZSM-12 samples studied. The selectivity to the main reaction products, camphene and limonene, remained essentially constant for the parent and desilicated materials. (Only upon applying severe *hydrothermal desilication* the selectivity to camphene rose to 45%.).

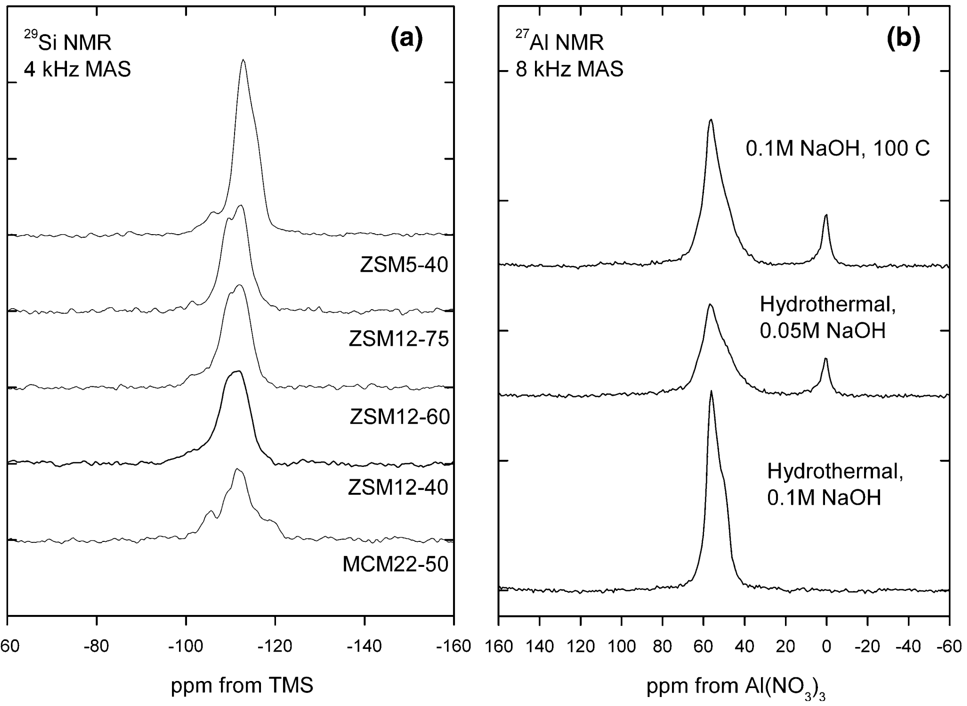

Fig. 4 ^{29}Si MAS NMR spectra of ZSM-5, ZSM-12, MCM-22 (**a**) and ^{27}Al MAS NMR spectra of desilicated MCM-22 samples (**b**)

Table 2 A comparison of the conversion and selectivity in the isomerization of α-pinene for chosen catalysts (reaction time: 60 min)

Sample	NaOH (M)	*T* (°C)	*X* (%)	S_{cam} (%)	S_{lim} (%)	Y_{cam} (%)	Y_{lim} (%)
ZSM-5 unmod	–	75	11.4	33.6	34.3	3.8	3.9
		90	10.0	33.6	34.5	3.3	3.4
d500585	0.05	75	14.7	32.6	32.3	4.8	4.7
		90	8.7	27.5	34.9	2.4	3.0
d50185	0.1	75	9.3	31.4	30.8	2.9	2.9
		90	9.5	29.3	30.3	2.8	2.9
d50585	0.5	75	17.1	33.7	33.1	5.8	5.7
		90	17.2	34.6	32.0	5.9	5.5
d5185	1.0	75	27.5	34.4	34.1	9.5	9.4
ZSM-12 unmod	–	75	43.0	43.0	31.0	18.5	13.3
		90	7.0	35.0	25.0	2.4	1.7
d0185	0.1	75	36.0	38.0	35.0	13.7	12.6
		90	42.0	38.0	35.0	16.0	14.7
d0585	0.5	75	69.0	39.0	34.0	26.9	23.5
d185	1.0	75	41.0	37.0	35.0	15.2	14.4
d01A	0.1	75	23.0	45.0	32.0	10.4	7.4
		90	15.0	31.0	32.0	4.7	4.8
MCM-22 unmod	–	75	77.0	35.0	45.0	26.9	34.6
		90	70.0	36.0	50.0	25.2	35.0
d00585	0.05	75	37.0	35.0	47.0	12.9	17.4
d0185	0.1	75	59.0	38.0	47.0	22.4	27.7
d01A	1.0	75	47.0	36.0	48.0	16.9	22.6

X-conversion, S_{cam}, selectivity to camphene; S_{lim}, selectivity to limonene; Y_{cam}, yield of camphene; Y_{lim}, yield of limonene; *T*, reaction temperature. Samples labelling: d0585, desilicated with 0.5 M NaOH at 85 °C; d01A, desilicated with 0.1 M NaOH under hydrothermal conditions at 100 °C. Product distribution is given in mol%

The other material, MCM-22 type zeolite, exhibited high activity in α-pinene isomerization (70–77%), already if used in the unmodified form (Table 2). Interestingly, the selectivity to limonene was higher for this catalyst (45–50%), and, as for ZSM-12, was not much affected by the NaOH treatment. We did not observe suppressing the catalytic activity for reaction carried out at 90 °C. However, the MWW structure was much more sensitive to the alkali treatment than the MTW one (as MCM-22 samples treated with 0.5 and 1 M NaOH solutions became amorphous), and this had an impact on the catalytic behaviour. Similar to ZSM-12 zeolite, treatment of MCM-22 with diluted alkali solutions resulted in lowering the conversion level (crystallinity of the material was fully retained). In general, for the desilicated MCM-22 samples, suppression of catalytic activity was observed in comparison with the pristine sample. The sample treated with 0.1 M NaOH yielded the highest conversion among the desilicated MCM-22 materials studied.

Finally, the unmodified ZSM-5 sample gave the lowest activity in isomerization of α-pinene, with the conversion of ca. 10% at 75 and 90 °C. Desilication with 0.05 and 0.1 M NaOH solutions (at 85 °C) has not brought any changes to their catalytic activity. However, catalytic behaviour of the samples treated with more concentrated alkali solutions (0.5 and 1.0 M) was altered. Catalytic activity of materials modified with 0.5 and 1.0 M solutions improved, with the conversion levels of ca. 17 and 27%, respectively (reaction temperature 75 °C). Moreover, treatment with NaOH improved the catalytic performance of ZSM-5 for the reaction carried out at 90 °C.

3.2 A ZSM-12/MCM-41 Composite Material

Hydrothermal conditions were applied to synthesis of ZSM-12/MCM-41 composites [36]. We prepared such a sample for comparison purposes, adopting similar synthesis conditions for the composite. XRD pattern of the

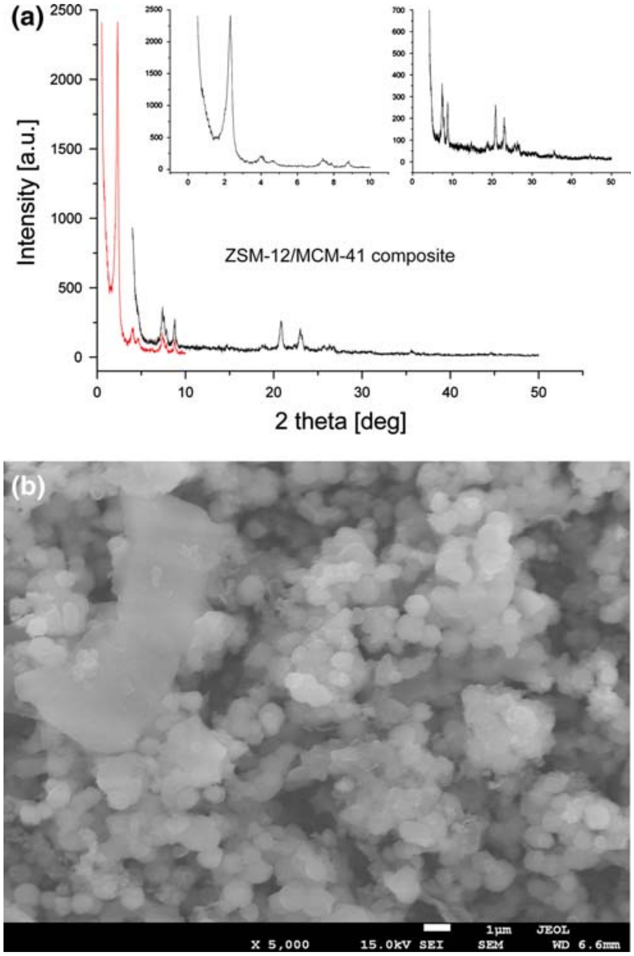

Fig. 5 XRD pattern of a ZSM-12/MCM-41 material (**a**) and its SEM micropohotograph (**b**)

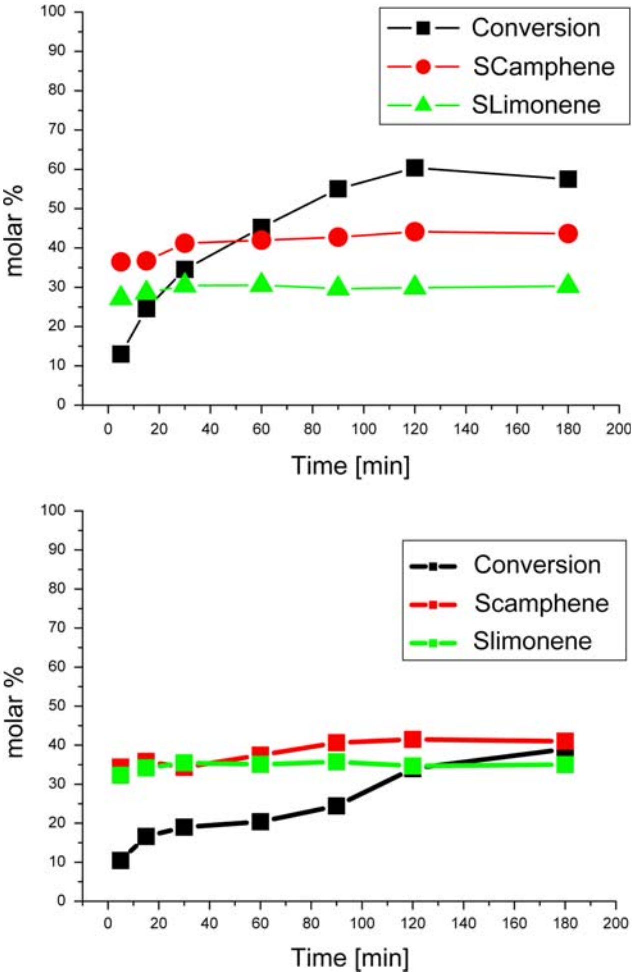

Fig. 6 Catalytic activity of ZSM-12 (*left*) zeolite and a ZSM-12/MCM-41 sample (*right*)

sample obtained showed reflexes characteristic both for ZSM-12 and MCM-41 structure (Fig. 5a). Close inspection of SEM microphotographs reveled that, in fact, the ZSM-12/MCM-41 material was rather a mixture of two phases (with large particles—corresponding to MCM-41 and the smaller ones—to ZSM-12 crystals), and not MCM-41 with included ZSM-12 domains (Fig. 5b).

As it can be seen from Fig. 6, the ZSM-12/MCM-41 sample exhibited lower catalytic activity in comparison to the unmodified ZSM-12 sample (data for the reaction carried out at 75 °C).

4 Conclusions

Desilication process affected pore structure and catalytic activity of the three zeolites of different architecture studied. Low-concentrated NaOH solutions "cleaned" the samples and removed mostly intercrystalline mesoporosity in both cases. The alkali treatment under hydrothermal conditions led to destruction of the MCM-22 structure (0.5 and 1 M NaOH solutions), whereas the ZSM-5 and ZSM-12 structures were not affected in a whole range of basic solutions and modification temperatures used. MCM-22 tend to be more fragile during the process of desilication, and therefore lower catalytic activity was observed for the desilicated samples. ZSM-5 type zeolite modified with 0.5 M and 1.0 M NaOH yielded materials with the improved catalytic activity in α-pinene isomerization. The selectivity to the main reaction products, camphene and limonene, remained essentially constant for all parent and desilicated materials studied here.

A ZSM-12/MCM-41 material was obtained in a form containing the mixture of the two phases. Catalytic activity of this sample was lower in comparison to pristine ZSM-12.

Finally, desilication of ZSM-12 under particular conditions, led to a very active catalyst; the α-pinene conversion was enhanced several times, to give nearly 70%. It was the best result observed up to now over zeolitic catalysts.

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