

# Selective production of light olefins from methanol over desilicated highly siliceous ZSM-5 nanocatalysts

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## ABSTRACT

Highly siliceous ZSM-5 nanocatalysts can dehydrate methanol to a wide range of hydrocarbons. In this study, the development of hierarchical H-ZSM-5 nanocatalysts (Si/Al=200) were reported for the methanol-to-olefins (MTO) reaction. The nanocatalysts were prepared through a hydrothermal technique and treated by NaOH desilication. The parent and desilicated nanocatalysts were characterized using FE-SEM, XRD, FTIR, NH<sub>3</sub>-TPD and N<sub>2</sub> adsorption-desorption techniques. The mesoporosity increased five times without significant collapse of the crystalline framework as a result of the appropriate desilication of H-ZSM-5 nanocatalyst. For the nanocatalyst, a high surface area of 189.5 m<sup>2</sup> g<sup>-1</sup>, mesopore volume of 0.35 cm<sup>3</sup> g<sup>-1</sup> and well-adjusted strong acidity of 0.16 mmol NH<sub>3</sub> g<sup>-1</sup> resulted in a high methanol conversion of 100%, high propylene selectivity of 43% and low light paraffins selectivity of <8% in the MTO reaction. A broad mesopore size of 2-10 nm suppressed coke deposition and provided a long catalytic life time of 75 h. The developed high silica nanocatalyst showed a high potential for industrial applications due to its stable performance. **Polyolefins J (2017) 5: 59-70**

**Keywords:** Hierarchical zeolites; ZSM-5; desilication; nanocatalyst, MTO.

## INTRODUCTION

Among petrochemical products, light olefins (ethylene and propylene) are highly demanded [1]. The current processes including steam cracking and fluid catalytic cracking (FCC) technologies are greatly energy consuming, low olefin yield and oil-dependent feed stock. The shortage of fossil fuel sources, continuously growing oil price and availability of huge natural gas resources have been led to try to find new routes for olefin production. Natural gas, biomass and coal as carbon sources can be converted to the synthesis gas

which, in turn, can be used for producing methanol [2, 3]. Acidic zeolite catalysts dehydrate methanol to a wide range of hydrocarbons. The product distribution in the methanol to olefins (MTO) reaction strongly depends on the catalyst type [4-7]. In general, olefin selectivity and catalytic lifetime are the main issues in the MTO catalyst development, which highlights the necessity of catalyst modification. Among catalyst properties, the acidity and textural specification of catalyst play a key role in the MTO reaction. Desilication treatment extracts silicon species from the zeolite structure, which results in acidity and pore size modification. In preparation

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of a hierarchical catalyst several parameters, for example, type of zeolite, Si/Al ratio, and operational conditions influence its performance [8-11]. Fathi et al. [12] modified ZSM-5 (Si/Al=15) catalyst by alkaline treatment ( $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and NaOH solution) at  $75^\circ\text{C}$  for 3 h and evaluated its properties for using in the methanol to gasoline (MTG) reaction. They found that NaOH treatment (0.1 M) reduced the acidity and created mesoporous structure more than other solutions. The sample treated by  $\text{Na}_2\text{CO}_3$  provided the highest  $\text{C}_{5+}$  cut yield (ca. 43 %) and the longest catalytic lifetime (4 h). Ahn et al. [13] tuned diffusion and acid sites concentration of H-ZSM-5 catalyst (Si/Al=36) for the methylation of toluene. They applied 0.2 M NaOH solution at  $67^\circ\text{C}$  under stirring for 0.75 h. The treatment increased the surface area ( $482 \text{ m}^2 \text{ g}^{-1}$ ), mesopore volume ( $0.05 \text{ cm}^3 \text{ g}^{-1}$ ) and total acidity ( $537 \text{ pyridine } \mu\text{mol g}^{-1}$ ). Desilication decreased effective diffusion length which led to the high toluene turnover rate. Yingping et al. [14] studied desilication of ZSM-5 (Si/Al=13) by tetrapropyl ammonium hydroxide (TPAOH) solution ( $0.1 \text{ mol L}^{-1}$ ) for different treatment durations (24, 48 and 72 h) at  $170^\circ\text{C}$ . The modification increased the surface area, mesopore volume and total acidity, which resulted in the lifetime increasing (170 h) in the MTG reaction.

Ghavipour et al. [15] reported the desilication of H-ZSM-5 catalyst (Si/Al=19) with 0.2 M NaOH solution at  $80^\circ\text{C}$  for 3 h. The treated catalyst represented the high methanol conversion (ca. 98 %) and propylene selectivity of ca. 19.3 % after 6 h time on stream. Bleken et al. [16] studied the effect of desilication on the deactivation of H-ZSM-5 (Si/Al=50) catalyst through the methanol to hydrocarbon (MTH) reaction. The catalyst was treated with 0.3 M NaOH solution ( $33 \text{ cm}^3 \text{ g}^{-1}$ ) for 30 min at  $70^\circ\text{C}$ . They found that the desilicated catalyst included more external coke than the parent sample, which could be explained by the lower diffusion resistance and faster hydrocarbon exit. Kim et al. [17] prepared mesopore MFI zeolite catalyst (Si/Al=25) using 0.2 M NaOH solution at  $60^\circ\text{C}$  for 30 min and applied for the MTO reaction. The modified catalyst included the high surface area ( $402 \text{ m}^2 \text{ g}^{-1}$ ) and mesopore volume ( $0.19 \text{ cm}^3 \text{ g}^{-1}$ ). The desilication increased the catalytic lifetime up to 80 h due to facile diffusion of coke precursors from the micropores to the external surface. They concluded a roughly linear correlation between the mesoporosity and H-ZSM-5 catalytic lifetime in the MTO reaction. Mochizuki et al. [18] studied the desilication of H-ZSM-5 (Si/Al=50) by alkaline treatment (0.05, 0.1 and 0.2 M

NaOH) at  $80^\circ\text{C}$  for 1-5 h and characterized in hexane cracking. The high NaOH concentration provided the high surface area ( $520 \text{ m}^2 \text{ g}^{-1}$ ) and less acid concentration ( $0.34 \text{ mmol NH}_3 \text{ g}^{-1}$ ). Schmidt et al. [19] synthesized hierarchical ZSM-5 zeolites (Si/Al=50, 140 and 300) by alkaline desilication including N,N,N-trimethylhexadecylammonium bromide (CTAB) as surfactant. 0.5 M NaOH solution including 0.05 M CTAB resulted in the high surface area ( $663 \text{ m}^2 \text{ g}^{-1}$ ) and total pore volume ( $0.7 \text{ cm}^3 \text{ g}^{-1}$ ). The treatment increased the catalytic life time up to 100 h including the maximum propylene selectivity of ca. 27 % in the MTO reaction. It is reported that the desilication of ZSM-5 depends on treatment temperature, alkaline solution concentration and time [8, 20, 21].

Only a few research has been performed on the desilication of high silica H-ZSM-5 catalyst and its application for the MTO reaction. However, it is accepted that the mentioned catalyst represents the best performance including the high methanol conversion and olefin selectivity [10, 22, 23]. Consequently, development of an appropriate desilication treatment for the high silica H-ZSM-5 nanocatalyst favors development of an appropriate MTO catalyst. In this study, the main aim was to adjust the acidity and textural properties of high silica H-ZSM-5 nanocatalyst for the MTO reaction through desilication. The appropriate desilication conditions provided a hierarchical nanocatalyst with the high mesoporosity, the less framework destruction and the improved catalytic performance.

## EXPERIMENTAL

### Materials

All the reagents, including silicic acid ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , > 99 wt. %), sodium aluminate ( $\text{NaAlO}_2$ ,  $\text{Al}_2\text{O}_3$  wt. % = 55), tetrapropyl ammonium bromide (TPABr,  $\text{C}_{12}\text{H}_{28}\text{BrN}$ , >99 wt. %), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , 99 wt. %), sodium hydroxide (NaOH, 99.6 wt. %) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98 wt. %) were purchased from Merck company (Germany).

### Nanocatalyst preparation

High silica H-ZSM-5 zeolite catalyst (Si/Al=200) was synthesized by hydrothermal technique. A solution containing NaOH (5.58 g), sodium aluminate (0.46 g) and deionized water ( $66 \text{ cm}^3$ ) was stirred for 30 min. TPABr (13 g) was then added and stirred for 1

h (solution A). Simultaneously, silicic acid (67 g) was dissolved in 100 cm<sup>3</sup> of deionized water (solution B). The solution A was added to the solution B drop by drop under continuous agitation and stirred for 2 h. An appropriate amount of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 %, Merck) was used to adjust the pH of solution (10.5). The final solution included the molar composition of 20SiO<sub>2</sub>: 0.05Al<sub>2</sub>O<sub>3</sub>: 1TPABr: 1.5Na<sub>2</sub>O: 200H<sub>2</sub>O. The crystallization was carried out in a static stainless-steel autoclave at 180°C under autogenous pressure for 48 h. The synthesized powder was filtered, washed, dried at 110°C overnight and then calcined at 540°C for 24 h (3°C/min) in air. The H-form ZSM-5 was prepared by four times ion-exchange with using 1M NH<sub>4</sub>NO<sub>3</sub> (99 wt. %, Merck) solution for 10 h at 90°C under continuous agitation, followed by calcination at 540°C for 12 h (3°C/min) in air. The parent nanocatalyst was denoted as PZ.

Hierarchical nanocatalysts were prepared from calcined ZSM-5 zeolite. The treatment was done in 0.3 M aqueous solution of NaOH at 65°C for different durations (30 and 60 min). The modified solid was filtered, washed and dried at 110°C for 12 h. The H-form of powder was prepared by ion-exchange with a 1M NH<sub>4</sub>NO<sub>3</sub> (99 wt. %, Merck) solution for 10 h at 90°C under continuous agitation, followed by calcination at 540°C for 12 h (3°C/min) in air. The prepared hierarchical nanocatalysts were denoted as DSZ<sub>x</sub>, where x is the time of desilication process.

### Characterization techniques

X-ray diffraction (XRD) experiments were carried out with a D8 Advance Bruker AXS X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation ( $\lambda=0.15418$  nm) and  $2\theta$  variations in the range of 4-50° at 40 kV. A KYKY (Model, EM3200) equipment determined field-emission scanning electron microscopy (FE-SEM) images at a potential difference of 26 kV. Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD, Micromeritics, USA) with an on-line TCD detector characterized acidity. 53.6 mg of each sample was pretreated at 550°C for 4 h. The powders were saturated with NH<sub>3</sub> for 1 h in the micro reactor and helium flow passed over the sample with a heating rate of 10°C min<sup>-1</sup>. The range of desorption temperature was 100-700°C. N<sub>2</sub> adsorption-desorption technique at -196.2°C (Quantachrome, USA) analyzed textural properties. The powders were degassed at 300°C for 3 h and then Brunauer-Emmet-Teller (BET) surface

area was measured. The total surface area (S<sub>BET</sub>) and total pore volume (V<sub>total</sub>) were determined using the BET isothermal equation and the nitrogen adsorbed volume at P/P<sub>0</sub> = 0.99, respectively. The t-plot method provides the micropore volume (V<sub>micro</sub>). The mesopore volume (V<sub>meso</sub>) is difference of the calculated total data and the corresponding micropore data. FTIR measurements were in a Nexus model infrared spectrophotometer (Nicolet Co, USA) at the resolution of 4 cm<sup>-1</sup>. The samples were prepared as self-supported wafers containing 1 wt. % of the powder in KBr.

### Catalyst testing

Methanol was converted to olefins over the nanocatalysts in a fixed-bed continuous-flow reactor set-up including a stainless steel tube reactor (450 mm length, 11 mm ID) [24]. A temperature-controlled three-zone furnace provided a constant temperature to the entire reactor. A K-type thermocouple probe near the nanocatalyst bed monitored the operational temperature. The operational condition was set as 480°C, atmospheric pressure and methanol weight hourly space velocity (WHSV) of 0.9 h<sup>-1</sup>. The nano catalysts were stabled, crushed and sieved to get 16-25 mesh particle size for the experiments. The nanocatalysts loading was 4 g and a HPLC infusion pump supplied the feed (methanol/water = 1 wt. /wt.). The activation of nanocatalysts was examined in-situ at 300°C for 2 h (heating rate of 3°C min<sup>-1</sup>) under N<sub>2</sub> flow. A heat-traced tube (120°C) was applied to avoid hydrocarbon condensation through the transfer line between the reactor and separator vessel. A micro gas chromatograph (Varian CP-4900) equipped with a TCD detector analyzed the up-stream of separator vessel (gas phase). The bottom stream in both aqueous and organic parts was separated. An off-line gas chromatograph (Varian CP-3800) equipped with TCD and FID detectors characterized the aqueous part. The organic part was analyzed by the off-line gas chromatograph (Varian CP-3800) equipped with an FID detector.

## RESULTS AND DISCUSSION

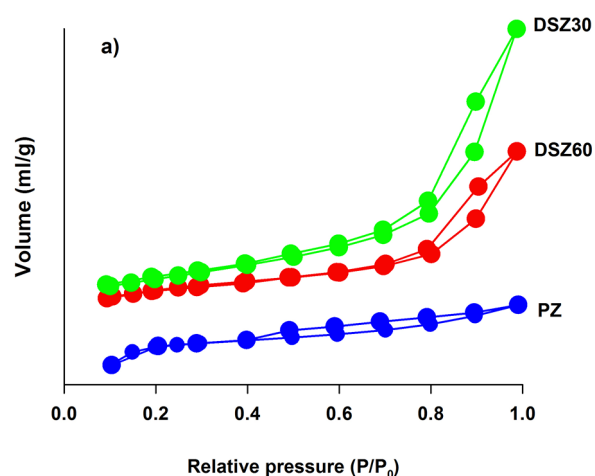
### Structural and textural parameters of nanocatalysts

XRD patterns confirm that the resulting hierarchical nanocatalysts include the zeolite structure and the ap-

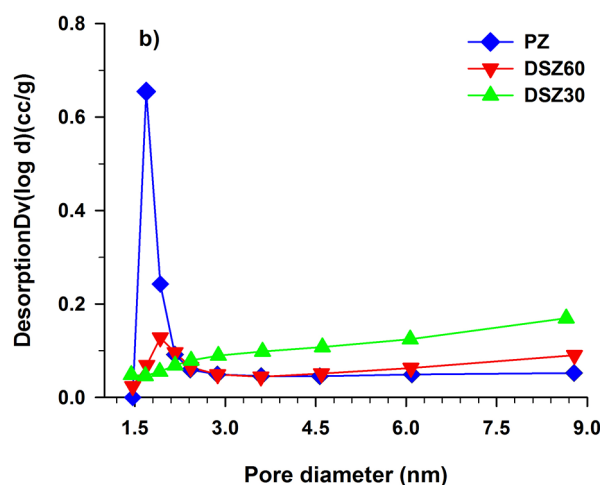
plied desilication have not changed the structure significantly. The relative crystallinity is the ratio of the large peak area found at  $2\theta=22.5-25^\circ$  to that of the parent nanocatalyst. The alkali treatment decreases the relative crystallinity from 100 % to 82 % (Table 1) due to the slightly destruction of zeolite framework during Si extraction [25]. The microporous and mesoporous structures of nanocatalysts lead to the common Langmuir isotherms including types I and IV (Figure 1). Capillary condensation in mesoporous structures occurs at the high relative pressure of adsorbate. The mesoporosity in the alkali-treated ZSM-5 nanocatalysts includes both inter- and intraparticle mesopores. The isotherms represent a hysteresis loop in  $N_2$  adsorption-desorption of the nanocatalysts as result of intraparticle mesopores (Figure 1). The isotherms show a sub-step in the low relative pressure ( $P/P_0=0.1-0.2$ ) due to fluid-to-crystalline like phase transition of the adsorbed nitrogen [26]. This common phenomenon does not indicate the additional mesopore formation [27]. It worth to note that the isotherms of treated nanocatalysts show a sharp increasing in the high relative pressure ( $P/P_0=1$ ). It reveals the interparticle mesopores formation between the ZSM-5 zeolite particles. The crystal agglomeration results in mesoporous structure in the form of interparticle spaces which is different from the intraparticle mesopores.

The pore size distribution of nanocatalysts confirms the formation of mesopores in the structures (Figure 1). The broad maximum in diameter shifts from ca. 1.70 nm to ca. 2.2 nm for the DSZ30 nanocatalyst. The DSZ60 nanocatalyst includes mesopores with a broad pore size distribution (2-10 nm) as a result of the high treatment temperature ( $65^\circ\text{C}$ ) and the longer treatment duration (60 min). Groen et al. [20] reported that the mesopore size can be adjusted by temperature and time of alkali treatment. The calculated textural data reveal the high surface area and mesopore volume of treated nanocatalysts (Table 1). The surface area reduction can be explained by the zeolite framework destroying owing to Si extraction and extra-framework formation through desilication.

Long-time desilication (DSZ60) extracts more Si



(a)



(b)

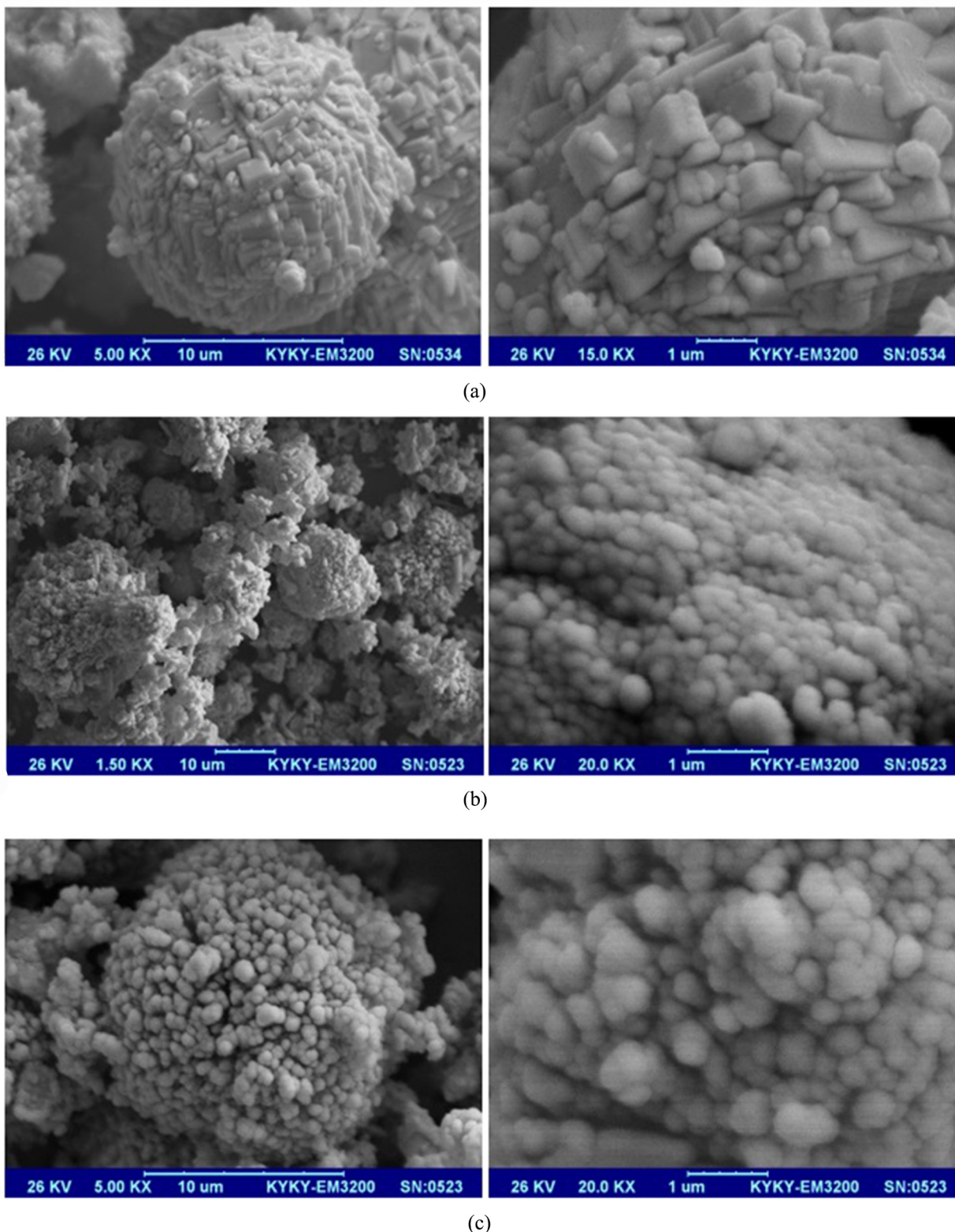
**Figure 1.**  $N_2$  adsorption-desorption isotherms and BJH pore size distribution of the nanocatalysts.

which leads to more reduction in the crystallinity. The results are in consistent with the XRD results. You et al. [25] studied desilication of ZSM-5 catalyst ( $\text{Si}/\text{Al}=12$ ) using 0.2-0.6 M aqueous solution of NaOH at  $65^\circ\text{C}$  for 2 h. They found that framework Al (FAL) content decreased significantly through the harsh desilication (0.4 M NaOH solution) owing to the formation of more extra framework Al (EFAL) content. Furthermore, long-time desilication favored the mesopore volume formation but decreased the micropore volume.

**Table 1.** Crystallinity and textural data.

Sample	Crystallinity (%)	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	$V_{\text{total}}$ ( $\text{cm}^3\text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3\text{g}^{-1}$ )	$V_{\text{meso}}$ ( $\text{cm}^3\text{g}^{-1}$ )
PZ	100.00	263.30	0.16	0.10	0.06
DSZ30	88.14	161.90	0.23	0.02	0.21
DSZ60	82.45	189.50	0.36	0.01	0.35





**Figure 2.** FE-SEM images of the nanocatalysts (a) PZ; (b) DSZ60; (c) DSZ30.

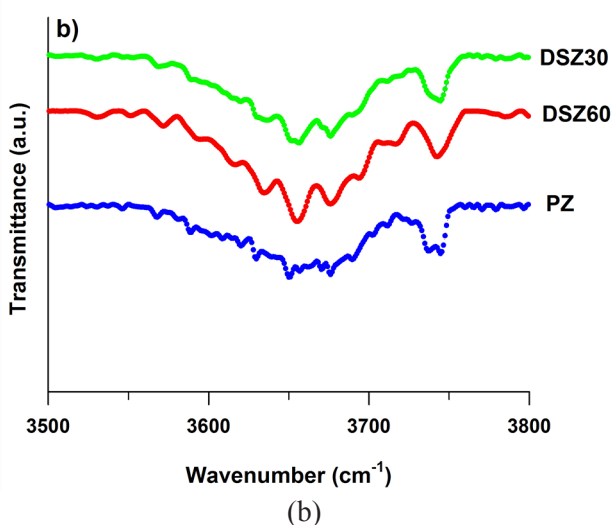
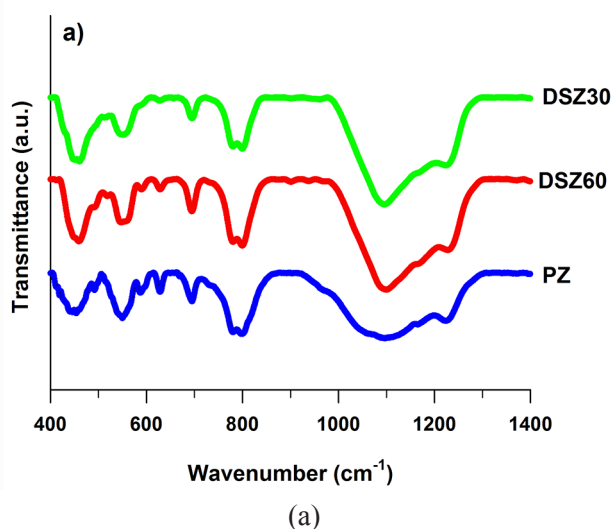
FE-SEM images show relatively uniform surface morphology (Figure 2). The nanocatalysts are in the form of spherical aggregation. TEM images of individual microsphere surface confirmed that nanosized crystals aggregation formed the microspheres [28, 29]. It

worth noting that the applied desilication process does not destroy morphology which agrees with the XRD results. The surface of nanocatalysts becomes rough after treatment and the edges of ZSM-5 particles have been melted and taken spherical shape. The results are

in agreement with literature [30, 31].

### FTIR analysis of nanocatalysts

FTIR spectra of the nanocatalysts were recorded in the range of 400-4000  $\text{cm}^{-1}$ . Internal  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral lead to the band near ca. 450  $\text{cm}^{-1}$  (Figure 3a). The band around ca. 550  $\text{cm}^{-1}$  indicates the ZSM-5 zeolite with five membered rings. The adsorptions at ca. 800  $\text{cm}^{-1}$  and ca. 1100  $\text{cm}^{-1}$  can attribute to the symmetric stretching of external and internal linkages, respectively. The existence of structures with four chains of 5-rings results in the band at ca. 1225  $\text{cm}^{-1}$ . FTIR spectra in the range of 3500-3800  $\text{cm}^{-1}$  can be used to investigate surface hydroxyl (OH) groups (Figure 3b). The band at ca. 3610  $\text{cm}^{-1}$  is assigned to the vibration of bridging Si-OH-Al groups [32, 33].



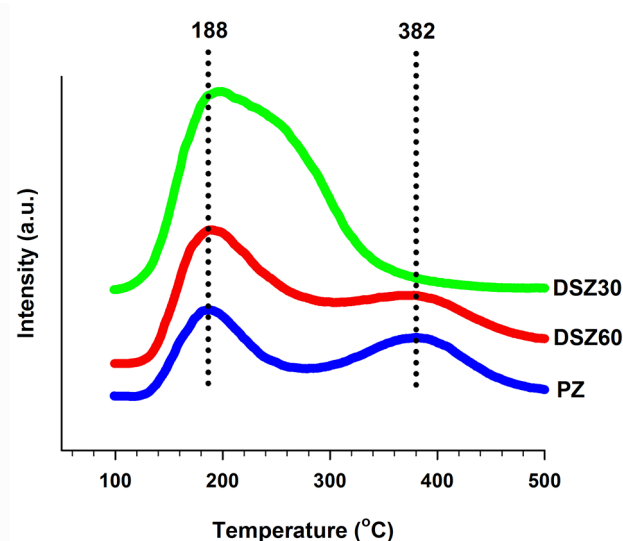
**Figure 3.** FTIR spectra of the nanocatalysts in the range of (a) 400-1400  $\text{cm}^{-1}$ ; (b) 3500-3800  $\text{cm}^{-1}$ .

The intensity of 3610  $\text{cm}^{-1}$  band increases through the alkali treatment. This phenomenon can be explained by the selective Si atom extraction and formation of the Si(OH)Al groups [34]. The band at 3680  $\text{cm}^{-1}$  characterizes EFAl species (Al-OH) in the nanocatalysts [35]. The band at ca. 3750  $\text{cm}^{-1}$  can be assigned to the vibrations of the isolated Si-OH silanols located on the external surface or mesopores surface [8]. The intensity of 3750  $\text{cm}^{-1}$  band for the DSZ60 nanocatalyst is higher than that for the parent nanocatalyst which reveals the secondary mesopores generation and supports the  $\text{N}_2$  adsorption-desorption results.

### $\text{NH}_3$ -TPD analysis of nanocatalysts

The parent and DSZ30 nanocatalysts represent similar  $\text{NH}_3$ -TPD pattern including different strength and amount of the acid sites (Figure 4). According to the method of Ramirez [36], the relative concentrations of weak (100-200 $^{\circ}\text{C}$ ), medium (200-300 $^{\circ}\text{C}$ ) and strong (>300 $^{\circ}\text{C}$ ) acid sites were determined (Table 2). Alkali treatment decreases the percentage of strong acid sites while increases the weak and medium acidity. Desilication for the long time removes the strong acid sites and thereby the DSZ60 nanocatalyst represents no peak in the high temperature range. You et al. [25] found that alkali treatment of H-ZSM-5 zeolite with NaOH solutions (0.2 and 0.4 M at 65 $^{\circ}\text{C}$  for 2 h) eliminated the strong acid sites and increased the strength and concentration of weak acid sites.

Tarach et al. [21] reported that desilication process resulted in the formation of acid sites which were located individually inside micropores. The maximum



**Figure 4.**  $\text{NH}_3$ -TPD profiles of the nanocatalysts.

**Table 2.** Acidity of the nanocatalysts.

Sample	Acidity (mmol NH <sub>3</sub> g <sup>-1</sup> )		
	PZ	DSZ30	DSZ60
Weak	0.17 (24 %)	0.27 (24 %)	0.64 (31 %)
Medium	0.20 (28 %)	0.42 (37 %)	1.25 (61 %)
Strong	0.34 (48 %)	0.44 (39 %)	0.16 (8 %)
Total	0.71	1.13	2.05

temperature of peaks shifts toward the higher temperatures which indicates the higher strength of acid sites for the treated nanocatalysts compared with the parent nanocatalyst. The results are in consistent with literature [37-39].

It worth mentioning that the concentration of strong and weak acid sites attribute to Si and Al content in zeolite framework, respectively. The strength of acidity is in the order of Al>>Si [40, 41]. Consequently, the preferential removing of framework Si and the increased Al concentration by formation of more Al-OH groups result in the high strength and concentration of weak acid sites in the alkali-treated nanocatalysts. The weak acid sites assigned to EFAl and the strong acid sites depend on the -OH groups of FAI[42, 43]. The NH<sub>3</sub>-TPD results support the FTIR results.

### Catalytic test in MTO reaction

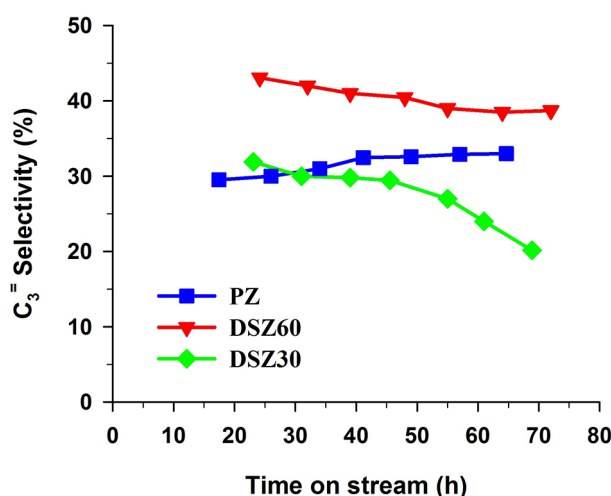
Methanol dehydration is an acid-catalyzed reaction which provides wide range of hydrocarbons. The MTO reaction was carried out in a fixed bed reactor over the parent and hierarchical nanocatalysts. The operational conditions were 480°C, atmospheric pressure, methanol WHSV of 0.9 h<sup>-1</sup> and 50 wt. % methanol in water solution as feed. The high methanol conversion (100 %) was obtained over the nanocatalysts for the long time on stream. Both acidic properties and accessibility of acid sites to the molecules of reagent influence the catalytic activity of the nanocatalysts. It is well accepted that the framework structure, pore architecture and acidity of zeolite catalysts control their performance in the MTO reaction [44-46].

Based on the hydrocarbon pool mechanism, the MTO reaction includes the following three main steps: i) methanol dehydration and dimethyl ether (DME) formation, ii) the initial C-C bond formation, and iii) higher production of hydrocarbons from the primary products.

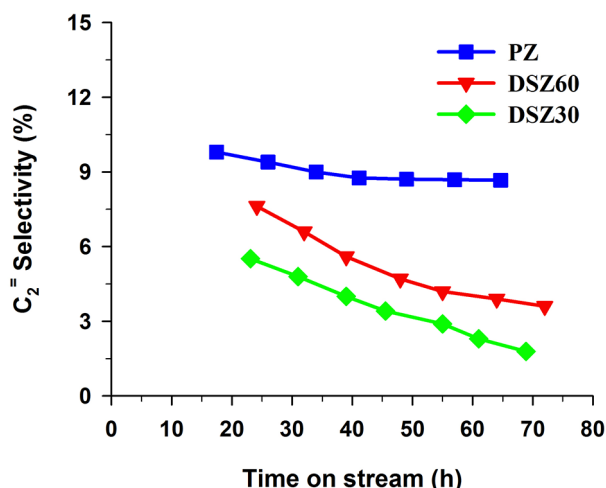
The weak acid sites carry out methanol to DME conversion [24, 47] as well as alkylation and methylation reactions [48]. The strong acid sites initiate C-C bond generation and also coke formation in the

MTO reaction [35, 49]. Therefore, the strong acidity of catalyst leads to the shorter catalytic lifetime due to the fast deactivation. The high surface area and mesopore volume facilitate the component diffusion out of the pores and decrease the diffusion resistance which hinder pore blocking by coke deposition. In this regards, the DSZ60 nanocatalyst represents the highest propylene selectivity (ca. 43 %) in the MTO reaction (Figure 5). The prolonged treatment (60 min) at alkaline solution results in the high surface area (189.5 m<sup>2</sup> g<sup>-1</sup>) and high mesopore volume (0.35 cm<sup>3</sup> g<sup>-1</sup>). The mesopore formation is beneficial for the more accessibility of surface acid sites to the reactants. The acidity of catalyst is a crucial parameter for catalytic activity through the MTO reaction [47, 50]. The variation of acid sites influences product distribution and rate of deactivation. The weak and medium acid sites enhance propylene production through the alkylation and methylation reactions. The strong acid sites are the main active sites for the conversion of light olefins to paraffins, aromatics, naphthenes and higher olefins. The medium acidity results in more light olefins, less low-value hydrocarbons, less coke formation and long catalytic lifetime [51-53]. Therefore, the high concentration of weak and medium acid sites for the DSZ60 nanocatalyst supports the high propylene selectivity.

The higher concentration and strength of strong acid sites compared with the parent nanocatalyst lead to the high rate of alkene methylation reactions over the DSZ30 nanocatalyst which produces more heavy hydrocarbons (C<sub>5+</sub>). Sevell et al. [54] considered trimethylbenzene (triMB) as main hydrocarbon pool interme-



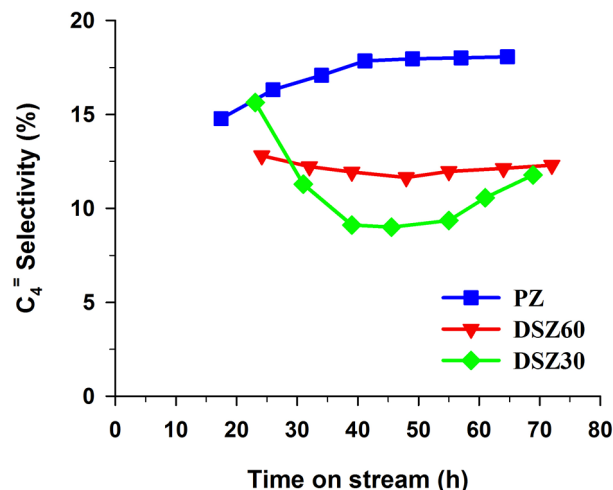
**Figure 5.** Propylene selectivity over the nanocatalysts with time on stream (reaction conditions: T=480°C, WHSV=0.9 h<sup>-1</sup>, P=1 atm, methanol/water 1:1 by weight).



**Figure 6.** Ethylene selectivity over the nanocatalysts with time on stream (reaction conditions:  $T=480^{\circ}\text{C}$ ,  $\text{WHSV}=0.9\text{ h}^{-1}$ ,  $P=1\text{ atm}$ , methanol/water 1:1 by weight).

diates for the MTO reaction over the H-ZSM-5 catalyst. They found that the MTO reaction occurred through a dual-cycle mechanism. Ethylene and toluene are the products of triMB cracking (cycle I), while alkene methylation and cracking reactions produce propylene and higher olefins (cycle II). The results show that the small pore dimension forces the hydrocarbon pool via smaller aromatics intermediates which favors ethylene production. Consequently, compared with the pore size of the parent nanocatalyst, the large pore size of alkaline-treated nanocatalysts leads to low ethylene selectivity (Figure 6). Deactivation of strong acid sites with time on stream decreases the triMB cracking rate as well as the rate of ethylene production. As a result, the drop in the ethylene selectivity with time on stream over the nanocatalysts is in agreement with the dual-cycle mechanism.

The methylation of light olefins produces butene through the MTO reaction [54]. Wu et al. [55] found that  $\text{C}_4=$  oligomerization produced  $\text{C}_8=$  olefin. In general, butene selectivity decreases over the alkali-treated nanocatalysts (Figure 7). This phenomenon can be explained by the catalyst deactivation which reduces cracking rate. Increasing trend of  $\text{C}_4=$  selectivity



**Figure 7.** Butene selectivity over the nanocatalysts with time on stream (reaction conditions:  $T=480^{\circ}\text{C}$ ,  $\text{WHSV}=0.9\text{ h}^{-1}$ ,  $P=1\text{ atm}$ , methanol/water 1:1 by weight).

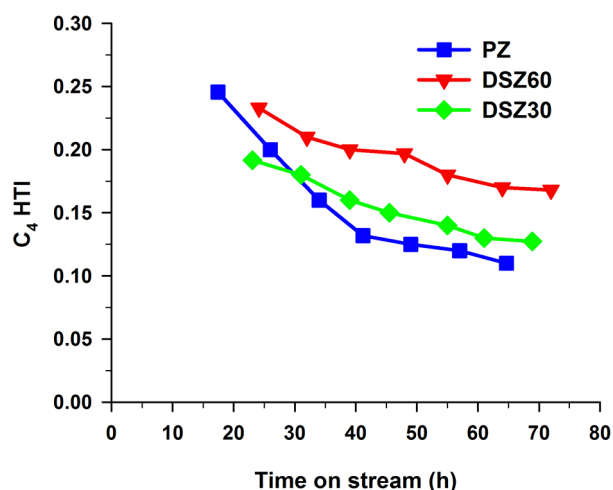
over the PZ nanocatalyst can be attributed to the low strength of strong acid sites and thereby the low rate of  $\text{C}_4=$  oligomerization. The high butene selectivity at the end of time on stream over the DSZ60 nanocatalyst indicates the fast deactivation of nanocatalyst.  $\text{C}_4$  hydrogen transfer index (HTI) reveals the progress of hydrogen transfer reactions over the nanocatalyst [56].  $\text{C}_4$  HTI is the ratio of butane yield (iso- $\text{C}_4$  and n- $\text{C}_4$ ) to the total  $\text{C}_4$  hydrocarbons yield (alkanes and alkenes). The nanocatalysts represent decreasing trend of  $\text{C}_4$  HTI (Figure 8) because coke formation reduces the acid sites density as well as the rate of hydrogen transfer and cyclization reactions.

The high  $\text{C}_4$  HTI of DSZ60 nanocatalyst is in consistent with the overall decreasing trend of  $\text{C}_4=$  selectivity. The high weak and medium acidity of DSZ60 nanocatalyst promotes butene consumption by methylation reaction. The prolonged alkali treatment (DSZ60) generates more mesopore structures which leads to the high heavy hydrocarbons selectivity (Table 3). The high mesopore volume accelerates olefins desorption. The large pore size is beneficial for the easy exit of heavy hydrocarbons and the low rate of coke formation.

**Table 3.** Average heavy hydrocarbons selectivity for the nanocatalysts.

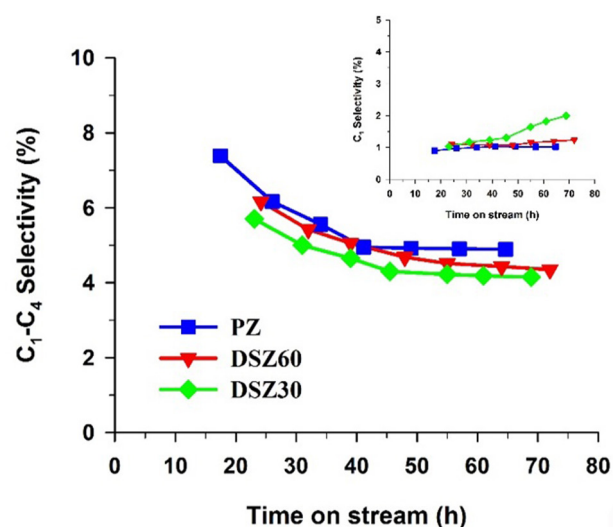
Characteristic	Selectivity (%)						
	$\text{C}_5$	$\text{C}_6$	$\text{C}_7$	$\text{C}_8$	$\text{C}_9$	$\text{C}_{10+}$	Total
PZ	3.56	7.46	0.87	1.60	0.68	0.20	14.37
DSZ30	4.28	11.18	1.48	3.37	2.98	1.29	24.58
DSZ60	5.08	13.57	1.98	3.19	2.47	0.58	26.87





**Figure 8.** C<sub>4</sub>-HTI for the nanocatalysts with time on stream (reaction conditions: T=480°C, WHSV=0.9 h<sup>-1</sup>, P=1 atm, methanol/water 1:1 by weight).

The nanocatalysts represent a similar trend for the light paraffins (C<sub>1</sub>-C<sub>4</sub>) selectivity (Figure 9). Catalyst deactivation decreases the selectivity with time on stream. Coke formation blocks the pores and does not allow the methanol molecules to access to the acid sites. Hence, more methanol molecules are adsorbed on the basic sites and decomposed to CO, CO<sub>2</sub> and CH<sub>4</sub> components. The parent nanocatalyst produces less aromatics and more paraffins, which agree with the low mesopore volume and high strong acidity. The low light paraffins selectivity over the hierarchical nanocatalysts (< 6 %) confirms their stable performance. The large pore size suppresses the coke deposition and catalyst deactivation. Furthermore, the high



**Figure 9.** Light paraffins selectivity over the nanocatalysts with time on stream (reaction conditions: T=480°C, WHSV=0.9 h<sup>-1</sup>, P=1 atm, methanol/water 1:1 by weight).

mesopore volume increases the access of methanol molecules to the internal acid sites.

## CONCLUSION

High silica hierarchical H-ZSM-5 nanocatalysts have prepared and characterized for the MTO reaction. The appropriate desilication process extracted Si species with no change in the structure of parent nanocatalyst. Alkali treatment increased the mesoporosity and medium acidity by more than five and two folds, respectively. Consequently, the developed hierarchical nanocatalyst represented the high propylene selectivity for the long catalytic lifetime. The reported desilication process is an excellent post treatment for the high silica H-ZSM-5 nanocatalyst which enhances its catalytic activity under conditions relevant to the industrial MTO process. The results could improve the comparability of the MTO process with the conventional processes for production of light olefins.

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