Contents lists available at ScienceDirect

# Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

# Enhancing activity without loss of selectivity – Liquid-phase alkylation of benzene with ethylene over MCM-49 zeolites by TEAOH post-synthesis



# Yanchun Shi, Enhui Xing, Wenhua Xie, Fengmei Zhang\*, Xuhong Mu, Xingtian Shu

State Key Laboratory of Catalytic Materials and Reaction Engineering, Research Institute of Petroleum Processing, Sinopec, Beijing 100083, China

#### ARTICLE INFO

Article history: Received 29 November 2014 Received in revised form 3 March 2015 Accepted 5 March 2015 Available online 19 March 2015

Keywords: MCM-49 Tetraethylammonium hydroxide Post-synthesis Liquid-phase alkylation Ethylebenzene

#### ABSTRACT

As-synthesized and calcined MCM-49 zeolites were post-synthesized by tetraethylammonium hydroxide to tailor their morphology, texture properties, acid sites and catalytic performances. With post-synthesis by tetraethylammonium hydroxide, both as-synthesized and calcined MCM-49 zeolites have showed remarkable morphology change from rose-like shape into disorderly packed irregular MWW sheets, and improved surface areas, pore volumes and acid sites without obvious loss of crystallinity. The samples before and after tetraethylammonium hydroxide treatment were used as catalysts in liquid-phase alkylation of benzene with ethylene. Importantly, a prominent increase in ethylene conversion was observed without loss of ethylbenzene selectivity over post-synthesized MCM-49 catalysts in liquid-phase alkylation of benzene with ethylene.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Ethylbenzene (EB) is an important chemical intermediate for plastic and rubber production with a current capacity of  $3.5 \times 10^7$  tons per year, growing at by 3.3% annually over the next decade of the forecast [1,2]. Compared with conventional AlCl<sub>3</sub> process, two zeolite-based EB processes, vapor-phase (ZSM-5) and liquid-phase processes (USY, Beta, MCM-22), show combined virtues of easy separation, low corrosion, high activity and shape selectivity [3–8]. Due to low reaction temperature, there are obvious advantages such as high EB selectivity and long catalyst life in the liquid-phase process. Regardless of somewhat low in catalytic activity, MWW zeolites inspire much more focus due to superior EB selectivity at lower benzene/ethylene molar ratio for the sake of energy consumption [9–11].

MWW zeolites [12–21] contain PSH-3, ERB-1, SSZ-25, MCM-22, MCM-49, MCM-56, MCM-36, ITQ-1, ITQ-2 and UZM-8 zeolites. As well known, hexamethyleneimine (HMI), as an effective structuredirecting agent, is potent to synthesize MWW zeolites. Because of its effective structure-directing capability in the formation of MWW zeolites, it is difficult to avoid the accumulation of MWW layers and realize the morphology control of MWW zeolites. Typically,

E-mail address: zhangfm.ripp@sinopec.com (F. Zhang).

http://dx.doi.org/10.1016/j.apcata.2015.03.005 0926-860X/© 2015 Elsevier B.V. All rights reserved. MWW zeolite crystals are in the form of sheet-like discs or aggregates of cross-linked discs of  $2-5\,\mu m$  in diameter and  $10-40\,nm$  in thickness [22,23], and there are the typical pores of MWW topology structure: 12 MR "cups" ( $0.71 \text{ nm} \times 0.71 \text{ nm} \times 0.91 \text{ nm}$ ) on the external surface, the supercages defined by 12 MR (0.71 nm outside diameter  $\times$  1.82 nm height) through 10 MR opening windows  $(0.41 \text{ nm} \times 0.54 \text{ nm})$ , and the two-dimensional sinusoidal 10 MR pores ( $0.41 \text{ nm} \times 0.54 \text{ nm}$ ). It has been verified that active centers of MWW zeolites are mainly located in 12 MR "cups" on the outer surface to be more easily accessed in liquid-phase alkylation of benzene with ethylene, using 2,4,6-trimethyl-pyridine  $(0.62 \text{ nm} \times 0.56 \text{ nm})$  as probe molecules [10,24,25]. It is deduced that 12 MR "cups" on the outer surface show little restriction on the diffusion of reactant toward the active centers. Therefore, these active centers are believed to be responsible for the unique catalytic performance of MWW catalysts, referred to as "surface pocket catalysis" [26,27]. Generally, the morphology, textural properties and acidities of MWW zeolites significantly affect the accessibility of active centers and their catalytic properties in liquid-phase alkylation of benzene with ethylene.

To increase the accessibility and amount of active centers, equal to improving the alkylation performances, many efforts have been devoted to synthesizing MWW zeolites as follows: preparing small grain size [28], pillaring [18,29], swelling [30], interlayer-expansion [31,32], delaminating [33,34], and introducing mesopores by acidic [35] or alkaline treatments [36–38]. Particularly, post-synthesis of MWW zeolites in acidic or alkaline solution is an efficient



<sup>\*</sup> Corresponding author. Research Institute of Petroleum Processing Sinopec, Xueyuan Road 18, Beijing, China. Tel.: +86 010 82368698.

way to introduce mesopores to tailor their catalytic properties. Most of researchers have studied that the calcined MWW zeolites were treated in NaOH solution, and mesopores were assuredly introduced into the frameworks of zeolites by desilication. Xu et al. [38] reported that when template-containing MCM-22 zeolite was alkali-treated, desilication mainly occurred in the Al-poor regions, which broke the crystal sheets into smaller particles. However, there were still two problems in post-synthesis of MWW zeolites in NaOH solution: firstly, in such harsh alkaline conditions, mesopores were generated by obvious desilication (parent zeolites SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 50-60, product zeolites SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 20-30) inevitably led to loss of crystallinity, which usually resulted in the disappointing performances of post-synthesized MWW zeolites. On the whole, due to tight connection between MWW layers and harsh NaOH treatment, it was difficult to control the degree of desilication (loss of  $SiO_2/Al_2O_3$ ), and this post-synthesis usually led to the loss of crystallinity, especially uncontrollable crystallinity loss of outer surface. It is well known that liquid-phase alkylation of benzene with ethylene mainly proceed in the 12 MR "cups" on the outer surface of MWW zeolites. The loss of crystallinity in NaOH solution would inevitably cause the loss of crystallinity on the outer surface firstly, which is really a disaster for liquid-phase alkylation of benzene with ethylene. Secondly, with intermediate EB as the target product in a consecutive reaction, the other contradictory issue is the trade-off between ethylene conversion and EB selectivity, which is usually featured by "improved ethylene conversion and decreased EB selectivity". As well known, the relationship between conversion and selectivity of intermediate product in a consecutive reaction has been well described in research papers and classic textbooks on reaction engineering [39,40], and there is a common phenomenon that the intermediate as the target product selectivity is almost 100% at low conversion, and the increase of conversion is accompanied by the decrease of intermediate product selectivity.

Considering the fact of the layered MCM-49 zeolites not enduring a harsh treatment in NaOH solution, in this paper, organicalkaline was selected to post-synthesize MCM-49 zeolites with preservation of crystallinity and to tailor their morphology, textural properties, acidities, and catalytic performances. Till now, there have been few reports on the post-synthesis of MCM-49 zeolites by organic-alkali treatment only. It is well summarized that \*BEA and MWW zeolites are excellent catalysts for liquid-phase alkylation of benzene with ethylene, due to their special topology structure directed by tetraethylammonium hydroxide (TEAOH) and HMI, respectively. Obviously TEAOH with larger molecular dimensions than HMI directs the larger channels of \*BEA than MWW. As for \*BEA zeolite, liquid-phase alkylation of benzene with ethylene proceed with high ethylene conversion within the 12 MR channels due to little restriction. However there is low ethylene conversion over MWW zeolite because of its structure restriction on liquidphase alkylation of benzene with ethylene. HMI is weeded out because of its strong capability in formation and connection of MWW layers. Therefore, TEAOH with lower alkalinity than NaOH is intentionally selected to post-synthesize MCM-49 zeolites with the preservation of crystallinity to tailor their morphology, texture properties, acidities, and catalytic performances in liquid-phase alkylation of benzene with ethylene. As-synthesized and calcined MCM-49 zeolites (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios at about 21) were chosen as parent zeolites to control the degree of desilication during post-synthesis.

### 2. Experimental

#### 2.1. Preparation of MCM-49 zeolites and H-type catalysts

Hydrothermal synthesis of MCM-49 zeolite: Parent MCM-49 zeolite was synthesized in the  $1 \text{ m}^3$  demonstration unit

in Hunan Jianchang Petrochemical Company, Sinopec via temperature-controlled phase transfer hydrothermal synthesis [41]. The batch composition in terms of molar ratio was:  $SiO_2/Al_2O_3 = 25$ ,  $NaOH/SiO_2 = 0.18$ ,  $HMI/SiO_2 = 0.3$ , aniline/ $SiO_2 = 0.2$ ,  $H_2O/SiO_2 = 15$ . The synthesis was carried out at  $145 \,^{\circ}C$  for 72 h with stirring speed at 15 Hz. The product was filtered, washed with deionized water until pH value 7, and dried at  $100 \,^{\circ}C$  overnight. Samples were calcined at  $550 \,^{\circ}C$  in ambient air for 6 h in a muffle furnace to remove organics.

Post-synthesis of MCM-49 in TEAOH solution: As-synthesized and calcined MCM-49 zeolites were treated in TEAOH solution. The typical batch composition in terms of molar ratio was: TEAOH/SiO<sub>2</sub> = 0.1, H<sub>2</sub>O/SiO<sub>2</sub> = 15. Post-synthesis of MCM-49 zeolites was carried out in a Teflon-lined autoclave at 150 °C under rotating conditions (30 r min<sup>-1</sup>) for various time (8 h, 16 h, 24 h). The products were recovered by filtration, washed with deionized water until pH value 7 and dried in oven at 100 °C overnight in order to remove the physically adsorbed water molecules. Subsequently, post-synthesized samples of as-synthesized MCM-49 and calcined MCM-49 in TEAOH solution were named as TMP-*x* with HMI, and TMC-*x* without HMI, respectively; *x* represented treatment time (h).

*H-type zeolites*: H-MCM-49 zeolite was prepared by twice liquidphase ion-exchange with NH<sub>4</sub>NO<sub>3</sub> solution at 90 °C for 2 h, filtrated and dried at 100 °C overnight, finally calcined at 550 °C for 6 h. Postsynthesized MCM-49 zeolites needed just one time ion-exchange because of the ion-exchange between TEAOH and Na<sup>+</sup> during the post-synthesis. The composition among MCM-49 zeolites, NH<sub>4</sub>NO<sub>3</sub>, and deionized water on the basis of mass ratio was: 1:1:20. Assynthesized MCM-49 zeolite was named as H-MCM-49 zeolite, according to treatment time at 16 h, post-synthesized MCM-49 zeolites were named as H-TMP-16 (as-synthesized MCM-49 as the parent zeolite), and H-TMC-16 (calcined MCM-49 as the parent zeolite) zeolites, respectively.

*Catalyst preparation*: The NH<sub>4</sub>-type samples (70 wt.%) with Na<sub>2</sub>O content less than 0.05 wt.% and Al<sub>2</sub>O<sub>3</sub> (30 wt.%) were mixed and extruded. The Al<sub>2</sub>O<sub>3</sub>, which showed almost no activity in liquid-phase alkylation of benzene with ethylene, was used as binder to increase the mechanical strength of catalysts. The extruded catalysts were then crushed and the -16/+20 mesh fraction was collected and subjected to calcinations at 550 °C for 6 h to obtain corresponding H-type catalysts. The H-type catalysts derived from TMP-16 (as-synthesized MCM-49 as the parent zeolite) and TMC-16 (calcined MCM-49 as the parent zeolite) zeolites were named as H-TMP-16 and H-TMC-16 catalysts.

### 2.2. Characterization

X-ray diffraction (XRD) patterns of samples were collected on X'pert X-ray diffractometer (PANalytical Corporation, Netherlands) with filtered Cu K $\alpha$  radiation at a tube current of 40 mA and a voltage of 40 kV. The scanning range of  $2\theta$  was 5–35°. The relative crystallinity of the samples was calculated according to the sum of the peak intensities at  $2\theta$  of 14.3°, 22.7°, 23.7° and 26.0° of calcined zeolites through calcination at 550 °C for 6 h, and the crystallinity of calcined MCM-49 zeolite via temperature-controlled phase transfer hydrothermal synthesis was defined as the reference with relative crystallinity at 100%. The crystal morphology was measured on a FEI Quanta scanning electron microscopy (SEM). The elemental analyses of the solids were performed on an X-ray fluorescence (XRF) spectrometer MagiX (Philips). Nitrogen adsorption-desorption isotherms were recorded on a Micromeritics ASAP 2010 instrument. The samples were first out gassed under vacuum at 90 °C for 1 h and at 350 °C for 15 h. The total surface area was obtained by application of the BET equation using the relative pressure range of 0.05–0.16 in the nitrogen adsorption isotherm

as range of linearity (using a molecular cross-sectional area for  $N_2$  of 0.162 nm<sup>2</sup>). The micropore volume was calculated by the *t*-plot method.

The acidic properties of H-type zeolites were measured by Fourier transform infrared spectrometer (FTIR), using pyridine (Py) as probe molecules. Py-FTIR spectra were obtained on a FTS3000 FTIR spectrometer by scans of 64 with a resolution of 4 cm<sup>-1</sup>. Selfsupporting thin wafers were pressed and placed in a quartz IR cell with CaF<sub>2</sub> windows, which used in pyridine adsorption studies. Prior to the measurements, each sample was dehydrated under vacuum 10<sup>-3</sup> Pa at 350 °C for 1 h, and then cool down to 50 °C for pyridine adsorption. The IR spectra of the samples before pyridine adsorption were recorded at different temperatures (50 °C, 200 °C and 350 °C), and after adsorbing pyridine for 10 s, the samples were purged under vacuum  $10^{-3}$  Pa to higher temperatures at a heating rate of 10 °C min<sup>-1</sup>. Then the IR spectra of pyridine on samples were recorded at different temperatures (50 °C, 200 °C and 350 °C). All the spectra given in this work were difference spectra. The amounts of Brønsted and Lewis acid sites were calculated according to the acid sites of adsorbed pyridine area.

<sup>29</sup>Si MAS NMR experiments were performed on a Bruker AVANCE III 500WB spectrometer at a resonance frequency of 99.3 MHz using a 7 mm double-resonance MAS probe. The magicangle spinning speed was 5 kHz in all experiments, and a typical π/6 pulse length of 1.8 μs was adopted for <sup>29</sup>Si resonance. The chemical shift of <sup>29</sup>Si was referenced to tetramethylsilane (TMS).

<sup>27</sup>Al MAS NMR experiments were performed on a Bruker AVANCE III 600WB spectrometer at a resonance frequency of 156.4 using a 4 mm double-resonance MAS probe at a sample spinning rate of 13 kHz. The chemical shift of <sup>27</sup>Al was referenced to 1 M aqueous Al(NO<sub>3</sub>)<sub>3</sub>. <sup>27</sup>Al MAS NMR spectra were recorded by smallflip angle technique using a pulse length of 0.4 µs (< $\pi$ /15) and a recycle delay of 1 s.

<sup>13</sup>C CP/MAS NMR experiments were performed on a Bruker AVANCE III 600WB spectrometer at a resonance frequency of 150.9 MHz using a 4 mm double-resonance MAS probe at a sample spinning rate of 7.5 kHz. The chemical shift of <sup>13</sup>C was determined using a solid external reference, hexamethylbenzene (HMB). <sup>13</sup>C CP/MAS NMR spectra were recorded by using a recycle delay of 5 s and a contact time of 2 ms.

The liquid <sup>13</sup>C NMR experiments were performed on a Varian INOVA 500 spectrometer at a resonance frequency of 125.6 MHz using a 5 mm double-resonance probe. The chemical shift of <sup>13</sup>C was referenced to tetramethylsilane. <sup>13</sup>C NMR spectra were recorded by small-flip angle technique using a pulse length of 3.2 ms ( $\pi/6$ ) and a recycle delay of 4 s.

#### 2.3. Liquid-phase alkylation of benzene with ethylene

The liquid-phase alkylation of benzene with ethylene was carried out in a stainless-steel fixed bed reactor. 8 mL catalyst was located in the center of the reactor and loaded with nitrogenpurged. Benzene was pumped into reactor to fully fill the bed under reaction pressure, and then the temperature was raised up to 200 °C before ethylene was introduced. The alkylation conditions were as follows: 3.5 MPa of pressure, 3 h<sup>-1</sup> of weight hourly space velocity (WHSV) of benzene, and 12/1 of benzene/ethylene molar ratio, 200–260 °C of temperature. At each temperature the reaction was given at least 15 h to reach a steady state condition before samples were collected for analysis. The reaction products were analyzed by an Agilent 6890 gas chromatograph (GC) equipped with a flame ionization detector and a capillary column. It is well known that the alkylation of benzene with ethylene was a consecutive reaction, and the reaction products were made up of ethylbenzene (EB), para-diethylbenzene (p-DEB), ortho-diethylbenzene (o-DEB), meta-diethylbenzene (m-DEB), triethylbenzenes (TEB), other

by-products (diphenylethane) in our work. The ethylene conversion, EB selectivity, DEB selectivity and DEB distribution of selectivity were calculated based upon these formulas as follows:

$$H = \frac{x_{\text{EB}}}{M_{\text{EB}}} + \frac{2x_{\text{DEB}}}{M_{\text{DEB}}} + \frac{3x_{\text{TEB}}}{M_{\text{TEB}}} + \frac{x_{\text{diphenylethane}}}{M_{\text{diphenylethane}}};$$

 $x_{\text{DEB}} = x_{\text{p-DEB}} + x_{\text{o-DEB}} + x_{\text{m-DEB}};$ 

*M*: molar mass (g/mol); *x*: mass percentage concentration (wt.%) from GC analysis; *H*: molar number percentage concentration (mol%) of ethyl.

- (1) Ethylene conversion (%):  $C_{\text{ethylene}} = H/(H + x_{\text{ethylene}}/M_{\text{ethylene}}) \times 100\%$
- (2) EB selectivity (%):  $S_{EB} = x_{EB}/(x_{EB} + x_{DEB} + x_{TEB} + x_{diphenylethane}) \times 100\%$
- (3) DEB selectivity (%):  $S_{\text{DEB}} = x_{\text{DEB}} / (x_{\text{EB}} + x_{\text{DEB}} + x_{\text{TEB}} + x_{\text{diphenylethane}}) \times 100\%$
- (4) DEB distribution of selectivity:

 $m(p-DEB)/m(DEB) = x_{p-DEB}/(x_{p-DEB} + x_{m-DEB} + x_{o-DEB}) \times 100\%;$   $m(m-DEB)/m(DEB) = x_{m-DEB}/(x_{p-DEB} + x_{m-DEB} + x_{o-DEB}) \times 100\%;$  $m(o-DEB)/m(DEB) = x_{o-DEB}/(x_{p-DEB} + x_{m-DEB} + x_{o-DEB}) \times 100\%.$ 

#### 3. Results and discussion

#### 3.1. Post-synthesis of MCM-49 zeolites

In the following experiments, as-synthesized and calcined MCM-49 zeolites were treated in TEAOH (TEAOH/SiO<sub>2</sub> = 0.1,  $H_2O/SiO_2 = 15$ ) solution at 150 °C for various time (8h, 16h, and 24 h). The XRD patterns of the parent and organic-alkaline treating samples are shown in Fig. 1, and it can be observed that the diffraction patterns of all treated samples are in good agreement with parent MCM-49 zeolites. The crystallinity of all samples was calculated according to the sum of the peak intensities at  $2\theta$  of 14.3°, 22.7°, 23.7° and 26.0° of calcined samples, and the relative crystallinity of calcined MCM-49 zeolite via the temperature-controlled phase transfer hydrothermal synthesis was defined as the reference with relative crystallinity at 100% for all post-synthesized samples from both as-synthesized and calcined MCM-49 zeolites. It could be clearly seen that the relative crystallinity of post-synthesized samples first decreased and then increased. The relative crystallinity of TMP-8 (Fig. 1A) and TMC-8 (Fig. 1B) samples decreased to 94% firstly, which might be attributed to the slight destruction of MCM-49 framework in TEAOH solution. Interestingly, the relative crystallinity of TMP-16 and TMP-24 samples in Fig. 1A increased with longer treatment time, reaching up to 100% and 102%, and so did TMC-16 and TMC-24 samples approaching to 96% in Fig. 1B. The results indicated that the first thing was to destroy the framework of MCM-49 slightly in TEAOH solution at the initial treatment time, and then it was possible for TEAOH to incorporate into MWW layers. Therefore, one thing was that TEAOH could act as a filling-space agent, and the other thing was that the amorphous aluminosilicate could be removed by TEAOH to purify zeolitic pores and crystals, which might contribute to their relative crystallinity for post-synthesized samples at longer treatment time. It can be clearly proved that the relative crystallinity of TMP-x samples was higher than those of TMC-x, indicating that the presence of HMI within as-synthesized MCM-49 zeolite would serve a protective agent for MWW framework in TEAOH treatment, but as for calcined MCM-49 zeolite, TEAOH might only clean the pores and crystals to purify the zeolite and acted as a space-filling agent.

To further clarify the interaction between TEAOH and MWW layer structure, liquid <sup>13</sup>C NMR and solid <sup>13</sup>C CP/MAS NMR measurements were performed to offer an insight into the post-synthesis of as-synthesized and calcined MCM-49 zeolites in



**Fig. 1.** XRD patterns of parent and post-synthesized MCM-49 zeolites (A: postsynthesis of as-synthesized MCM-49 zeolite, a: calcined MCM-49, b: TMP-8, c: TMP-16, d: TMP-24; B: post-synthesis of calcined MCM-49 zeolite, a: calcined MCM-49, b: TMC-8, c: TMC-16, d: TMC-24).

TEAOH solution. The <sup>13</sup>C NMR spectra of TMP-16 and TMC-16 mother liquor were shown in Fig. 2A. Compared with TEAOH solution, TEAOH did not decompose during the post-synthesis with the same resonances at 8 and 54 ppm without any other resonances detected, and there were some other resonances at 26, 27 and 47 ppm in mother liquor of TMP-16 in agreement with those of HMI [22]. The results indicated that some HMI was replaced or exchanged by TEAOH into mother liquor during the post-synthesis. There were also two new resonances at 11 and 49 ppm in the mother liquor obtained from TMP-16 (as-synthesized MCM-49 zeolite by TEAOH treatment) in Fig. 2A-b, and these two resonances were in accordance with those of triethylamine in water, which indicated that TEAOH might decompose to form triethylamine on the basis of Hofmann degradation during the post-synthesis. However interestingly, there were not any typical resonances at 11 or 49 ppm in the mother liquor obtained from TMC-16 (calcined MCM-49 zeolite by TEAOH treatment) in Fig. 2A-c.

Additionally, Fig. 2B displays the <sup>13</sup>C CP/MAS NMR spectra of as-synthesized and calcined MCM-49 samples treated in TEAOH (TEAOH/SiO<sub>2</sub> = 0.1, H<sub>2</sub>O/SiO<sub>2</sub> = 15) solution at 16 h. As well known, there were three resonances of HMI in the parent MCM-49 zeolite: the C1 resonances of HMI occurred at 48 and 57 ppm, and the C2, C3 resonances overlapped at 27 ppm; the C1 resonances at 48 and 57 ppm were ascribed respectively to HMI located in the intra-layered and inter-layered regions [22]. For as-synthesized MCM-49 zeolite in this paper, the C1 resonance at 48 ppm was



**Fig. 2.** Liquid <sup>13</sup>C NMR of TEAOH and mother liquor (A: a: TEAOH solution, b: mother liquid of TMP-16, c: mother liquid of TMC-16); <sup>13</sup>C/P MAS NMR spectra of parent and post-synthesized MCM-49 zeolites (B: a: as-synthesized MCM-49, b: TMP-16, c: TMC-16)

retained, while the C1 resonance at 57 ppm seemed very weak due to the involvement of aniline into the hydrothermal synthesis [41]. For TMP-16 (Fig. 2B-b) and TMC-16 (Fig. 2B-c) samples, it was obvious to see that post-synthesized MCM-49 samples showed new strong intensity resonances at 8 and 54 ppm, which meant that TEAOH molecules could incorporate into both as-synthesized and calcined MCM-49 zeolites. Besides, there was an obvious new resonance at 48 ppm for TMC-16 sample, which may be ascribed to triethylamine formed via the Hofmann degradation of TEAOH during the post-synthesis process in Fig. 2B-c. According to the result of liquid <sup>13</sup>C NMR (Fig. 2A-c), there were not any typical resonances at 11 or 49 ppm in the mother liquor obtained from TMC-16 (calcined MCM-49 zeolite by TEAOH treatment) in, which was proposed that TEAOH incorporated into MCM-49 zeolite and then some decomposed within MCM-49 zeolite, not decomposed in the mother liquor. It was difficult for triethylamine molecules to get out of framework and to enter into mother liquor because of blocking effects of calcined MCM-49 zeolite with rigid 3D structure and tight connection between MWW layers. As for TMP-16 sample, the resonance at 48 ppm (triethylamine) overlapped with that of at 49 ppm (HMI), which was in agreement with the result of liquid <sup>13</sup>C NMR spectra of TMP-16 mother liquor in Fig. 2A-b. Based on above results, post-synthesis of as-synthesized and calcined



Fig. 3. SEM images of as-synthesized and corresponding post-synthesized MCM-49 zeolites (a: as-synthesized MCM-49, b: TMP-8, c: TMP-16, d: TMP-24).

MCM-49 zeolites in TEAOH solution was achieved by the incorporation of TEAOH into parent zeolites.

As shown in Fig. 3 (as-synthesized MCM-49 as the parent zeolite) and Fig. 4 (calcined MCM-49 as the parent zeolite), the morphology of post-synthesized samples has been tailored remarkably. Although the morphology showed their irregular sheets packed disorderly, post-synthesized MCM-49 samples showed high relative crystallinity in Fig. 1, indicating that they were well crystallized but packed in disorder. The morphology was obviously different from rose-like shape of the parent MCM-49 zeolite in Fig. 3a (assynthesized MCM-49 as the parent zeolite) and Fig. 4a (calcined MCM-49 as the parent zeolite). Particularly, it was more disorder for as-synthesized MCM-49 zeolite treated in TEAOH solution in Fig. 3b and c demonstrating that it is easier to be tailored into smaller MWW sheets by TEAOH in with HMI incorporated in MCM-49 zeolite. With prolonging the treatment time, these irregular MWW sheets packed in disorder had a tendency to accumulate together again in Fig. 3d. The results of SEM images directly show the interaction of TEAOH, HMI and MWW layers, and because of the incorporation of TEAOH into MWW layers, post-synthesized MCM-49 zeolites has been tailored significantly from rose-like shape into small MWW sheets packed in disorder. What is more, due to little structure-directing performance of TEAOH for synthesizing MWW zeolites, the connection between the MWW layers became loose and not such tight. The special morphology of post-synthesized MCM-49 zeolites would affect their textural properties and acidity, furthermore, the irregular MWW sheets packed disorderly of postsynthesized MCM-49 zeolites would offer more opportunities for reactants to access the active centers than those of parent MCM-49 zeolite, which could be benefit for their catalytic performances.

Table 1 presents the textural properties of parent and postsynthesized samples. The  $SiO_2/Al_2O_3$  of post-synthesized samples at 18, were lower than that of the parent MCM-49 zeolite because of somewhat desilication in TEAOH solution. With long treatment time, the  $SiO_2/Al_2O_3$  of post-synthesized samples did not change, just at 18, which was close to the lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> limit of MCM-49 by conventional hydrothermal synthesis. As well known, the lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of MCM-49 zeolites could offer the more acid sites and the better acid density, which would be beneficial for the liquid-phase alkylation of benzene with ethylene. With the preservation of the crystallinity, the surface areas and pore volumes of post-synthesized samples increased obviously, but for TMC-8 sample. On one hand, as for calcined MCM-49 by TEAOH treated at 8 h, the surface area, micro surface area, pore volume and micro pore volume of TMC-8 sample were  $471 \text{ m}^2 \text{ g}^{-1}$ ,  $401 \text{ m}^2 \text{ g}^{-1}$ , and  $0.51 \text{ cm}^3 \text{ g}^{-1}$ , respectively, which was lower than those of TMP-8 sample  $(494 \text{ m}^2 \text{ g}^{-1}, 410 \text{ m}^2 \text{ g}^{-1}, \text{ and } 0.58 \text{ cm}^3 \text{ g}^{-1}, \text{ respec-}$ tively). These results suggest that the presence of HMI within as-synthesized MCM-49 zeolite could serve a protective agent for the MWW framework in TEAOH treatment: but as for calcined MCM-49 zeolite. TEAOH might only clean the pores and crystals to purify the zeolite pore system. On the other hand, the micro pore volume of TMC-8 sample was  $0.19 \text{ cm}^3 \text{ g}^{-1}$ , higher than that of TMP-8 sample, which indicated that TEAOH could clean easily the amorphous phase in the MWW layers for calcined MCM-49 zeolite in absence of HMI.

TMP-16 and TMC-16 samples with high relative crystallinity, the surface areas increased obviously from  $460 \text{ m}^2 \text{ g}^{-1}$  to  $503 \text{ m}^2 \text{ g}^{-1}$  and  $494 \text{ m}^2 \text{ g}^{-1}$ , the micro surface areas increased from  $371 \text{ m}^2 \text{ g}^{-1}$  to  $416 \text{ m}^2 \text{ g}^{-1}$  and  $420 \text{ m}^2 \text{ g}^{-1}$ , but the exterior surface areas decreased from  $89 \text{ m}^2 \text{ g}^{-1}$  to  $87 \text{ m}^2 \text{ g}^{-1}$  and  $74 \text{ m}^2 \text{ g}^{-1}$ , respectively; the total volumes increased from  $0.56 \text{ cm}^3 \text{ g}^{-1}$  to  $0.68 \text{ cm}^3 \text{ g}^{-1}$  and  $0.63 \text{ cm}^3 \text{ g}^{-1}$ , and the micro volumes had slight increase from  $0.17 \text{ cm}^3 \text{ g}^{-1}$  to  $0.19 \text{ cm}^3 \text{ g}^{-1}$ , and  $0.19 \text{ cm}^3 \text{ g}^{-1}$ . There was no obvious enhancement of surface areas and pore volumes for post-synthesized samples by increasing treatment time from 16 to 24 h. Obviously, TMP-x and TMC-x samples have better surface area, micro-surface area and pore volumes than the parent MCM-49 zeolite, indicating that MCM-49 zeolites may be tailored their textural properties in TEAOH solution with preservation of high



Fig. 4. SEM images of the calcined MCM-49 and corresponding post-synthesized MCM-49 zeolites (a: calcined MCM-49, b: TMC-8, c: TMC-16, d: TMC-24).

fable 1	
Texture properties of parent calcined MCM-49 zeolite and post-synthesized MCM-49 zeolites by TEAOH treatment.	

Sample no.	$SiO_2/Al_2O_3$	$S_{\rm BET} (m^2g^{-1})$	$S_{ m micro}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{ m micro}~( m cm^3~g^{-1})$	$V_{\rm total}~({ m cm^3~g^{-1}})$	RC (%)	Na <sub>2</sub> O (wt.%)	
a (MCM-49)	21	460	371	0.17	0.56	100	0.55	
(A) TEAOH + as-synthesized MCM-49 zeolite								
b-TMP-8 (8 h)	18	494	410	0.17	0.58	94	0.24	
c-TMP-16 (16 h)	18	503	416	0.19	0.68	100	0.22	
d-TMP-24 (24 h)	18	505	421	0.19	0.67	102	0.16	
(B) TEAOH + calcined MCM-49 zeolite								
b-TMC-8 (8 h)	18	471	401	0.19	0.51	94	0.21	
c-TMC-16 (16 h)	18	494	420	0.19	0.63	96	0.15	
d-TMC-24 (24 h)	18	495	421	0.19	0.64	96	0.16	

relative crystallinity. Also there was ion-exchange phenomenon during post-synthesis, showing that TEAOH assuredly incorporated into the parent MCM-49 zeolites. This was the reason why post-synthesized MCM-49 samples needed only one time ion-exchange to meet the requirement of Na<sub>2</sub>O contents (<0.05 wt.%). Additionally, TMC-*x* samples showed lower Na<sub>2</sub>O contents than those of TMP-*x* samples, mainly because the protective role of HMI for TMP-*x* samples decreased the efficiency of ion-exchanging capabilities between Na<sup>+</sup> and TEAOH. This post-synthesis in TEAOH solution offers an excellent way to increase surface areas and pore volumes with the preservation of high crystallinity.

Comparing TMP-x to TMC-x samples, it is easy to find that there was a clear advantage for as-synthesized MCM-49 zeolite by TEAOH treatment, with high crystallinity, surface area and pore volume. Calcined MCM-49 zeolite possessed the rigid 3D structure and tight connection of MWW layered structure, however, for as-synthesized MCM-49 zeolite, the layered structure did not connect so closely. Therefore, it is more effective to select as-synthesized MCM-49 zeolite as the parent zeolite for TEAOH post-synthesis. With the preservation of high relative crystallinity, post-synthesized MCM-49 zeolites showed the small MWW sheets and packs in disorder, and improved the surface areas and pore volumes. Generally, for

liquid-phase alkylation of benzene with ethylene, more disorderly packed the MWW sheets and higher pore volumes would offer less restriction of reactants and products, and better accessibility of active centers. Finally, TMP-16 and TMC-16 samples with high crystallinity, high surface areas and pore volumes, and especially irregular sheets packed in disorder, were selected to prepare H-type zeolites for characterizations, and alkylation catalysts to evaluate their catalytic performances, with the parent H-MCM-49 zeolite as a comparison.

# 3.2. Properties of H-type zeolites

As well known, there was desilication phenomenon during postsynthesis in TEAOH solution, and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio decreased from 21 (the parent MCM-49 zeolite) to 18 (post-synthesized samples), indicating that there were more acid sites and higher acid density of post-synthesized samples. The acidity distribution and the amount of acid sites of MCM-49 before and after TEAOH treatment were characterized by the Py-FTIR in Table 2. Remarkably, the amounts of both Lewis and Brønsted acid sites were increased by TEAOH treatment. Take an example of the results at 200 °C, for H-TMP-16 sample, Lewis acid sites increased from 189  $\mu$ mol g<sup>-1</sup> to

Table 2	
Acid properties of H-type zeolites.	

Samples 200 °C			350°C			
	Lewis acid (µmol g <sup>-1</sup> )	Brønsted acid ( $\mu mol g^{-1}$ )	B/L	Lewis acid ( $\mu mol g^{-1}$ )	Brønsted acid ( $\mu$ mol g <sup>-1</sup> )	B/L
a (H-MCM-49)	189	402	2.13	168	375	2.23
b (H-TMP-16)	327	518	1.58	261	450	1.72
c (H-TMC-16)	390	423	1.08	244	385	1.58

327  $\mu$ mol g<sup>-1</sup> and Brønsted acid sites increased from 402  $\mu$ mol g<sup>-1</sup> to 518  $\mu$ mol g<sup>-1</sup>, suggesting that there would be similar amount of newly generated Lewis and Brønsted acid sites on as-synthesized MCM-49 zeolite during TEAOH post-synthesis. Interestingly, for H-TMC-16 samples, Lewis acid sites increased from  $189 \,\mu mol g^{-1}$ to 390 µmol g<sup>-1</sup> and Brønsted acid sites increased slightly from 402  $\mu$ mol g<sup>-1</sup> to 423  $\mu$ mol g<sup>-1</sup>, indicating that there would be more Lewis acid sites newly emerged on calcined MCM-49 zeolite during TEAOH post-synthesis. This result shows us a way to adjust the distribution of acid types. For H-TMP-16 sample, the increase in both Lewis and Brønsted acid sites enlighten us to consider that the framework of MCM-49 zeolite could not only be protected appropriately, but also generated new Lewis and Brønsted acid sites with presence of HMI incorporated within MCM-49. On the contrary, for calcined MCM-49 zeolite in TEAOH solution, the increase of acid sites was almost Lewis acid sites. The increase of acid sites determined by Py-FTIR would offer better accessibility of acid sites, that is to say, post-synthesized MCM-49 zeolites (H-TMP-16 and H-TMC-16) would offer more active centers and better accessibility of active centers for reactants. During post-synthesis of MCM-49 zeolites, not only did it tailor the morphology and textural properties, but also increased the amount of acid sites. The special morphology of small MWW sheets and packs in disorder, the higher surface area and pore volumes, and the increase of the acid sites would offer less restriction, more opportunities for benzene to access the active centers, more active centers and better accessibility to active centers, which are benefit for their catalytic performance.

<sup>27</sup>Al MAS NMR spectra of post-synthesized samples were expected to give an insight into the effects of TEAOH treatment on the distribution of Al in Fig. 5A. Upon calcination, all the samples showed the occurrence of extra-framework aluminum with a sharp peak at about 0 ppm, which indicated that high temperature calcinations caused dealumination to some extent. The <sup>27</sup>Al MAS NMR spectra of MWW zeolites were both comprised of three tetrahedral Al resonances centered at 49, 56 and 61 ppm [42]. Particularly, there were two phenomena: an increasing tendency for the intensity of tetrahedral Al at 49 ppm and a decreasing tendency for the intensity of tetrahedral Al at 61 ppm after TEAOH treatment, which illustrated that the environment of Al sites in the tetrahedral frameworks had been changed during TEAOH treatment. As shown in Fig. 5B, the <sup>29</sup>Si MAS NMR spectra of the calcined samples are similar to those presented in parent MCM-49, with five peaks at about -99, -105, -111, -114, and -119 ppm. These peaks are mainly associated with Si sites of MWW zeolites as follows:  $-99 \text{ ppm} \sim \text{Si}$ (1Al) and  $-105 \text{ ppm to } -119 \text{ ppm } \sim \text{Si}(\text{OAl})$  [42].

#### 3.3. Alkylation performances of H-type catalysts

The initial goal in our paper is to post-synthesize MWW zeolites by TEAOH with the preservation of high crystallinity and improve their surface areas, pore volumes and acid sites. According to the above results, post-synthesized MWW zeolites not only truly have high relative crystallinity retained, but also have tailored the morphology, textural property, acidity and accessibility of active centers. With high crystallinity preserved irregular small



Chemical shift (ppm) Fig. 5. <sup>27</sup>Al (A)/<sup>29</sup>Si (B) MAS NMR spectra of H-type zeolites.

-110

-120

-130

-80

-90

-100

MWW sheets different from original rose-like shape, higher surface areas and pore volumes, and more amounts of acid sites, post-synthesized MCM-49 zeolites may offer more active sites and better accessibility for the reactants. We are really interested in how the morphology, texture property, acidity and accessibility of active centers influence the catalytic properties of H-type catalysts in the liquid alkylation of benzene with ethylene.

The alkylation performances of H-type catalysts are shown in Fig. 6A and B. As well known, the alkylation of benzene with ethylene is a consecutive reaction, and with EB as the target product, the trade-off between ethylene conversion and EB selectivity must be carefully weighed and considered, and it is usually featured by "improved ethylene conversion and decreased EB selectivity" [39,40]. All H-type catalysts showed somewhat increased



**Fig. 6.** Ethylene conversion (%, A) and ethylbenzene selectivity (%, B) of H-type catalysts (a: H-MCM-49; b: H-TMP-16; c: H-TMC-16; Liquid-phase alkylation conditions: 8 mL catalysts,  $T = 200-260 \circ C$ , p = 3.5 MPa, benzene WHSV<sup>-1</sup> =  $3.0 \text{ h}^{-1}$ , benzene/ethylene molar ratio = 12.0).

ethylene conversion with the rise of temperature, but presented slightly decreased EB selectivity. This result still falls into a rule like "see-saw", which is usually encountered in a consecutive reaction with intermediate product as the target product, that is, it is a common phenomenon that the ethylene conversion increased with the rise of temperature, and the EB selectivity decreased.

For H-TMP-16 and H-TMC-16 catalysts, the corresponding ethylene conversion has been improved remarkably, compared to the parent H-MCM-49 catalyst in Fig. 6A from 96.6% for H-MCM-49 to 99.9% for H-TMP-16 and 99.3% for H-TMC-16 just at 200 °C. Firstly, as for H-TMP-16 catalyst, obtained from as-synthesized MCM-49 zeolite by TEAOH treatment, the ethylene conversion had approached up to 100% from 200 to 260 °C, which indicated that there was excellent accessibility of active centers. Secondly, for H-TMC-16 catalyst from calcined MCM-49 zeolite by TEAOH treatment, the ethylene conversion increased gradually up to 100% by the rise of temperature. Compared to the parent H-MCM-49 catalyst, the superior activity of post-synthesized samples indicated that there might be more active centers and superior accessibility of active centers for liquid-phase alkylation of benzene with ethylene, especially for H-TMP-16 catalyst, which was in accordance with the results of characterizations, such as more irregular MWW sheets, higher surface areas, pore volumes, and more acid sites to offer more active centers and better accessibility.

Importantly, it is simultaneous for post-synthesized catalyst to achieve (or at least maintain) high EB selectivity in Fig. 6B. Take an example of EB selectivity at 200°C, it can be seen that there

were 95.4%, 95.5% and 95.6% for the parent H-MCM-49 catalyst, H-TMP-16 and H-TMC-16 catalysts, respectively. With the temperature increasing, the EB selectivity of post-synthesized samples maintained a little higher or at least no lower than that of the parent H-MCM-49 catalyst regardless of slight fluctuation, especially for H-TMP-16 catalyst. These results confirmed that an excellent method for catalyst preparation, with the preservation of high crystallinity, small MWW sheets packed in disorder and more active centers to offer more opportunities for benzene to access the active centers, can make a significant breakthrough for enhancing activity without loss of EB selectivity. In the evaluation, there was the identical benzene WHSV<sup>-1</sup> at 3 h<sup>-1</sup> and benzene/ethylene molar ratio at 12 for all catalysts. Because of the same feeding ethylene, the activity increase of post-synthesized catalysts means the more EB to be produced and the less ethylene for EB to produce DEB, TEB and other by-products. Therefore, it can be observed an increase in ethylene conversion without loss of EB selectivity over post-synthesized H-MCM-49 catalysts in liquid-phase alkylation of benzene with ethylene. That is, the postsynthesized H-MCM-49 catalysts by TEAOH treatment could make a significant breakthrough of the trade-off between ethylene conversion and EB selectivity, mainly because with the preservation of high relative crystallinity, post-synthesized H-MCM-49 catalysts possessed more irregular MWW sheets packed, higher surface area and pore volumes, more active centers, and better accessibility of active centers than those of the parent H-MCM-49 catalyst.

In all, with the preservation of high crystallinity, it could be post-synthesized MCM-49 zeolites in TEAOH solution, which improved surface areas, pore volumes, and acid sites to offer more active centers. Certainly, the morphology of MCM-49 has tailored dramatically from rose-like shape to small irregular sheets packed in disorder, which could also afford more opportunities for reactants to access active centers. Because of these advantages, post-synthesized H-MCM-49 catalysts performed superior alkylation performance, enhancing ethylene conversion without loss of EB selectivity in Fig. 6. For post-synthesized MCM-49 zeolites in TEAOH solution, the physical-chemical properties and catalytic performances were improved obviously. This result of alkylation performance may highlight a new strategy for enhancing both catalytic activity and intermediate selectivity. This synthesis concept should be applicable to many reactions that are diffusion limited, and require reaction occurring on the external surface due to the change of the morphology and improvements in accessibility to active centers.

DEB selectivity and DEB distribution: Fig. 7A and B shows that DEB selectivity and DEB distributions over H-type catalysts in the liquid-phase alkylation of benzene with ethylene. The DEB selectivity for all H-type catalysts increased by the rise of temperatures regardless of slight fluctuation for the parent H-MCM-49 catalyst. In alkylation, high EB selectivity would directly be related to low DEB selectivity. At low temperature, it can be seen that the high degree of selectivity over all H-type zeolites for o-DEB, as shown in Fig. 7B, and that o-DEB decreased by the temperature range from 200 °C to 260 °C. On the contrary, the low degree of selectivity for m-DEB gradually was generated. As well known, p-DEB has the smallest molecular diameter among of the three DEB isomers, while space-filling models have shown that the o-DEB has the most favorable configuration for active centers of H-type zeolites. With the temperature rising, more and more m-DEB was produced by the isomerization of o-DEB, and in the meantime, the selectivity of p-DEB almost had no change. Additionally, at high temperature, it is obvious to see the gradual trend of DEB isomers moving toward the thermodynamic equilibrium values with the mass ratios of DEB isomers were maintained as 64 (for m-DEB):30 (for p-DEB):6 (for o-DEB) [10], respectively. It could be worthy that less o-DEB (kinetically favorable) was generated over H-TMP-16 at initial reaction



**Fig. 7.** DEB selectivity (%, A) and distribution of DEB isomers (%, B) of H-type catalysts (a: H-MCM-49; b: H-TMP-16; c: H-TMC-16; liquid-phase alkylation conditions: 8 mL catalysts, T = 200-260 °C, p = 3.5 MPa, benzene WHSV<sup>-1</sup> = 3.0 h<sup>-1</sup>, benzene/ethylene molar ratio = 12.0).

temperature 200 °C than that of the parent H-MCM-49 catalyst. It is well known that improved ethylene conversion decreases the opportunities for further ethylation of EB to form DEB isomers indicated that there was less opportunity to produce kinetically favorable o-DEB over H-TMP-16. In other words, the lower DEB selectivity in Fig. 7A means the higher EB selectivity in Fig. 6B.

# 4. Conclusion

The post-synthesis of as-synthesized and calcined MCM-49 in TEAOH solution offers a special way to tailor the morphology, textural property, and acidity with high crystallinity retained. MWW layered structure should be slightly destroyed by TEAOH at first in order that TEAOH could incorporate into and post-synthesize MWW zeolites, which were in accordance with the fact that relative crystallinity of post-synthesized samples first decreased and then increased by increasing treatment time. Owing to TEAOH entering layered structure, the morphology of post-synthesized samples have been tailored dramatically from rose-like shape to small irregular sheets packed in disorder, the surface areas and pore volumes have increased, which would offer more opportunities for reactants to access the active centers. More importantly, the increase of acid sites mean offering more active centers, which is equal to enhancing the accessibility of active centers in the liquid-phase alkylation of benzene with ethylene. Increases of ethylene conversion were observed without loss of EB selectivity over post-synthesized MCM-49 catalysts, which were attributed to more active centers and better accessibility of active centers. This post-synthesis concept of MWW zeolites based on large size of organic–alkali and mild organic–alkali treatment, one is to tailor the morphology, textural property and acidity with the preservation of crystallinity, and the other is to enhance both catalytic activity and selectivity, which could be applicable to many diffusion limited or extra-surface reactions.

# Acknowledgments

This work was supported by the National Basic Research Program of China (973 Program, No. 2012CB224805). Special thanks to the Department of Analysis in Research Institute of Petroleum Processing Sinopec.

#### References

- [1] B. Yilmaz, U. Muller, Top. Catal. 52 (2009) 888-895.
- [2] B. Zhang, Y.J. Ji, Z.D. Wang, Y.M. Liu, H.M. Sun, W.M. Yang, P. Wu, Appl. Catal. A: Gen. 443–444 (2012) 103–110.
- [3] J. Cejka, A. Vondrova, B. Wichterlova, G. Vorbeck, R. Fricke, Zeolites 14 (1994) 147–153.
- [4] C. Perego, P. Ingallina, Catal. Today 73 (2002) 3–22.
- [5] W. Vermeiren, J.P. Gilson, Top. Catal. 52 (2009) 1131–1161.
- [6] G. Bellussi, G. Pazzuconi, C. Perego, G. Girotti, G. Terzoni, J. Catal. 157 (1995) 227–234.
- [7] Y.C. Du, H. Wang, S. Chen, J. Mol. Catal. A: Chem. 179 (2002) 253–261.
- [8] J.C. Cheng, C.M. Smith, D.E. Walsh, US 5493065 (1996).
- [9] J.C. Cheng, C.M. Smith, C.R. Venkat, D.E. Walsh, US 5600048 (1997).
   [10] J. Cheng, T. Degnan, J. Beck, Y. Huang, M. Kalyanaraman, J. Kowalski, C. Loehr, D. Mazzone, Stud. Surf. Sci. Catal. 121 (1999) 53-60.
- [11] D.Y. Jan, J.A. Johnson, R.J. Schmidt, G.B. Woodle, US 7268267 B2 (2007).
- [12] L. Puppe, J. Weisser, US 4439409 (1984).
- [13] G. Bellussi, G. Perego, M.G. Clerici, A. Giusti, EP 293032 (1988).
- [14] S.I. Zones, D.I. Holtermann, R.A. Innes, T.A. Pecoraro, D.S. Santilli, J.N. Ziemer, US 4826667 (1989).
- [15] M.K. Rubin, P. Chu, US 4954325 (1990).
- [16] J.M. Bennett, C.D. Chang. S.T. Lawton, M.E. Leonowicz, D.N. Lissy, M.K. Rubin, US 5236575 (1993).
- [17] A.S. Fung, S.T. Lawton, W.J. Roth, US 5362697 (1994).
- [18] C.T.-W. Chu, C.T. Kresge, W.J. Roth, K.G. Simmons, J.C. Vartuli, US 5292698 (1994).
- [19] M.J.D. Cabañas, M.A.C. Fernandez, C.C. Martires, A.C. Canos, US 6077498 (2000).
   [20] P.J.V.D. Brink, A.C. Canos, E.J. Creyghton, V.F. Segui, V.M. Soria, US 2003/0004382
- A1 (2003).
- [21] L.M. Rohde, G.J. Lewis, M.A. Miller, J.G. Moscoso, J.L. Gisselquist, R.L. Patton, S.T. Wilson, D.Y. Jan, US 6756030 B1 (2004).
- [22] S.L. Lawton, A.S. Fung, G.J. Kennedy, L.B. Alemany, C.D. Chang, G.H. Hatzikos, D.N. Lissy, M.K. Rubin, H.C. Timken, S. Steuernagel, D.E. Woessner, J. Phys. Chem. 100 (1996) 3788–3798.
- [23] I. Guray, J. Warzywoda, N. Bac, A. Sacco Jr., Microporous Mesoporous Mater. 31 (1999) 241–251
- [24] H. Du, D.H. Olson, J. Phys. Chem. B 106 (2002) 395-400.
- [25] P. Ayrault, J. Datka, S. Laforge, D. Martin, M. Guisnet, J. Phys. Chem. B 108 (2004) 13755–13763.
- [26] T.F. Dengnan Jr., C.M. Smith, C.R. Venkat, Appl. Catal. A: Gen. 221 (2001) 283-294.
- [27] J. Čejka, A. Krejčí, N. Žilková, J. Kotrla, S. Ernst, A. Weber, Microporous Mesoporous Mater. 53 (2002) 121–133.
- [28] X.Y. Yin, N.B. Chu, J.H. Yang, J.Q. Wang, Z.F. Li, Catal. Commun. 43 (2014) 218–222.
- [29] M. Kaldstroma, N. Kumara, T. Heikkilab, D.Yu. Murzina, Appl. Catal. A: Gen. 397 (2011) 13–21.
- [30] W.J. Roth, P. Chlubná, M. Kub, D. Vitvarová, Catal. Today 204 (2013) 8-14.
- [31] S. Inagaki, H. Imai, S. Tsujiuchi, H. Yakushiji, T. Yokoi, T. Tatsumi, Microporous
- Mesoporous Mater. 142 (2011) 354–362. [32] H. Xu, L.Y. Fu, J.G. Jiang, M.Y. He, P. Wu, Microporous Mesoporous Mater. 189 (2014) 41–48.
- [33] B. Onida, L. Borello, B. Bonelli, F. Geobaldo, E. Garrone, J. Catal. 214 (2003) 191-199.
- [34] J. Aguilar, S.B.C. Pergher, C. Detoni, A. Corma, F.V. Melo, E. Sastre, Catal. Today 133–135 (2008) 667–672.
- [35] Y. Wang, Y.M. Liu, L.L. Wang, H.H. Wu, X.H. Li, M.Y. He, P. Wu, J. Phys. Chem. C 113 (2009) 18753–18760.
- [36] V. Machadoa, J. Rochab, A.P. Carvalhoc, A. Martinsa, Appl. Catal. A: Gen. 445–446 (2012) 329–338.
- [37] K.F. Liu, S.J. Xie, G.L. Xu, Y.N. Li, S.L. Liu, L.Y. Xu, Appl. Catal. A: Gen. 383 (2010) 102–111.

Y. Shi et al. / Applied Catalysis A: General 497 (2015) 135-144

- [38] K.F. Liu, S.J. Xie, H.J. Wei, X.J. Li, S.L. Liu, L.Y. Xu, Appl. Catal. A: Gen. 468 (2013) 288–295.
- [39] J.G. van de Vusse, Chem. Eng. Sci. 21 (1966) 1239–1252.
  [40] L.D. Schemidt, The Engineering of Chemical Reactions, Oxford University Press, New York, 1998, pp. 157–168.
- [41] E.H. Xing, X.Z. Gao, W.H. Xie, F.M. Zhang, X.H. Mu, X.T. Shu, RSC Adv. 4 (2014) 24893–24899.
  [42] D. Vuono, L. Pasqua, F. Testa, R. Aiello, A. Fonseca, T.I. Koranyi, J.B. Nagy, Microporous Mesoporous Mater. 97 (2006) 78–87.