

Using ultrasound to improve the sequential post-synthesis modification method for making mesoporous Y zeolites

Rongxin Zhang¹, Peinan Zhong¹, Hamidreza Arandiyani², Yanan Guan³, Jinmin Liu³, Na Wang (✉)^{4,5,6},
Yilai Jiao (✉)³, Xiaolei Fan (✉)¹

¹ Department of Chemical Engineering and Analytical Science, School of Engineering, The University of Manchester, Manchester, M13 9PL, UK

² Laboratory of Advanced Catalysis for Sustainability, School of Chemistry, The University of Sydney, Sydney 2006, Australia

³ Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

⁴ Sino-Spanish Advanced Materials Institute, Shenyang University of Chemical Technology, Shenyang 110142, China

⁵ Advanced Manufacturing Institute of Polymer Industry (AMIPI), Shenyang University of Chemical Technology, Shenyang 110142, China

⁶ Key Laboratory of Materials and Advanced Equipment for Resource Chemical Technology (Ministry of Education), Shenyang University of Chemical Technology, Shenyang 110142, China

© The Author(s) 2020. This article is published with open access at link.springer.com and journal.hep.com.cn 2020

Abstract Mesoporous Y zeolites were prepared by the sequential chemical dealumination (using chelating agents such as ethylenediaminetetraacetic acid, H₄EDTA, and citric acid aqueous solutions) and alkaline desilication (using sodium hydroxide, NaOH, aqueous solutions) treatments. Specifically, the ultrasound-assisted alkaline treatment (i.e., ultrasonic treatment) was proposed as the alternative to conventional alkaline treatments which are performed under hydrothermal conditions. In comparison with the hydrothermal alkaline treatment, the ultrasonic treatment showed the comparatively enhanced efficiency (with the reduced treatment time, i.e., 5 min vs. 30 min, all with 0.2 mol·L⁻¹ NaOH at 65°C) in treating the dealuminated Y zeolites for creating mesoporosity. For example, after the treatment of a dealuminated zeolite Y (using 0.1 mol·L⁻¹ H₄EDTA at 100°C for 6 h), the ultrasonic treatment produced the mesoporous zeolite Y with the specific external surface area (S_{external}) of 160 m²·g⁻¹ and mesopore volume (V_{meso}) of 0.22 cm³·g⁻¹, being slightly higher than that by the conventional method (i.e., S_{external} = 128 m²·g⁻¹ and V_{meso} = 0.19 cm³·g⁻¹). The acidic property and catalytic activity (in catalytic cracking of *n*-octane) of mesoporous Y zeolites obtained by the two methods were comparable. The ultrasonic desilication treatment was found to be generic, also being effective to treat the dealuminated Y zeolites by citric acid. Additionally, the first step of chemical dealumination treatment was crucial to enable the effective creation of mesopores in the parent

Y zeolite (with a silicon-to-aluminium ratio, Si/Al = 2.6) regardless of the subsequent alkaline desilication treatment (i.e., ultrasonic or hydrothermal). Therefore, appropriate selection of the condition of the chemical dealumination treatment based on the property of parent zeolites, such as Si/Al ratio and crystallinity, is important for making mesoporous zeolites effectively.

Keywords zeolite Y, mesoporous zeolite, post-synthesis treatment, ultrasound, chemical dealumination treatment, alkaline desilication treatment

1 Introduction

Zeolites as a class of crystalline porous materials with intrinsic micropores (i.e., < 1 nm) are being used considerably by industry as adsorbents and catalysts due to their high specific surface areas, excellent hydrothermal stability, inclusion of acidity and ion exchange ability. For catalytic application, zeolite Y (faujasite, FAU type), with the intrinsic low silicon-to-aluminium (Si/Al) ratio of ~2.6 and 12-member ring windows of a three-dimensional (3D) channel system (with the pore width of ~0.74 nm), has been widely used in fluid catalytic cracking (FCC) after its successful synthesis by Breck in 1964 [1], representing the most important technical breakthrough in petrochemical conversions. The microporous structure of zeolite Y imposes the accessibility and diffusion limitation on their applications, which is one of the primary contributing factors to the catalyst deactivation [2], due to the coke deposition covering acidic sites and/or clogging the

Received June 7, 2019; accepted October 4, 2019

E-mails: iamwangna@syuct.edu.cn (Wang N),

yljiao@imr.ac.cn (Jiao Y),

xiaolei.fan@manchester.ac.uk (Fan X)

micropores [3,4]. Therefore, to improve the catalytic performance of zeolites, especially FAU zeolite Y for FCC, it is necessary to make zeolites with hierarchical meso-micro-pores (or mesoporous zeolites) to mitigate the accessibility and diffusion limitation. Common strategies for making hierarchical zeolites can be categorised into the destructive (top-down) and constructive (bottom-up) methods [5]. Although the bottom-up method can remarkably enhance pore accessibility by soft [6,7] or hard templating [8], the associated cost and environmental issues (of using templates) can be problematic for large-scale applications in industry [9]. The top-down method, which creates the intracrystalline mesopores by the post-synthesis dealumination and/or desilication (via steaming, chemical treatment, acid and base washing) [9–13], is simple and effective, as well as being practical for industrial adoption.

Dealumination involves the extraction of framework Al species, and it is commonly achieved by steaming, acid and chemical treatment using mineral (e.g., hydrochloric acid [14]) and organic chelating agents (or chelators such as ethylenediaminetetraacetic acid, H_4EDTA [15] and citric acid [16]). Chelators not only provide the hydronium ions (for the hydrolysis of framework Al species) but also complex non-framework Al species to water-soluble complexes which can be easily removed from the zeolite framework [15,17]. Particularly for the pristine FAU Y zeolite with low Si/Al ratios of 2.4–2.6, dealumination is also necessary to reduce the framework Al concentration, and thus improving its thermal stability for harsh FCC reaction (500°C–550°C) and regeneration (650°C–760°C) steps [2,18]. Desilication via the alkaline treatment is generally effective for zeolites with high Si/Al ratios (> 20), such as ZSM-5 (Mobile Five, MFI type) [19], beta (BEA type) [20], mordenite (MOR type) [12], to create hierarchical mesopores. Direct desilication of pristine Y zeolite is not effective since the high concentration of framework Al species protects the framework Si against the attack by OH^- . Accordingly, the sequential dealumination and alkaline treatments of zeolite Y were proposed, creating mesoporous Y zeolites effectively, in which the first step of dealumination helps to remove the framework Al partially from the pristine Y zeolite, and the second step of alkaline treatment has multiple functions, including (i) removing the debris remaining in the zeolite framework by dealumination treatment, (ii) enabling the desilication for improving the intracrystalline mesoporosity, and (iii) facilitating the recrystallisation to recover the crystallinity partially. Verboekend et al. performed the chemical treatment of a parent Y with Si/Al = 2.4 for dealumination (using H_4EDTA and ethylenediaminetetraacetic acid disodium salt, Na_2H_2EDTA , at 100°C for 6 h), and then alkaline treatment (using aqueous NaOH solution at 65°C for 30 min), and created hierarchical Y zeolites with high specific mesopore areas ($S_{external}$, up to 388 $m^2 \cdot g^{-1}$) and mesopore volumes ($V_{meso} > 0.1 \text{ cm}^3 \cdot g^{-1}$)

[21]. Accordingly, for the pristine Y zeolite, the preliminary dealumination to increase the bulk Si/Al ratio is the prerequisite for the subsequent alkaline treatment to be effective for desilication, and thus the creation of hierarchical mesoporosity [22,23].

Although the post-synthesis treatment is robust, effective and practical, the associated drawbacks, such as being energy intensive (e.g., the steam generation for steaming and lengthy operation at elevated temperatures for acid leaching and chemical treatment), still need to be addressed for improving the sustainability of such protocols and the resulting mesoporous zeolites. Over the past years, process intensification of zeolite synthesis using alternative energy such as microwave and ultrasound has been proposed and researched and found to be greener and safer than the conventional hydrothermal synthesis at high temperatures (80°C–200°C) and autogenous pressures of the aqueous synthesis solution [24]. Such process intensification strategies are also extended to post-synthesis modification of zeolites such as microwave-assisted dealumination [25,26] and desilication [27].

Ultrasound irradiation (with frequencies $> 20 \text{ kHz}$) has proven to be very useful in organic synthesis and synthesis of nanomaterials (known as sonochemistry) [28]. Ultrasound can be transmitted through solids, gases and liquids. In liquids, longitudinal vibrations of molecules cause cavitation (i.e., the rapid formation and collapse of cavities or bubbles in a liquid medium), being responsible for most of the ultrasonic physical and chemical effects [28]. For post-synthesis treatment systems for zeolite modification, i.e., liquid-solid systems of zeolite slurry, cavitation due to ultrasound irradiation may make the additional microscopic stirring effect, intensifying the treatments by improving the local mass transfer [29]. Ultrasound-assisted desilication of zeolite Y (Si/Al = 2.6) has been attempted by Oruji et al. for preparing Y zeolites with mesoporous features [30]. The alkaline treatments were performed with 0.5 $\text{mol} \cdot \text{L}^{-1}$ NaOH at 30°C for various treatment durations (i.e., 20, 40 and 60 min) under ultrasound irradiation (at 20 kHz with a probe sonicator). However, the use of ultrasound seemed not to intensify the post-synthesis alkaline treatment, and the ultrasonic treatment produced the resulting Y zeolites with mesopore surface area $< 10 \text{ m}^2 \cdot \text{g}^{-1}$ and volume $< 0.05 \text{ cm}^3 \cdot \text{g}^{-1}$, which can hardly be classified into mesoporous zeolites. Such results can be expected, as discussed above, because it is very difficult to achieve effective desilication due to the high concentration of framework Al species in the pristine Y zeolite. Even under severe alkaline conditions (e.g., $\geq 3 \text{ mol} \cdot \text{L}^{-1}$ NaOH and $\geq 65^\circ\text{C}$), mesoporosity cannot be introduced in zeolite Y effectively [23]. Therefore, to utilise ultrasound irradiation for intensifying desilication, either using the parent zeolites with high Si/Al ratios (i.e., > 20 , for the one-step direct alkaline treatment) or developing relevant sequential dealumination-alkaline treatment strategies for the parent zeolites with low Si/Al ratios, especially the pristine zeolite

Y, is necessary to realise the desired effect, i.e., making mesoporous zeolites.

In this work, we explored the possibility of using ultrasound irradiation to intensify the alkaline treatment step in the sequential post-synthesis treatment of pristine zeolite Y, aiming at preparing hierarchical Y zeolites more efficiently than the conventional sequential method under hydrothermal conditions. The first-step chemical treatment of the pristine Y zeolite for dealumination was performed under hydrothermal conditions using different chelating agents, concentrations and treatment time. Then the second step of alkaline treatment (of the dealuminated Y zeolites) was performed comparatively using the conventional hydrothermal treatment and ultrasound-assisted treatment in the NaOH solution at 65°C. The resulting Y zeolites are comprehensively characterised regarding their physical and chemical properties such as crystallinity, porosity, Si/Al ratio and acidity, as well as being assessed using the model cracking reactions, demonstrating the effectiveness of the developed ultrasonic treatment to improve the sequential post-synthesis treatment for making mesoporous Y zeolites.

2 Materials and methods

2.1 Sequential post-synthesis treatments under hydrothermal conditions

For all experiments in this study, the parent ammonium zeolite Y was purchased from Zeolyst International (i.e., CBV 300, molar Si/Al ratio = 2.6), and was used as received. H₄EDTA (titration, ≥99%, Aldrich), citric acid (ACS reagent, ≥99.5%, Aldrich) and NaOH (reagent grade, 97%, Aldrich) were all used as received.

For chemical treatment of the parent zeolite Y using different chelators, zeolite Y (4 g for each experiment) was dispersed in 50 mL of aqueous solution of citric acid and H₄EDTA with different concentrations (in a three-neck flask) and mixed well, then treated hydrothermally at 100°C (temperature was maintained by immersing the flask in an oil bath) under stirring and reflux for different durations from 30 min to 6 h. After the chemical treatment, the system was cooled down to room temperature, and the dealuminated sample was separated from the solution by centrifugation (at 4400 r·min⁻¹). Then, it was washed thoroughly with deionised water for 5 times and dried at 100°C in an oven overnight to obtain the dry dealuminated sample.

For alkaline treatment under the hydrothermal condition, a dry dealuminated sample was treated in 0.2 mol·L⁻¹ NaOH solution at 65°C under stirring for 30 min. The desilicated sample was then separated by centrifugation, washed with deionised water for 5 times and dried at 100°C before characterisation. The yield after the treatment was determined by comparing the dry mass of

the resulting material against the weight of the starting material.

2.2 Sequential post-synthesis treatments involving the ultrasound-assisted alkaline treatment

The same procedure was used to obtain the dry dealuminated sample. For ultrasound-assisted alkaline treatment, the dry dealuminated sample was dispersed in 0.2 mol·L⁻¹ NaOH solution and sonicated at 65°C for 5 min by immersing the flask in an ultrasonic bath (U500H, 50–60 Hz). The resulting sample was subject to the same work-up procedure before characterisation.

Loss of materials was inevitable during the sequential post-synthesis treatments and the work-up procedure. Therefore, blank experiments (i.e., treating the parent zeolite using the same procedures with the deionised water) were performed to estimate the sample weight loss due to the protocol. The relevant weigh losses for chemical and alkaline treatments are about 5% and 6%, respectively. The samples were named accordingly as *aY-b-c-d*, where *a* is the acronym of chelators used (i.e., EA for H₄EDTA and CA for citric acid) in chemical treatments, *b* is the concentration of chelator, *c* is the time of the chemical treatment, and *d* is the condition used for alkaline treatment of desilication (i.e., HT for the hydrothermal treatment and S for the ultrasonic treatment), respectively.

2.3 Characterisation of materials

Powder X-ray diffraction (XRD) patterns of materials were obtained using a Philips X'Pert X-ray diffractometer with monochromatised CuKα₁ radiation (40 kV, 30 mA, λ = 1.5406 Å). XRD data were recorded in the 2θ range of 5°–40° with an angular step size of 0.0168° and a counting time of 1.167°·min⁻¹. The relative crystallinity (RC, using the XRD pattern of the parent zeolite Y as the reference with 100% RC) of the modified zeolites was calculated using the Integrated Peak Area Method [31]. The total integrated peak area of the eight peaks corresponding to the 15.7°, 18.7°, 20.4°, 23.6°, 27.0°, 30.7°, 31.4°, and 34.1° was calculated for determining the RC values of the modified zeolites (Eq. (1)).

$$RC = \frac{\sum \text{Integrated peak area of the modified Y zeolite}}{\sum \text{Integrated peak area of the parent Y zeolite}} \times 100\%, \quad (1)$$

Nitrogen (N₂) adsorption-desorption analysis was performed at -195°C on a Micromeritics 3Flex Surface Characterisation Analyser to characterise the porous property of materials. Prior to the measurements, 120 mg samples was degassed at 350°C under vacuum overnight.

Specific surface areas of samples were calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) method using the adsorption branch of isotherms. The micropore surface area, micropore volume and external surface area were obtained by the t -plot method. The morphology of samples was obtained by field emission scanning electron microscope (SEM, FEI Inspect F50 operating at 5 kV accelerating voltage) and field emission transmission electron microscope (TEM, FEI Tecnai F20 with the operating voltage of 200 kV). An energy-dispersive X-ray fluorescence (EDXRF) spectrometer (PANalytical MiniPal 4 EDXRF) was used to determine the elemental composition of materials, and hence the calculation of bulk Si/Al ratio of zeolites. Ammonia temperature programmed desorption (NH_3 -TPD) analysis of the acidity of zeolites was carried out on a Micrometrics AutoChem II 2920 chemisorption analyser (100 mg sample), and the relevant technical details of NH_3 -TPD analysis are described elsewhere [32].

2.4 Catalysis

Selected zeolites were ion-exchanged using $1 \text{ mol} \cdot \text{L}^{-1}$ aqueous ammonium nitrate (NH_4NO_3 , $\geq 98\%$, Aldrich) solution at 80°C for 24 h and calcined at 500°C (heating rate = $5^\circ\text{C} \cdot \text{min}^{-1}$, 3 h) to be evaluated using cracking reactions with n -octane as the model compound. The catalysis was performed at 350°C using a fixed bed reactor (I.D. = 10 mm) with 1 g pelletised zeolite diluted with glass beads. Before the catalytic reaction, the catalyst bed was preheated at 350°C for 2 h, then n -octane ($0.1 \text{ mL} \cdot \text{min}^{-1}$ with N_2 as the inert carrier gas at $240 \text{ mL} \cdot \text{min}^{-1}$) was introduced to initiate the cracking. The cracking products were analysed using an in-line gas chromatograph (Agilent 7890B) equipped with a flame ionisation detector (FID) and Agilent PoraPLOT Q column.

3 Results and discussion

For the pristine Y zeolite with a low Si/Al ratio of ~ 2.6 , dealumination before the alkaline treatment is necessary to improve mesoporous structures. Therefore, to compare the effectiveness of hydrothermal (at 65°C for 30 min) and ultrasonic (at 65°C for 5 min) alkaline treatment in modifying the dealuminated Y zeolites, the treatment time (30–360 min) of the first-step chemical dealumination (with $0.1 \text{ mol} \cdot \text{L}^{-1}$ H_4EDTA solution) was varied. The yield of materials after the chemical treatment for dealumination (DA) and the overall sequential treatment are showed in Fig. 1. All yield values were corrected according to the blank experiments. By varying the time of DA treatment from 30 min to 6 h, the relevant yields are measured at $80\% \pm 5\%$, suggesting the extraction of Al species from the pristine zeolite Y. After the second step of alkaline

treatment, regardless of the ultrasonic or hydrothermal method, comparable overall yields were obtained at $70\% \pm 5\%$, indicating the removal of Si species under the alkaline conditions.

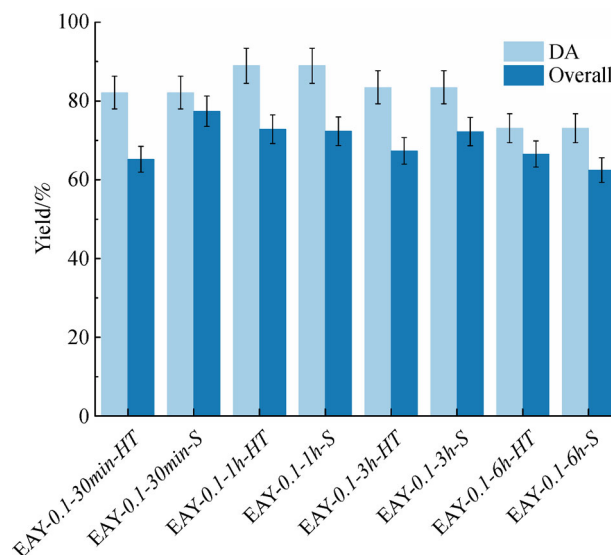


Fig. 1 Yields of EAY zeolites after the sequential chemical (using H_4EDTA) and hydrothermal/ultrasonic alkaline treatments of the pristine zeolite Y.

XRD patterns of EAY zeolites in reference to that of the parent zeolite Y are shown in Fig. 2, and the calculated RC values of the zeolites are summarised in Table 1. In general, EAY zeolites obtained by different post-synthesis treatments, regardless of the duration of the chemical dealumination treatment or the method used by desilication, show the analogous crystalline properties such as the characteristic diffraction peaks. However, it is noticeable

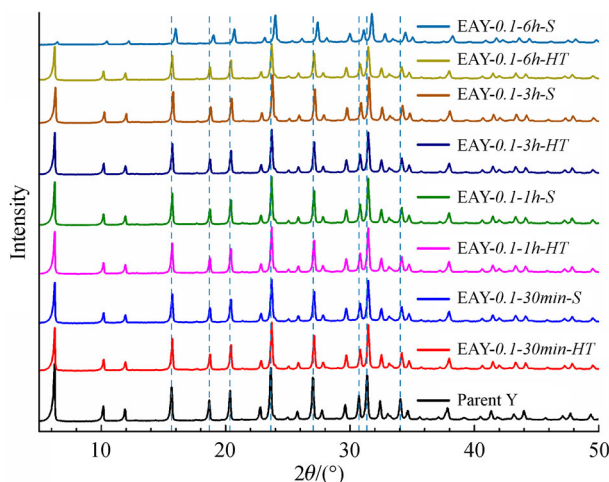


Fig. 2 XRD patterns of EAY zeolites obtained by the sequential post-synthesis treatments under different conditions.

Table 1 Si/Al ratios and RC values of the parent Y and EAY zeolites

Samples	Si/Al by XRF	RC by XRD
Parent Y	2.60	100%
EAY-0.1-30min-HT	3.88	89%
EAY-0.1-1h-HT	3.88	87%
EAY-0.1-3h-HT	4.05	85%
EAY-0.1-6h-HT	4.39	71%
EAY-0.1-30min-S	3.98	84%
EAY-0.1-1h-S	3.86	83%
EAY-0.1-3h-S	3.86	81%
EAY-0.1-6h-S	4.25	64%

that, in comparison with the parent zeolite Y, the relevant XRD characteristic peaks shifted towards high 2θ , suggesting the decrease of unit cell parameter [33]. Since the content of framework Al in the zeolite is proportional to unit cell parameter, the findings confirm the extraction of framework Al species during the sequential treatments. Especially for EAY-0.1-6h-HT and EAY-0.1-6h-S, the shift is comparably significant, suggesting the effective dealumination by treating the parent Y for 6 h. The extraction of Al species from the parent Y zeolite is also confirmed by XRF analysis, as shown in Table 1, showing that all EAY zeolites have larger Si/Al ratios than that of the parent Y (Si/Al of ~ 2.6). Specifically, based on the Si/Al ratios of the materials, the chemical treatment seems to require at least 3 h to be effective for dealumination, i.e., the Si/Al ratio of EAY zeolites treated for ≤ 3 h is comparable at 3.92 ± 0.07 , while that treated for 6 h has the ratio of 4.32 ± 0.1 .

Based on the calculated RC values, EAY zeolites became less crystalline with the extension of the treatment time used by the chemical dealumination treatment. By extending the time of dealumination from 30 min to 6 h, RC values of the resulting materials by the ultrasonic and hydrothermal alkaline treatment are about 89% and 71%, respectively. Comparing the alkaline treatments after the same dealumination treatment, EAY zeolites obtained by the ultrasonic treatment shows the relatively low crystallinity than that by the hydrothermal treatment, e.g., $RC_{EAY-0.1-6h-S} = 64\%$ vs. $RC_{EAY-0.1-6h-HT} = 71\%$.

The textural property of the resulting materials was analysed by N_2 physisorption, and the corresponding adsorption-desorption isotherms and the BJH pore size distributions (PSD, obtained from the adsorption branches of isotherms) are shown in Fig. 3. The parent Y exhibits a typical Type-I isotherm for microporous materials, whereas all EAYs show the hysteresis loop which is the evidence of the presence of mesoporous features in the materials. Concerning the mesoporosity in EAYs, the chemical treatment with the treatment time of < 3 h was less effective in comparison with the 6 h treatment. This is evidenced by the corresponding specific mesopore

volumes (V_{meso}) and external surface areas ($S_{external}$) presented in Table 2, in which the EAYs dealuminated for < 3 h show $V_{meso} = 0.1 \pm 0.01 \text{ cm}^3 \cdot \text{g}^{-1}$ and $S_{external} = 64 \pm 9 \text{ m}^2 \cdot \text{g}^{-1}$. Comparatively, for EAY-0.1-6h-S and EAY-0.1-6h-HT, the values for V_{meso} and $S_{external}$ are higher than $0.19 \text{ cm}^3 \cdot \text{g}^{-1}$ and $120 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. According to the previous work by Kerr [15,34], the chemical dealumination treatment of zeolite Y using EDTA relies on the hydrolysis of framework Al species, which needs hours to be effective to produce non-framework Al species. Conversely, the complexation of non-framework Al species using EDTA is relatively fast to extract Al species and create defective framework to make mesoporosity. Based on the same chemical dealumination treatment, the consecutive ultrasonic alkaline treatment was relatively more effective than the hydrothermal alkaline treatment and delivered better results regarding the mesoporous features of the relevant EAY zeolites. For example, V_{meso} values for EAY-0.1-6h-S and EAY-0.1-6h-HT are $0.19 \text{ cm}^3 \cdot \text{g}^{-1}$ and $0.22 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively. According to SEM and TEM analyses, exemplified by EAY-0.1-6h-S and EAY-0.1-6h-HT, surface defects and mesoporous structures were observed for EAY zeolites, suggesting the effectiveness of the sequential post-synthesis treatments under study for creating hierarchical mesoporous structures in the pristine zeolite Y. Also, as shown in Figs. 3(b), (d) and (f), PSDs of the obtained EAY zeolites all have the monomodal distribution centred on ~ 8.5 nm.

As discussed above, the ultrasound-assisted alkaline treatment of dealuminated zeolite Y is comparatively effective and efficient to make mesoporous Y zeolites, especially compared with the conventional alkaline treatment under the hydrothermal condition. The ultrasound irradiation enables the rapid extraction of Si species from the dealuminated zeolite framework [35], leading to the structural defects in the resulting EAY zeolites, and thus the relatively low crystallinity (Table 1, compared to the EAY zeolites obtained by the hydrothermal alkaline treatment). Previously, the direct ultrasound-assisted alkaline treatment of the pristine Y zeolite (Si/Al = 2.6) was reported, stating that the mesoporous Y zeolites were obtained [30]. However, the obtained zeolites only have insignificant mesoporous features, especially $V_{meso} < 0.1 \text{ cm}^3 \cdot \text{g}^{-1}$. Accordingly, it is difficult to classify such zeolites as mesoporous zeolites. By using the sequential chemical and ultrasound-assisted alkaline treatment, the EAY zeolites represent a 5-fold increase of the mesopore volume and a 14-fold increase of the mesopore area in comparison to the Y zeolites reported by Oruji et al. [30]. The findings of this study suggest that dealumination of the parent zeolite is necessary before the ultrasound-assisted alkaline treatment for preparing mesoporous zeolites via the post-synthesis modification of zeolites with low Si/Al ratios, exemplified by the Y zeolite.

The developed protocol facilitated by ultrasonication is generic, which was proved by using citric acid (CA) as the

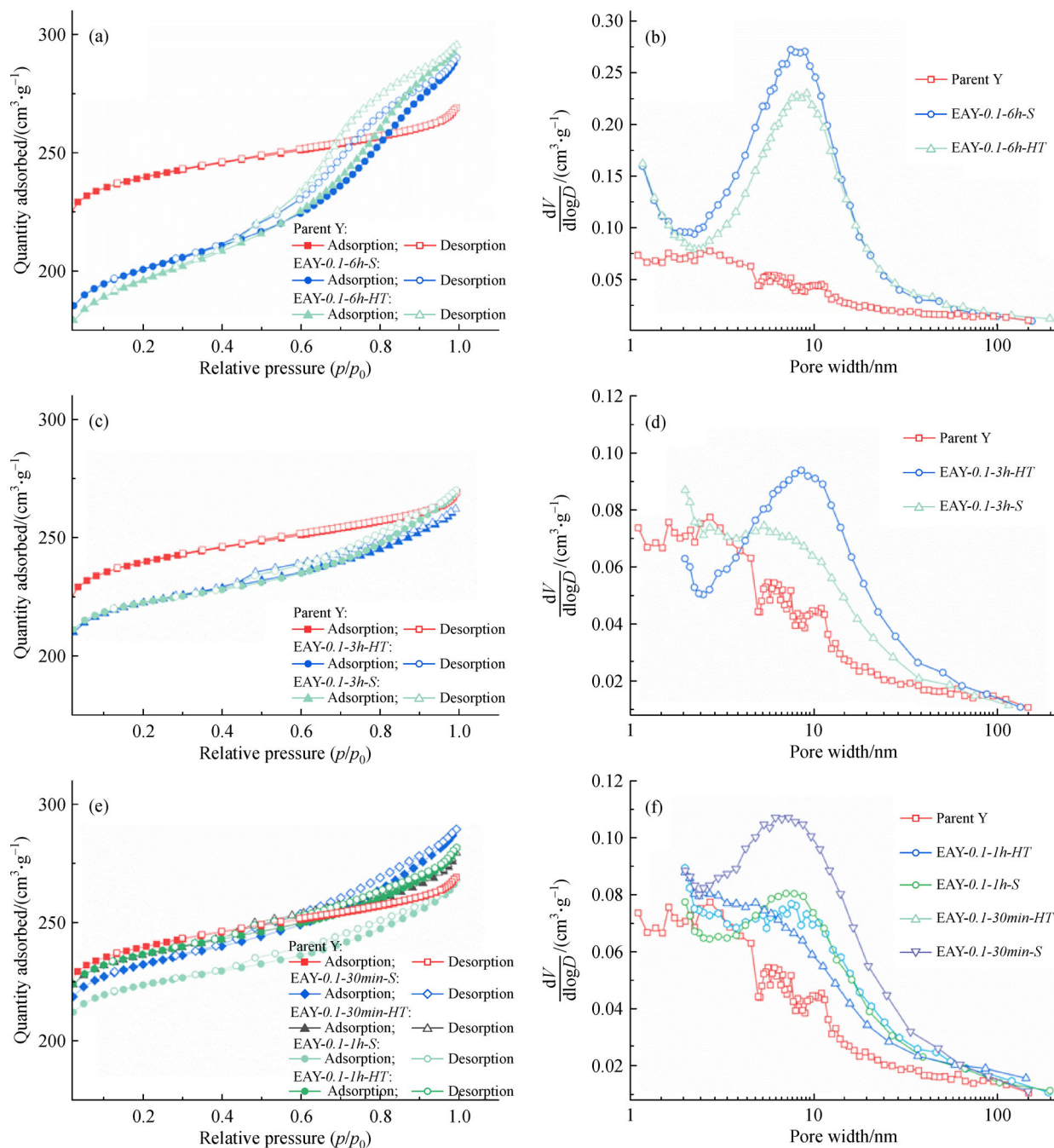


Fig. 3 N_2 adsorption-desorption isotherms and PSDs for (a and b) EAY-0.1-6h-HT and EAY-0.1-6h-S; (c and d) EAY-0.1-3h-HT and EAY-0.1-3h-S; (e and f) EAY-0.1-1h-HT, EAY-0.1-1h-S, EAY-0.1-30min-HT, and EAY-0.1-30min-S.

chelator in the chemical dealumination step. Citric acid has been used commonly in the post-synthesis dealumination of various zeolites such as ZSM-5 [36–38], zeolite beta [39–41] and zeolite Y [3,11,16,42,43] with few studies using CA in the sequential treatment [11,21,42]. For example, Xing et al. [42] performed the sequential hydrothermal treatment of zeolite Y using $0.17 \text{ mol}\cdot\text{L}^{-1}$ citric acid for dealumination (4 h) and $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH for desilication (6 h), and introduced a large amount of

mesopores in the resulting zeolite ($V_{\text{meso}} = 0.29 \text{ cm}^3\cdot\text{g}^{-1}$). Li et al. prepared the hierarchical Y zeolite with high mesoporosity with $V_{\text{meso}} = 0.34 \text{ cm}^3\cdot\text{g}^{-1}$ using a sequential chemical (with $0.15 \text{ mol}\cdot\text{L}^{-1}$ citric acid for 1 h) and alkaline treatment ($0.8 \text{ mol}\cdot\text{L}^{-1}$ NaOH for 0.5 h) [3]. However, the structure directing agent (SDA, i.e., tetrabutylphosphonium hydroxide, TBPH) was employed during the alkaline treatment to enable the mesopore formation. Although the reported methods are effective in

Table 2 Porous properties of the parent Y zeolite and EAY zeolites

Samples	Specific surface areas $/(m^2 \cdot g^{-1})$			Specific pore volumes $/(cm^3 \cdot g^{-1})$		
	$S_{micro}^a)$	$S_{external}^a)$	BET	$V_{micro}^a)$	$V_{meso}^b)$	$V_{total}^c)$
Parent Y	858	9	867	0.35	0.01	0.36
EAY-0.1-30min-S	722	82	804	0.33	0.12	0.45
EAY-0.1-30min-HT	757	61	818	0.34	0.09	0.43
EAY-0.1-1h-S	713	60	773	0.33	0.10	0.41
EAY-0.1-1h-HT	759	59	818	0.34	0.09	0.43
EAY-0.1-3h-S	706	63	769	0.32	0.10	0.42
EAY-0.1-3h-HT	711	59	770	0.32	0.09	0.41
EAY-0.1-6h-S	568	128	696	0.25	0.19	0.45
EAY-0.1-6h-HT	521	160	681	0.23	0.22	0.46

a) by the t -plot method; b) pore size range = 2–50 nm, calculations were based on the cumulative pore volume using the BJH method; c) single point adsorption total pore volume at $p/p^0 = 0.99$.

creating mesopore in Y zeolite, they require lengthy treatment time and SDAs, which may be improved using the developed ultrasonic method in the sequential treatment. Therefore, the sequential chemical treatment of the parent Y zeolite using citric acid for dealumination and followed by the hydrothermal and ultrasonic alkaline

treatment were performed to demonstrate the effectiveness of using ultrasound irradiation to improve the alkaline treatment.

During the chemical dealumination treatment using citric acid, two treatment durations of 1 h and 3 h and three citric acid concentrations (i.e., 0.1, 0.14 and $0.16 \text{ mol} \cdot \text{L}^{-1}$) were used, and the relevant yields and XRD patterns of the resulting CAY zeolites are presented in Fig. 5. Overall, the findings regarding the yield and XRD analysis of CAY are in line with that of EAY zeolites. An increase of the treatment time of chemical dealumination from 1 h to 3 h with citric acid caused the slight decrease of DA and overall yields (Fig. 5(a)), revealing the insignificant effect of treatment time ($< 3 \text{ h}$) on the extent of dealumination. The RC value and Si/Al ratio of CAY zeolites are shown in Table 3, showing that the two features do not have the strong correlation with the chemical treatment time under study (i.e., $< 3 \text{ h}$). By comparing the two methods used for the alkaline treatment, they showed the comparable performance regarding the yield. Again, the ultrasonic desilication treatment was found more intensive than the hydrothermal one, as shown in Table 3, producing the CAY zeolites with lower RC values, e.g., 86% for CAY-0.1-1h-HT vs. 83% for CAY-0.1-1h-S. Figure 5(b) presents the XRD patterns of the materials, showing that the characterised peaks of CAY zeolites from the ultrasonic treatment shift more to high 2θ compared to that by the conventional hydrothermal desilication. All findings confirm the effectiveness of the ultrasound irradiation in the alkaline desilication treatment, being able to extract Si species from the dealuminated Y zeolites efficiently.

Compared to the method using H_4EDTA as the chelator, the one employing citric acid delivered the mesoporous Y zeolites with similar yields and RC values after the sequential treatments. Since the ability of citric acid for removing framework Al species is comparable with that of EDTA, the effective dealumination with the concentrated citric acid and short treatment time may be possible. This

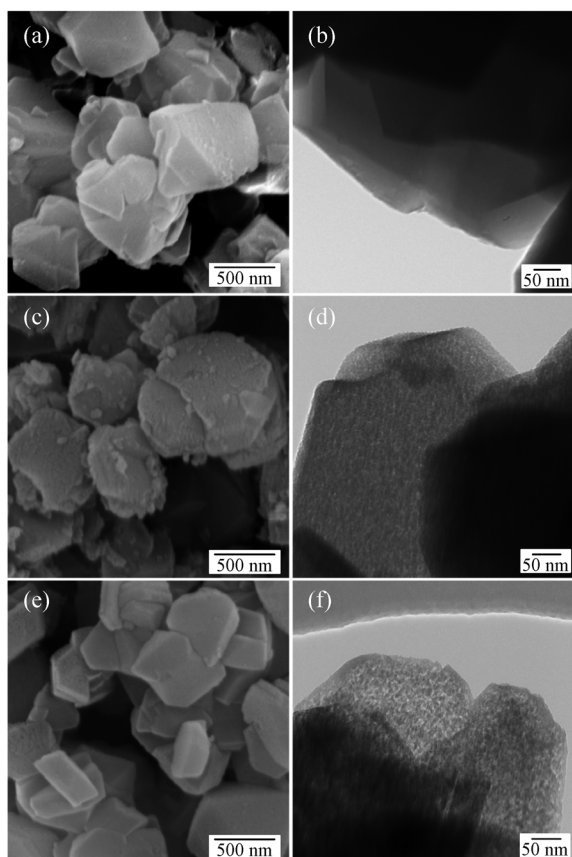


Fig. 4 SEM and TEM micrographs of (a and b) the parent zeolite Y, (c and d) EAY-0.1-6h-HT, and (e and f) EAY-0.1-6h-S.

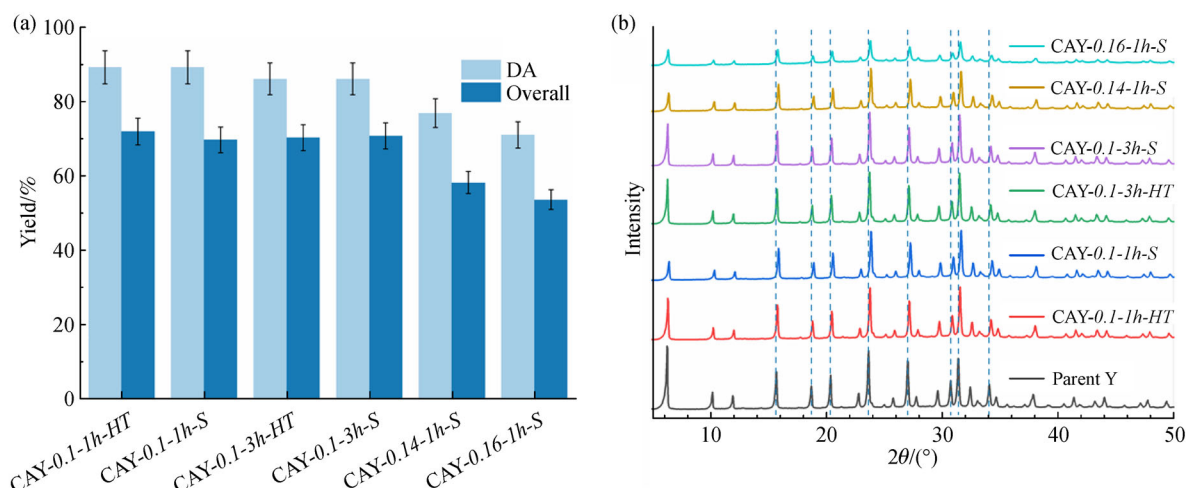


Fig. 5 (a) Yields of CAY zeolites after the sequential chemical (using citric acid) and hydrothermal/ultrasonic alkaline treatments of the pristine zeolite Y; (b) XRD patterns of CAY zeolites after the sequential post-synthesis treatments under different conditions.

Table 3 Si/Al ratios and values of relative crystallinity (RC) of the parent Y and CAY zeolites

Samples	Si/Al by XRF	RC by XRD
Parent Y	2.60	100%
CAY-0.1-1h-HT	3.95	86%
CAY-0.1-3h-HT	4.02	82%
CAY-0.1-1h-S	3.94	83%
CAY-0.1-3h-S	3.95	81%
CAY-0.14-1h-S	4.40	73%
CAY-0.16-1h-S	4.92	69%

hypothesis was confirmed by the relevant yield and XRD data of CAY-0.14-1h-S and CAY-0.16-1h-S, as shown in Fig. 5(a) and Table 3. Moreover, for the comparatively severely dealuminated Y zeolites, i.e., the CAY zeolites produced using concentrated citric acid solutions (i.e., 0.14 and 0.16 mol·L⁻¹), the ultrasound-assisted alkaline treatment was also very effective.

All CAY zeolites were analysed by N₂ physisorption analysis, as shown in Fig. 6. It is clear that after the sequential treatment (using citric acid for dealumination), all samples present hysteresis loops at the middle to high relative pressure, which are typical features for mesoporous zeolite with the Type IV isotherm. These hysteresis loops and high crystallinity (without amorphous phase), as well as the TEM analysis of the selected CAY zeolites (as shown in Fig. 7), prove that intracrystalline mesopores were successfully introduced into the parent Y zeolite. N₂ isotherms of the hydrothermally desilicated CAYs show similar uptake values at low relative pressure, but being slightly smaller than that of the ultrasonically desilicated

CAYs and the parent Y. When 0.1 mol·L⁻¹ citric acid was used for dealumination, the subsequent ultrasonic alkaline treatment showed relatively better effectiveness than the hydrothermal treatment, as shown by the comparison of mesoporous features of the resulting CAY zeolites in Table 4 (e.g., values of S_{external}). Additionally, by comparing the CAY zeolites with the relevant EAY zeolites (both treated using 0.1 mol·L⁻¹ chelating agents for 1 h and 3 h), it was found that citric acid is more effective than H₄EDTA to perform the first-step chemical dealumination, which led to the comparatively improved mesoporous features in the resulting zeolites (Tables 2 and 4). PSDs of CAY-0.1-1h and CAY-0.1-3h zeolites are shown in Fig. 6(b), showing that the mesopores in these samples are centred around 9 nm.

Based on the ultrasonic desilication treatment, the effect of citric acid concentration (i.e., 0.1, 0.14 and 0.16 mol·L⁻¹) used in the chemical dealumination treatment on the mesoporosity of the resulting CAY zeolites was studied. As expected, an increase in the concentration of citric acid in the dealumination step caused the decrease of the yield (Fig. 5(a)) and relative crystallinity (Table 3), as well as the increase of the Si/Al ratio of the final CAYs, suggesting the important role of the chelator concentration in removing the framework Al (based on the same treatment time), and hence the effectiveness of mesopore formation at the end of the sequential treatment.

By comparing the relevant N₂ isotherms, CAY-0.16-1h-S shows the lowest uptake at the low relative pressure compared to CAY-0.1-1h-S and CAY-0.14-1h-S, suggesting severe dealumination, and hence the damage of the microporous crystalline domain. Table 4 shows that the micropore surface area of CAY-0.16-1h-S is appreciably low at only 236 m²·g⁻¹, while that of CAY-0.1-1h-S and

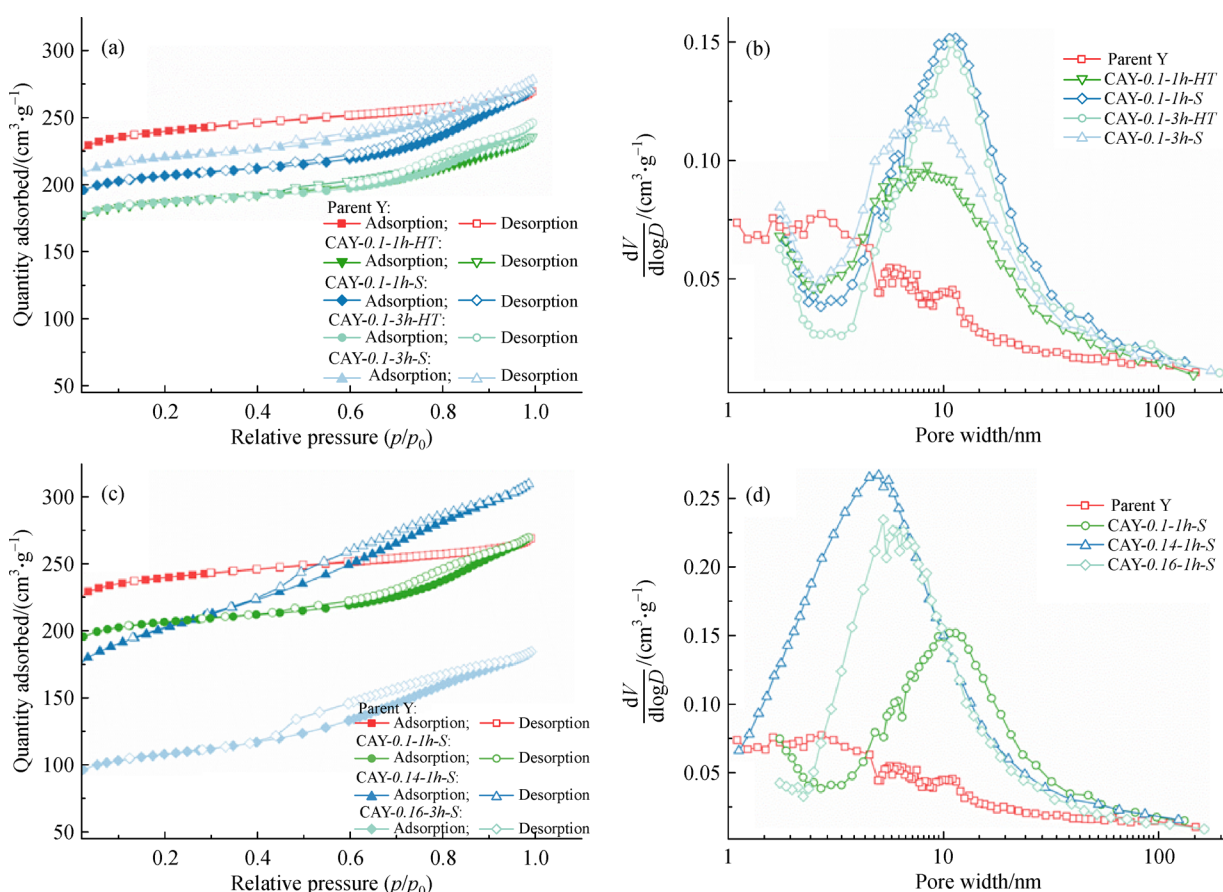


Fig. 6 (a and c) N_2 adsorption-desorption isotherms and (b and d) PSDs for CAY zeolites produced using different sequential post-synthesis treatments.

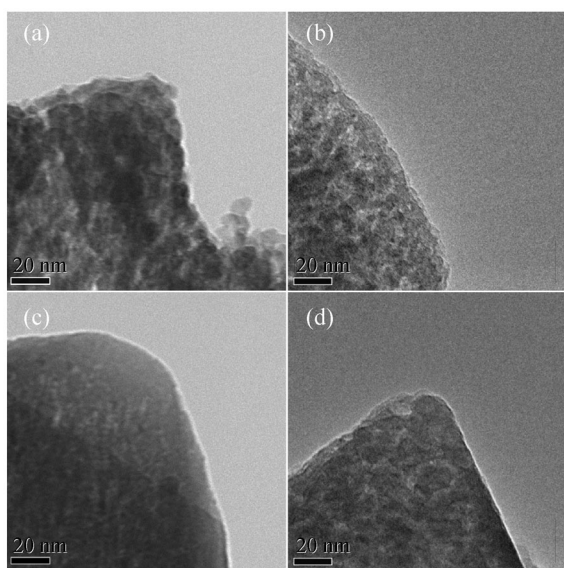


Fig. 7 TEM micrographs for (a) CAY-0.1-1h-HT, (b) CAY-0.1-1h-S, (c) CAY-0.14-1h-S and (d) CAY-0.16-1h-S.

CAY-0.14-1h-S is above $530 \text{ m}^2 \cdot \text{g}^{-1}$. Comparatively, CAY-0.14-1h-S possesses the best combination of the mesoporous and microporous features with high external and micropore surface area of 206 and $531 \text{ m}^2 \cdot \text{g}^{-1}$, respectively, as well as the specific pore volumes (Table 4). Considering the mesoporous property of the resulting zeolites, the developed sequential method employing ultrasound is as effective as the previously reported ones such as the sequential chemical treatment (using EDTA [21] or citric acid [44])-alkaline treatment, sequential steaming-chemical treatment (using EDTA) [45,46], sequential chemical treatment (using citric acid)-surfactant-templating method [16,47] and sequential acid leaching (using HCl)-alkaline treatment [21]. For CAY-0.16-1h-S, the sequential treatment using the highly concentrated citric acid caused the excessive Al extraction, and hence the destruction of the zeolite framework, leading to the collapse of the framework. This is also reflected by comparing the RC values of the relevant samples, and CAY-0.16-1h-S shows the lowest one at 69%.

Selected samples were ion-exchanged and analysed by NH_3 -TPD to compare the effect of different sequential

treatments on the acidic property of the resulting materials in reference to the parent Y, and the obtained results are presented in Fig. 8(a) and Table 5. All zeolites exhibited the typical NH_3 desorption behaviour corresponding to the Y zeolite, being in line with the previous findings [31]. The desorption peaks can be deconvoluted into two which are related to the weak ($< 200^\circ\text{C}$) and strong acidic sites ($> 300^\circ\text{C}$), respectively (Table 5). Compared to the acidic property of the parent Y, the sequential post-synthesis treatments, regardless of the chelator and the desilication method used, caused the decrease of strong acidity, i.e.,

$0.818 \text{ mmol} \cdot \text{g}^{-1}$ for the parent Y vs. $< 0.618 \text{ mmol} \cdot \text{g}^{-1}$ for the mesoporous Y. Based on the same first-step chemical treatment, the conventional hydrothermal and the proposed ultrasound-assisted alkaline treatments are equivalently effective, producing mesoporous zeolites with the comparable acidic property, as shown in Table 5. The selected mesoporous zeolites along with the parent Y were assessed by the comparative catalytic cracking of *n*-octane at 350°C . Figure 8(b) shows the absolute conversion of *n*-octane over different zeolites as a function of time-on-stream. All catalysts show the comparable initial activity close to

Table 4 Porous properties of the parent Y zeolite and CAY zeolites

Samples	Specific surface areas $/(\text{m}^2 \cdot \text{g}^{-1})$			Specific pore volumes $/(\text{cm}^3 \cdot \text{g}^{-1})$		
	$S_{\text{micro}}^{\text{a)}$	$S_{\text{external}}^{\text{a)}$	BET	$V_{\text{micro}}^{\text{a)}$	$V_{\text{meso}}^{\text{b)}$	$V_{\text{total}}^{\text{c)}$
Parent Y	858	9	867	0.35	0.01	0.36
CAY-0.1-1h-S	545	82	627	0.28	0.14	0.42
CAY-0.1-1h-HT	491	76	567	0.26	0.10	0.36
CAY-0.1-3h-S	581	87	668	0.30	0.12	0.42
CAY-0.1-3h-HT	499	68	567	0.26	0.12	0.38
CAY-0.14-1h-S	531	206	737	0.23	0.25	0.48
CAY-0.16-1h-S	236	101	337	0.12	0.16	0.28

a) *t*-plot method; b) pore size range = 2–50 nm, calculations were based on $V_{\text{total}} - V_{\text{micro}}$

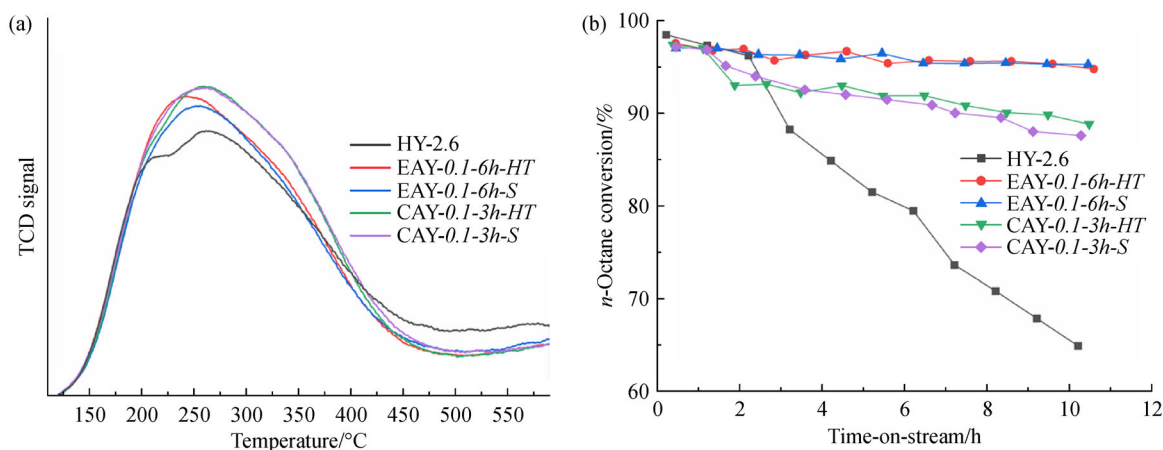


Fig. 8 (a) NH_3 -TPD spectra and (b) catalytic cracking activity (regarding the absolute conversion of *n*-octane) of the parent Y and selected mesoporous Y zeolites (including EAY-0.1-6h-HT, EAY-0.1-3h-S, CAY-0.1-3h-HT and CAY-0.1-3h-S).

Table 5 Analysis of NH_3 -TPD data for the parent Y and selected mesoporous Y zeolites

Catalysts	<i>T</i> of desorption peaks/ $^\circ\text{C}$		Weak acidity $/(\text{mmol} \cdot \text{g}^{-1})$	Strong acidity $/(\text{mmol} \cdot \text{g}^{-1})$	Total acidity $/(\text{mmol} \cdot \text{g}^{-1})$
	First peak	Second peak			
HY-2.6	202.1	296.5	0.396	0.818	1.214
EAY-0.1-6h-HT	227.0	331.5	0.895	0.458	1.353
EAY-0.1-6h-S	225.0	315.9	0.743	0.544	1.287
CAY-0.1-3h-HT	227.5	325.5	0.815	0.618	1.433
CAY-0.1-3h-S	227.5	328.6	0.840	0.606	1.446

~97%. The parent Y deactivated significantly (deactivation rate = $-3.4\% \cdot \text{h}^{-1}$), and the conversion of *n*-octane was about 65% after 10 h test. Conversely, the mesoporous Y zeolites demonstrated the improved catalytic performance, especially the EAY zeolites, which almost sustained their activity during the test. By comparing the EAY and CAY zeolites used in the catalytic tests, the former possesses the better mesoporosity ($\sim 0.21 \text{ cm}^3 \cdot \text{g}^{-1}$) than the latter (about $0.12 \text{ cm}^3 \cdot \text{g}^{-1}$). Therefore, although the strong acidity is relatively low in EAY zeolites (compared to the CAY zeolites, Table 5), the well-developed mesopores facilitate the accessibility and diffusion of molecules in their frameworks, leading to the improved performance in the cracking reaction. CAY zeolites deactivated gradually over time at the rate of about $-1\% \cdot \text{h}^{-1}$. More importantly, the catalytic tests show that during the sequential post-synthesis treatments, the developed ultrasound-assisted method (in the alkaline treatment) is as effective as the conventional hydrothermal method, however, the efficiency of the ultrasonic method is better than the hydrothermal one, i.e., the reduction in the treatment time by 6-fold.

4 Conclusions

Mesopore zeolites are practical solutions to solve the accessibility issues experienced by the pristine microporous zeolites in the important chemical conversions, especially petrochemicals. Therefore, the continuous development and innovation of preparing various types of mesoporous zeolites are necessary to improve the sustainability of zeolites and the processes (not limited to the catalytic petrochemical conversions) using zeolites, contributing to the sustainable development of the industry and society. In this work, sequential post-synthesis chemical dealumination and desilication of the pristine Y zeolite (with Si/Al of ~ 2.6 , the most important catalyst for FCC to produce gasoline range organics) was performed to prepare mesoporous Y zeolites. H_4EDTA was first used as the chelating agent in the study, and the effect of the dealumination treatment time (30 min to 6 h) and the method for desilication, i.e., hydrothermal and ultrasonic desilication, on the creation of mesoporosity was investigated. It was found that, for the pristine Y zeolite, the condition used by the dealumination step in the sequential treatment is critical for creating mesopores. When $0.1 \text{ mol} \cdot \text{L}^{-1} \text{H}_4\text{EDTA}$ was used, if the dealumination treatment was performed for $< 3 \text{ h}$, the sequential method was not very effective for making zeolites with mesoporous features, e.g., $S_{\text{external}} < 100 \text{ m}^2 \cdot \text{g}^{-1}$. More importantly, the ultrasound-assisted desilication treatment of the dealuminated zeolites was found effective in the sequential treatment method to facilitate the creation of mesopores, being more efficient than the conventional hydrothermal

dealumination treatment with the reduced treatment time, i.e., 5 min vs. 30 min. The effect of the ultrasound irradiation on the desilication is generic, which was confirmed by the comparative work using the citric acid dealuminated Y zeolites. In addition, based on the same first-step chemical treatment, the developed ultrasonic alkaline treatment method was as effective as the hydrothermal alkaline treatment, which was evidenced by the analysis of the porous, acidic and catalytic properties of the selected mesoporous zeolite analogues. The findings from this work emphasised that the ultrasound irradiation is a promising alternative to the conventional hydrothermal heating, being more energy- and time-efficient, in the sequential post-synthesis dealumination-desilication method for making hierarchical mesoporous zeolites.

Acknowledgements Yilai Jiao thanks the China Scholarship Council for his academic visiting fellowship in the UK (File No. 201604910181). Na Wang thanks the National Natural Science Foundation of China (Grant No. 51973124) for supporting her research.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. Barrer R, Makki M. Molecular sieve sorbents from clinoptilolite. *Canadian Journal of Chemistry*, 1964, 42(6): 1481–1487
2. van Donk S, Janssen A H, Bitter J H, de Jong K P. Generation, characterization, and impact of mesopores in zeolite catalysts. *Catalysis Reviews*, 2003, 45(2): 297–319
3. Li W, Zheng J, Luo Y, Da Z. Effect of hierarchical porosity and phosphorus modification on the catalytic properties of zeolite Y. *Applied Surface Science*, 2016, 382: 302–308
4. Paweewan B, Barrie P J, Gladden L F. Coking and deactivation during *n*-hexane cracking in ultrastable zeolite Y. *Applied Catalysis A, General*, 1999, 185(2): 259–268
5. Li K, Valla J, Garcia-Martinez J. Realizing the commercial potential of hierarchical zeolites: New opportunities in catalytic cracking. *ChemCatChem*, 2014, 6(1): 46–66
6. Inayat A, Knoke I, Spiecker E, Schwieger W. Assemblies of mesoporous FAU-type zeolite nanosheets. *Angewandte Chemie International Edition*, 2012, 51(8): 1962–1965
7. Jin J, Peng C, Wang J, Liu H, Gao X, Liu H, Xu C. Facile synthesis of mesoporous zeolite Y with improved catalytic performance for heavy oil fluid catalytic cracking. *Industrial & Engineering Chemistry Research*, 2014, 53(8): 3406–3411

8. Tao Y, Kanoh H, Kaneko K. Uniform mesopore-donated zeolite Y using carbon aerogel templating. *Journal of Physical Chemistry B*, 2003, 107(40): 10974–10976
9. Chal R, Gerardin C, Bulut M, Van Donk S. Overview and industrial assessment of synthesis strategies towards zeolites with mesopores. *ChemCatChem*, 2011, 3(1): 67–81
10. Triantafillidis C S, Vlessidis A G, Evmiridis N P. Dealuminated H-Y zeolites: Influence of the degree and the type of dealumination method on the structural and acidic characteristics of H-Y zeolites. *Industrial & Engineering Chemistry Research*, 2000, 39(2): 307–319
11. Xiao L, Mao J, Zhou J, Guo X, Zhang S. Enhanced performance of HY zeolites by acid wash for glycerol etherification with isobutene. *Applied Catalysis A, General*, 2011, 393(1): 88–95
12. van laak Adri N C, Gosselink R W, Sagala S L, Meeldijk J D, de Jongh P E, de Jong K P. Alkaline treatment on commercially available aluminum rich mordenite. *Applied Catalysis A, General*, 2010, 382(1): 65–72
13. Qin Z, Shen B, Gao X, Lin F, Wang B, Xu C. Mesoporous Y zeolite with homogeneous aluminum distribution obtained by sequential desilication-dealumination and its performance in the catalytic cracking of cumene and 1,3,5-triisopropylbenzene. *Journal of Catalysis*, 2011, 278(2): 266–275
14. Lee E F T, Rees L V C. Dealumination of sodium Y zeolite with hydrochloric acid. *Journal of the Chemical Society, Faraday Transactions I*, 1987, 83(5): 1531–1537
15. Kerr G T. Chemistry of crystalline aluminosilicates. V. Preparation of aluminum-deficient faujasites. *Journal of Physical Chemistry*, 1968, 72(7): 2594–2596
16. García-Martínez J, Johnson M, Valla J, Li K, Ying J Y. Mesoporous zeolite Y-high hydrothermal stability and superior FCC catalytic performance. *Catalysis Science & Technology*, 2012, 2(5): 987–994
17. Apelian M R, Fung A S, Kennedy G J, Degnan T F. Dealumination of zeolite β via dicarboxylic acid treatment. *Journal of Physical Chemistry*, 1996, 100(41): 16577–16583
18. Vogt E, Weckhuysen B. Fluid catalytic cracking: Recent developments on the grand old lady of zeolite catalysis. *Chemical Society Reviews*, 2015, 44(20): 7342–7370
19. Verboekend D, Mitchell S, Milina M, Groen J C, Pérez-Ramírez J. Full compositional flexibility in the preparation of mesoporous MFI zeolites by desilication. *Journal of Physical Chemistry C*, 2011, 115(29): 14193–14203
20. Tarach K, Góra-Marek K, Tekla J, Brylewska K, Datka J, Mlekodaj K, Makowski W, Igualada López M C, Martínez Triguero J, Rey F. Catalytic cracking performance of alkaline-treated zeolite Beta in the terms of acid sites properties and their accessibility. *Journal of Catalysis*, 2014, 312: 46–57
21. Verboekend D, Vilé G, Pérez-Ramírez J. Hierarchical Y and USY zeolites designed by post-synthetic strategies. *Advanced Functional Materials*, 2012, 22(5): 916–928
22. Verboekend D, Mitchell S, Pérez-Ramírez J. Hierarchical zeolites overcome all obstacles: Next stop industrial implementation. *CHIMIA International Journal for Chemistry*, 2013, 67(5): 327–332
23. Verboekend D, Nuttens N, Locus R, Van Aelst J, Verolme P, Groen J C, Perez-Ramirez J, Sels B F. Synthesis, characterisation, and catalytic evaluation of hierarchical faujasite zeolites: Milestones, challenges, and future directions. *Chemical Society Reviews*, 2016, 45(12): 3331–3352
24. Meng X, Xiao F S. Green routes for synthesis of zeolites. *Chemical Reviews*, 2014, 114(2): 1521–1543
25. Fan X, Manchon M G, Wilson K, Tennison S, Kozynchenko A, Lapkin A A, Plucinski P K. Coupling of Heck and hydrogenation reactions in a continuous compact reactor. *Journal of Catalysis*, 2009, 267(2): 114–120
26. Fan X, Jiao Y. A microwave-assisted chelation protocol to create mesoporosity in zeolites. 2018, GB1814932.8
27. Abelló S, Pérez-Ramírez J. Accelerated generation of intracrystalline mesoporosity in zeolites by microwave-mediated desilication. *Physical Chemistry Chemical Physics*, 2009, 11(16): 2959–2963
28. Baig R N, Varma R S. Alternative energy input: Mechanochemical, microwave and ultrasound-assisted organic synthesis. *Chemical Society Reviews*, 2012, 41(4): 1559–1584
29. Askari S, Alipour S M, Halladj R, Farahani M H D A. Effects of ultrasound on the synthesis of zeolites: A review. *Journal of Porous Materials*, 2013, 20(1): 285–302
30. Oruji S, Khoshbin R, Karimzadeh R. Preparation of hierarchical structure of Y zeolite with ultrasonic-assisted alkaline treatment method used in catalytic cracking of middle distillate cut: The effect of irradiation time. *Fuel Processing Technology*, 2018, 176: 283–295
31. Zhang R, Xu S, Raja D, Khusni N B, Liu J, Zhang J, Abdulridha S, Xiang H, Jiang S, Guan Y, et al. On the effect of mesoporosity of FAU Y zeolites in the liquid-phase catalysis. *Microporous and Mesoporous Materials*, 2019, 278: 297–306
32. Jiao Y, Fan X, Perdjon M, Yang Z, Zhang J. Vapor-phase transport (VPT) modification of ZSM-5/SiC foam catalyst using TPAOH vapor to improve the methanol-to-propylene (MTP) reaction. *Applied Catalysis A, General*, 2017, 545: 104–112
33. Pagis C, Prates A R M, Bats N, Tuel A, Farrusseng D. High-silica hollow Y zeolite by selective desilication of dealuminated NaY crystals in the presence of protective Al species. *CrystEngComm*, 2018, 20(11): 1564–1572
34. Kerr G T, Shipman G F. Reaction of hydrogen zeolite Y with ammonia at elevated temperatures. *Journal of Physical Chemistry*, 1968, 72(8): 3071–3072
35. Svelle S, Sommer L, Barbera K, Vennestrom P N, Olsbye U, Lillerud K P, Bordiga S, Pan Y H, Beato P. How defects and crystal morphology control the effects of desilication. *Catalysis Today*, 2011, 168(1): 38–47
36. Vieira S S, Magriotis Z M, Ribeiro M F, Graça I, Fernandes A, Lopes J M F M, Coelho S M, Santos N A V, Sazk A A. Use of HZSM-5 modified with citric acid as acid heterogeneous catalyst for biodiesel production via esterification of oleic acid. *Microporous and Mesoporous Materials*, 2015, 201: 160–168
37. Feng R, Yan X, Hu X, Wang Y, Li Z, Hou K, Lin J. Hierarchical ZSM-5 zeolite designed by combining desilication and dealumination with related study of *n*-heptane cracking performance. *Journal of Porous Materials*, 2018, 25(6): 1743–1756
38. Fan Y, Bao X, Lin X, Shi G, Liu H. Acidity adjustment of HZSM-5 zeolites by dealumination and realumination with steaming and citric acid treatments. *Journal of Physical Chemistry B*, 2006, 110

- (31): 15411–15416
39. Xie Z, Chen Q, Zhang C, Bao J, Cao Y. Influence of citric acid treatment on the surface acid properties of zeolite beta. *Journal of Physical Chemistry B*, 2000, 104(13): 2853–2859
40. Bai G, Han J, Zhang H, Liu C, Lan X, Tian F, Zhao Z, Jin H. Friedel-Crafts acylation of anisole with octanoic acid over acid modified zeolites. *RSC Advances*, 2014, 4(52): 27116–27121
41. Zhai L, Liu M, Dong X, Song C, Guo X. Dehydration of 2-(4'-ethylbenzoyl)-benzoic acid to 2-ethylanthraquinone over H β zeolite modified with organic acids. *Chinese Journal of Catalysis*, 2009, 30 (1): 9–13
42. Xing C, Yang G, Wu M, Yang R, Tan L, Zhu P, Wei Q, Li J, Mao J, Yoneyama Y, Tsubaki N. Hierarchical zeolite Y supported cobalt bifunctional catalyst for facilely tuning the product distribution of Fischer-Tropsch synthesis. *Fuel*, 2015, 148: 48–57
43. Al-Ani A, Darton R J, Sneddon S, Zholobenko V. Nanostructured Zeolites: The introduction of intracrystalline mesoporosity in basic faujasite-type catalysts. *ACS Applied Nano Materials*, 2018, 1(1): 310–318
44. Verboekend D, Keller T C, Mitchell S, Pérez-Ramírez J. Hierarchical FAU- and LTA-type zeolites by post-synthetic design: A new generation of highly efficient base catalysts. *Advanced Functional Materials*, 2013, 23(15): 1923–1934
45. Agudelo J L, Mezari B, Hensen E J M, Giraldo S A, Hoyos L J. On the effect of EDTA treatment on the acidic properties of USY zeolite and its performance in vacuum gas oil hydrocracking. *Applied Catalysis A, General*, 2014, 488: 219–230
46. Agudelo J L, Hensen E J M, Giraldo S A, Hoyos L J. Effect of USY zeolite chemical treatment with ammonium nitrate on its VGO hydrocracking performance. *Energy & Fuels*, 2016, 30(1): 616–625
47. Etim U J, Xu B, Zhang Z, Zhong Z, Bai P, Qiao K, Yan Z. Improved catalytic cracking performance of USY in the presence of metal contaminants by post-synthesis modification. *Fuel*, 2016, 178: 243–252