An efficient microwave-assisted chelation (MWAC) post-synthetic modification method to produce hierarchical Y zeolites

Samer Abdulridha [a, 1], Rongxin Zhang [a,1], Shaojun Xu [a], Aleksander Tedstone [a], Xiaoxia Ou [a], Jiacheng Gong [a], Boyang Mao [b], Mark Frogley [c], Carlo Bawn [d], Zhaoxia Zhou [e], Xinran Zhang [d], Sarayute Chansai [a], Stuart M. Holmes [a], Christopher Hardacre [a], Arthur A. Garforth [a], Sihai Yang [d,*], Yilai Jiao [a, f, **], Xiaolei Fan [a, ***]

[a] *Department of Chemical Engineering and Analytical Science, School of Engineering, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom*
[b] *Department of Department of Engineering, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0FA, United Kingdom*
[c] *Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom*
[d] *Department of Chemistry, School of Natural Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom*
[e] *Loughborough Materials Characterisation Centre, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom*
[f] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China Oxford Road, Manchester, M13 9PL, United Kingdom*

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ABSTRACT

We report a low-cost, highly energy efficient microwave-assisted chelation (MWAC) method, which enabled the post-synthetic modification of synthetic zeolites for adopting hierarchical structures within minutes. Exemplified by Zeolite Y, hierarchical Y zeolites prepared in this way showed exceptional specific external surface areas of >300 m^2 g^{1} and mesopore volumes of >0.46 cm^3 g^{1}. Comparative assessments revealed that developed zeolites have shown significantly improved catalytic activities for catalysis involving large substrates, such as catalytic cracking and hydrocracking of plastics.

1. Introduction

Synthetic zeolites dominate the global zeolites market, and the worldwide synthetic zeolites market is estimated at several billions of U. S. dollars [1,2]. They are principally used in industries as heterogeneous catalysts [3]. For example, faujasite (FAU) type Y zeolites are the most important material in petroleum refinery catalysts for fluid catalytic cracking (FCC) and hydrocracking [4], being estimated to account for a share of 61.1% of the total market of synthetic zeolites in 2018, regarding value [2]. The intrinsic micropores of these zeolites (<1 nm) lead to the long standing challenge of limitation on accessibility and diffusion during catalysis [5], for example, the reduced accessibility of active sites within the pore structure to the reactants and the slow diffusion rate of the products from the pores to the bulk media. The

former leads to low reaction rates, while the latter yields coke that partially or completely blocks the active sites. Various strategies have been explored to enhance the accessibility of the active sites within zeolite frameworks [4,6] such as: (i) design of zeolites with intrinsic large pores [7] or nanosized crystals [8,9]; (ii) templating methods to endow zeolites with mesoporous features [10–12]; and (iii) post-synthetic treatments of pristine zeolites to create hierarchical meso-/micro-porous structures [13–15]. The last strategy based upon dealumination and desilication [6,13,15–17] is robust and low-cost and thus particularly attractive for practical applications [16]. State-of-the-art post-synthetic dealumination and desilication are per-formed primarily by steaming, calcination and hydrothermal (HT) treatments in the presence of acids, bases or chelating agents (e.g., ethylenediaminetetraacetic acid, EDTA) [6,16]. Although being

effective, these processes are generally energy intensive and time-consuming [16], restricting the sustainable features of the resultant hierarchal zeolites. For creating mesopores in the aluminium-rich zeolites, especially zeolite Y (with the intrinsically low silicon-to-aluminum ratio, SAR, of ~2.4), compared with the steaming and acid leaching methods, chelation dealumination (also referred as chemical treatment) is relatively mild, being advantageous for making hierarchical Y with retained framework crystallinity and stability [14].

Microwave (MW) irradiation shows high efficiency in many chemical processes, such as the metal extraction from soils and plants [18,19]. In zeolite chemistry, synthesis of zeolites under MW conditions has been proven to be more energy-efficient and time-saving than the conven-tional synthesis under the hydrostatic HT conditions [20]. Additionally, MW-assisted post-synthetic modification of zeolites and zeotypes (in the liquid-phase) regarding the acidity [21–24] and porosity [25–28] was also attempted using the mineral acids and bases. Especially, our recent work has shown that the combination of chelation dealumination with the microwave irradiation was highly efficient to prepare mesoporous zeolitic materials [29,30].

Here we report the extended investigation of the post-synthetic treatment protocol involving chelation dealumination under MW irra-diation (i.e., MW-Assisted Chelation, MWAC [29,30]) for producing the modified synthetic zeolites with hierarchical pore structures. Specif-ically, and significantly, the MWAC method has enabled the preparation of hierarchical FAU zeolite Y on the minute timescale, and the obtained Y zeolites show exceptional hierarchical mesoporous features with the specific external surface area ($S_{ext.}$) >300 m^2 g^{-1} and mesopores volume (V_{meso}) > 0.46 cm^3 g^{-1}. As a result, the relevant zeolite catalysts exhibited notably enhanced catalytic activity and stability in catalytic cracking and hydrocatalytic decomposition (of plastics) reactions, compared with the commercial and conventional mesoporous Y zeolites. The MWAC method is generic for the post-synthetic modification of Y zeolite with different chelating agents, as well as other zeolites, showing significantly enhanced efficiency compared with the conventional HT processes.

2. Materials and methods

Chemicals and materials used by this work are detailed in the Sup-porting Information, SI. The hierarchical Y zeolites were prepared using the MWAC method with EDTA as the model chelating agent in aqueous solutions, and followed by a workup procedure to remove the detrital materials from the framework. Specifically, MWAC treatment of zeolite Y was performed in a monomode microwave reactor (CEM Discover SP-D MW reactor) at 100 ◦C or 50 ◦C with the variable MW power input of maximum 150 W. To prepare the mixture, 1.667 g zeolite Y was first charged into the EDTA aqueous solution (25 ml, EDTA concentration = 0.05–0.2 M) in a 35 ml Pyrex pressure vessel under stirring. The vessel containing the mixture was then inserted into the MW reactor and treated at the set temperature under stirring (at ca. 570 rpm) for various treatment times. After the MWAC treatment, the relevant zeolite sam-ples were obtained after the workup procedure. Typically, the mixture was quenched using an ice water bath for 15 min, and separated by centrifugation at 4400 rpm to separate the solid from the solution. The resulting solid samples were washed using deionized water four times and dried at 70 ◦C in an oven overnight. The dry sample was then washed using 0.2 M NaOH aqueous solution at 65 ◦C for 30 min under stirring to remove the detrital material remained in the zeolite pores. Finally, the sample was washed thoroughly using deionized water to obtain the final products, which were dried at 70 ◦C overnight prior to the characterisation. The resultant samples are denoted as MWAC-Y-*a-b-c*, in which *a, b* and *c* represent for the EDTA concentration (M), treat-ment time (min) and treatment temperature (◦C), respectively. By contrast, HT-Y-0.1-360-100 is the control mesoporous Y produced following the literature procedure [13,14] by the conventional HT treatment with 0.1 M EDTA at 100 ◦C for 360 min (SI).

Materials prepared were comprehensively characterised using various techniques such as powder X-ray diffraction (XRD), nitrogen (N$_2$) physisorption, scanning electron and scanning transmission mi-croscopy (SEM and S/TEM), Helium ion microscopy (HIM) and in situ infrared (IR) microspectroscopy, and relevant details of these techniques are provided in SI.

Comparative catalytic assessments of the zeolite catalysts were car-ried out using catalytic cracking of 1,3,5-triisopropylbenzene (TiPB, at 325 ◦C under atmospheric pressure), hydro-catalytic cracking of poly-proplylene and catalytic aldol condensation. All experimental informa-tion regarding catalysis is presented in SI in detail.

3. Discussion

By exposing zeolite Y, suspended aqueous EDTA solutions, to MW radiation at 150 W and 100 ◦C for varying reaction time, hierarchical Y zeolites with mesoporous features were produced, surpassing those of both the parent and HT-Y-0.1-360-100 zeolites (Table 1). At 100 ◦C, by varying the treatment time from 1 to 90 min, the obtained MWAC- ze-olites show the specific external surface areas ($S_{ext.}$) at 439 ± 112 m^2 g^{-1} and mesopores volumes (V_{meso}) at 0.55 ± 0.05 cm^3 g^{-1}, revealing an increase of a factor of ~3 in comparison to that of HT-Y-0.1-360-100. Indeed, these characteristic values of $S_{ext.}$, V_{meso} and V_{total} are amongst the highest ones reported to date for the post-synthetically modified Y zeolites (Table S1). By comparing the porosity of MWAC-Y zeolites, the effect of treatment time of the MWAC method is insignificant. For example, the value of V_{meso} has increased by only 16% on extending the MWAC treatment time from 1 to 90 min. A control experiment using the MWAC method at 50 ◦C was performed; and the resulting MWAC-Y-0.1-1-50 showed distinct mesoporous features with $S_{ext.}$ = 306 m^2 g^{-1} and V_{meso} = 0.46 cm^3 g^{-1} (Table 1), which are also higher than that of HT-Y. The findings demonstrate that the mesoporous characteristics of MWAC-Ys are not strictly related to the dielectric heating of the bulk water or the bulk thermal effect in the MWAC system. The micro- and meso-pore size distributions (PSDs) of MWAC-Ys can be readily tuned by varying the concentration of the chelating agent (Fig. S1, results related to the control blank experiments are shown in Figs. S2–S4 and Tables S1–S2), and the relevant crystallinity and solid yield data of the materials are presented in Fig. S4 and Table S2. Comparatively, samples obtained by the MWAC method using 0.1 M EDTA showed the optimal combination of micro- and meso-pores (Table 1), as well as the relative crystallinity of 62 ± 1.2% and SAR of 3.9 ± 0.9 (Table S2).

The presence of hierarchical mesopores of MWAC-Ys was evidenced by the observation of H1 type hysteresis loops in N$_2$ adsorption-desorption isotherms of MWAC-Y-0.1-1-100 and MWAC-Y-0.1-30-100 compared with that of the parent Y and HT-Y (Fig. 1a), as well as the comparison of the cumulative pore volume (Fig. 1b) and differential PSD (Fig. 1c). The local Al environment of the zeolite across different stages of the treatment (after 1 min) was studied by ^{27}Al MAS NMR (Fig. 1d–f), which suggests that, under the MW conditions, chelating agents can interact with the framework Al effectively (at ca. 60 ppm) to produce the

Table 1

Textural properties of the parent zeolite Y and hierarchical Y zeolites.

| Sample	Specific surface areas (m^2 g^{-1})			Specific pore volumes (cm^3 g^{-1})		
	BET	S_{micro}	$S_{ext.}$	V_{total}	V_{micro}	V_{meso}
Parent Y	867	858	9	0.36	0.35	0.01
HT-Y-0.1-360-100	762	626	137	0.48	0.28	0.20
MWAC-Y-0.05-90-100	1117	804	312	0.73	0.33	0.40
MWAC-Y-0.1-90-100	930	523	407	0.79	0.22	0.57
MWAC-Y-0.15-90-100	506	67	439	0.63	0.03	0.60
MWAC-Y-0.1-30-100	986	415	571	0.82	0.24	0.58
MWAC-Y-0.1-10-100	835	495	340	0.70	0.21	0.49
MWAC-Y-0.1-1-100	822	491	331	0.70	0.21	0.49
MWAC-Y-0.1-1-50	811	502	306	0.68	0.22	0.46
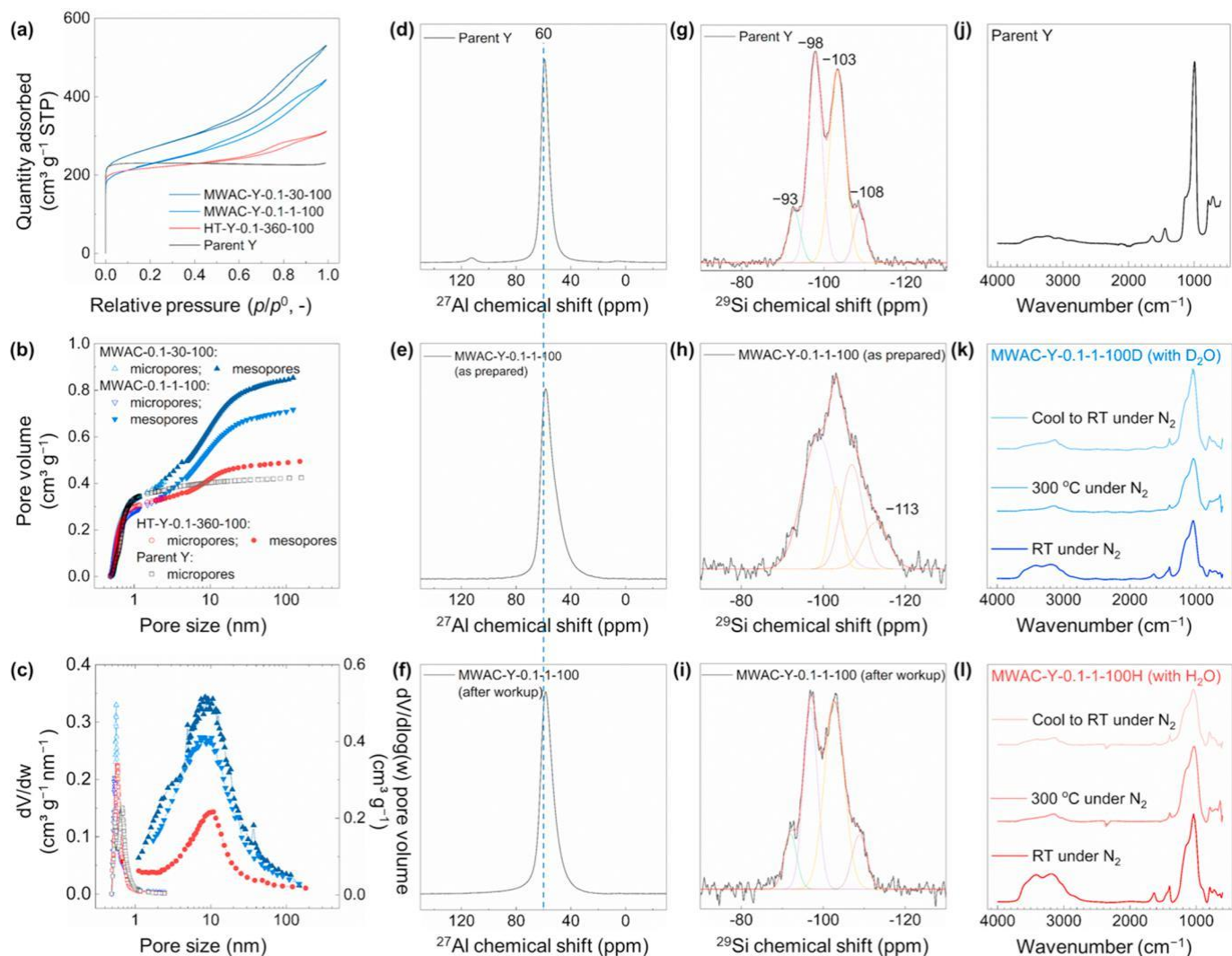
Fig. 1. Comparative characterisation of hierarchical Y zeolites under investigation. (a) N_2 adsorption-desorption isotherms, (b) Cumulative PSDs, and (c) Differential PSDs of the parent Y, HT-Y and MWAC-Y zeolites; (d to f) 27Al MAS NMR spectra, and (g to i) 29Si MAS NMR spectra of the parent Y and MWAC-Y-0.1-1-100 zeolites; (j) Reference IR spectrum of the parent Y zeolite; (k to l) In situ IR micro-spectroscopic spectra of the as-synthesized MWAC-Ys prepared using hydrogen and deuterium labelling.

tetrahedral non-framework Al sites [31], which was reflected by the broaden NMR spectrum (Fig. 1e). This is also evidenced by the ^{29}Si MAS NMR spectra of the parent and MW treated Y samples (Fig. 1g–i), which show the disappearance of NMR signal at ca. 93 ppm for Si(3Al) spe-cies and development of Si(4Si) signal at ca. 113 ppm on the treatment. After the workup, MWAC-Y-0.1-1-100 showed similar ^{27}Al and ^{29}Si MAS NMR spectra (Fig. 1f–i) to that of parent Y (Fig. 1d–g), but signal broadening is observed for both spectra, suggesting the variation of local Al/Si coordination within the framework after the post-treatment.

In situ infrared (IR) microspectroscopy study of MWAC-Y-0.1-1-100 zeolites treated using water and deuterium oxide (D_2O) show that deuterium as the labelling isotope in the MWAC was not incorporated in the resulting framework, labelled as MWAC-Y-0.1-1-100D (Fig. 1k). Both MWAC-Y-0.1-1-100H (MWAC-Y using water as the solvent, Fig. 1j) and MWAC-Y-0.1-1-100D show the main symmetric and asymmetric stretching (in the range of 3000–3600 cm^{-1}) and bending (at ca. 1635 cm^{-1}) bands of lattice water, suggesting the MWAC method promotes the direct chelation of framework Al by EDTA which sequentially pro-duced water [32]. These bands disappeared gradually by treating the samples under heating (up to 300 °C in a flow cell) under a dry N_2 flow due to the desorption of the lattice water from the framework. In the –OH stretching region (Fig. 1k and j, Fig. S5 and S6), the band at 3130

cm^{-1} emerged gradually during the in situ thermal treatment for both samples (in comparison to the spectrum of the parent zeolite, Fig. 1j), which confirmed the creation of the surface –OH groups through the MW-EDTA-zeolite interaction rather than the hydrolysis (Scheme 1). The –OH groups are stable at 300 °C and can be exchanged by deuterium (by introducing D_2O vapour in N_2), causing the predicted redshift of the IR spectra (Fig. S5). Importantly, by contrast, the post-synthetic treat-ment of zeolite Y using mineral acids (e.g. hydrochloric acid and nitric acid at 0.1 M) under MW irradiation was not effective in creating mes-oporous structures (Table S1).

The hierarchical nature of MWAC-Y zeolites has also been studied by the scanning transmission electron microscopy (S/TEM) and helium (He) ion microscopy (HIM), as shown in Fig. 2, S7–S8. High-resolution TEM micrographs (Fig. 2a–b) show distinct comparison between the parent zeolite and MWAC-Y-0.1-1-100. The parent Y shows the typical dense zeolite phase with well-aligned lattice fringes, while MWAC-Y demonstrates the co-existence of the intra-crystalline mesopores (ca. 5–10 nm) and crystal lattice fringes. The accessible hierarchical porosity of MWAC-Ys was confirmed by high-angle annular dark-field (HAADF) and focused He-ion beams imaging. Comparative TEM (Fig. 2c) and HAADF-S/TEM (Fig. 2d) images of MWAC-Y-0.1-30-100 show the opening of mesopores at the edges of the zeolite Y crystal. The feature
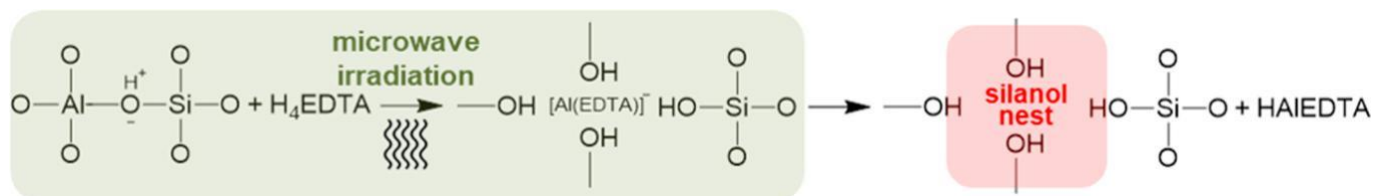
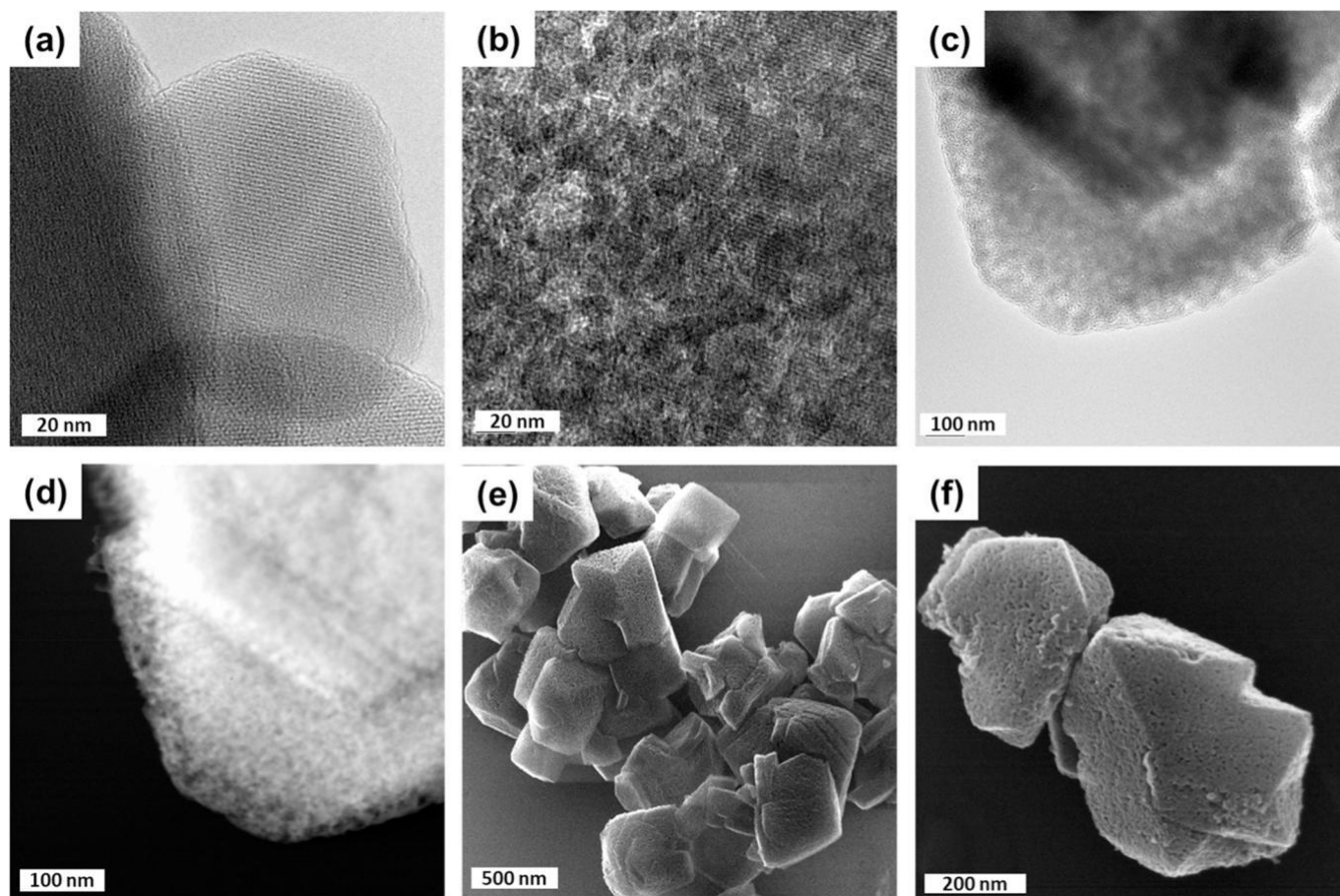**Scheme 1.** Dealumination of Y zeolite by the MWAC method with EDTA.

Fig. 2. (a) TEM micrograph of the parent Y; (b) TEM micrograph of the crystal domain and intracrystalline mesopores of MWAC-Y-0.1-1-100; (c and d) Comparative TEM and HAADF-STEM images of MWAC-Y-0.1-30-100; (e and f) HIM images of MWAC-Y-0.1-1-100.

was also evidenced by direct HIM imaging of the zeolite particle surface of MWAC-Y (Fig. 2e–f), clearly showing the hierarchical mesopores that exist on the surfaces (similar features were also recorded by the low voltage scanning electron microscopy (SEM, Figs. S8e and S9). The crystalline nature of the MWAC-Y is also confirmed by selected area electron diffraction (SAED) patterns of discrete spots (Fig. S8b).

Stable hierarchical FAU Y zeolites (Figs. S10–S11) are important industrial catalysts, particularly for reactions involving bulky substrates. We assessed the catalytic properties of the selected MWAC-Ys using (i) catalytic cracking of a bulky aromatic hydrocarbon 1,3,5-triisopropyl-benzene (TiPB), (ii) hydro-catalytic cracking of polypropylene (PP, using platinum, Pt, impregnated zeolites) and (iii) catalytic aldol condensation (for producing a bulky fragrance chemical, i.e. jasmi-naldehyde) (Figs. S12–S14) with direct comparison to the parent Y and/ or commercial mesoporous Y and HT-Y zeolites. The MWAC-Y zeolites demonstrate exceptional performance on cracking TiPB (Fig. 3a), yielding quantitative conversions of TiPB as well as high selectivity to propylene (Fig. S13a), over the entire course of study. Conversely, the parent Y and HT-Y deactivated gradually due to the coke formation

(Fig. S15). Given that the total acidity of the MWAC-Y zeolites is comparable to that of HT-Y (Fig. S11), the excellent catalytic activity of MWAC-Ys in cracking reactions is primarily due to the much enhanced hierarchical mesoporosity promoted by the MWAC method.

Comparative catalysis using the Pt supported on zeolite catalysts for the hydrocracking of plastics (polypropylene as the model plastic) was performed as well, as shown in Fig. 3b and c. The catalysts based on the MWAC-Y-0.1-1-100 and HT-Y-0.1-360-100 zeolites showed the comparable performance regarding the conversion of polypropylene (at ~78%), whereas the catalysts supported on the commercial mesoporous Y and Parent Y only enabled the conversions at about 67% and 39%, respectively. All Pt catalysts supported on Y zeolites gave similar distributions of hydrocarbon products, centered at around C4, i.e. butane and isobutene, as shown in Fig. 3c. In addition to the light hydrocarbons produced (Fig. S14), gel permeation chromatography (GPC) analysis showed that the weight average molecular weight (M_w) of the polymer retrieved after the hydrocracking reaction was reduced significantly compared with that of the pristine polypropylene. More importantly, the catalyst based on the MWAC-Y-0.1-1-100 showed the smallest M_w value,
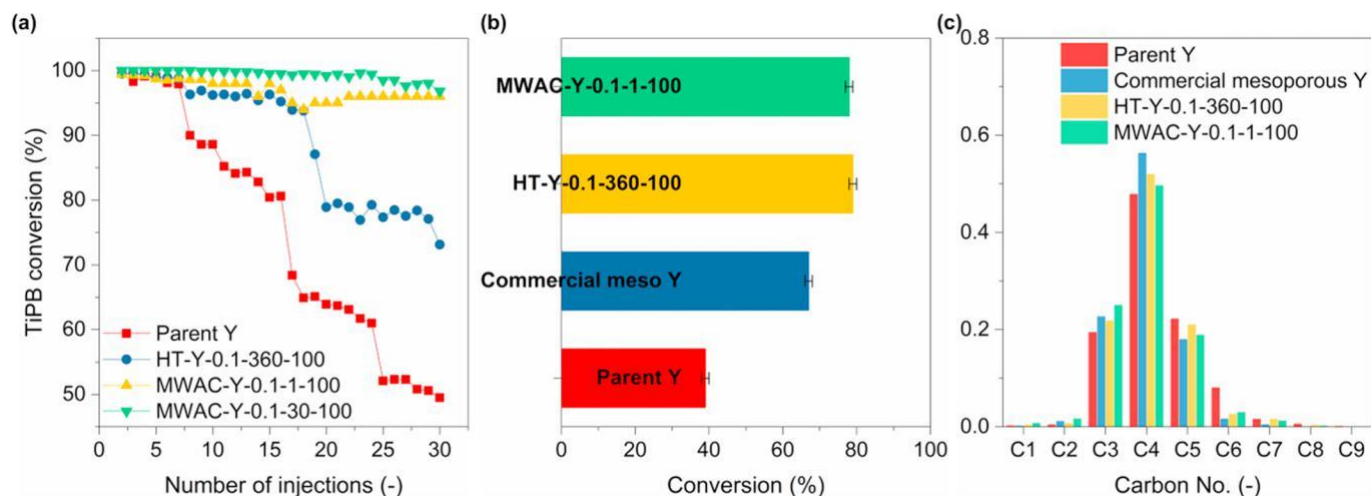
Fig. 3. Catalytic performance of the Y zeolite catalysts. (a) TiPB conversions over the Y zeolites as a function of injection numbers in catalytic cracking; (b) Polypropylene conversion over the Pt supported on Y zeolites catalysts in hydrocracking of polypropylene; (c) Weight average Mw of the pristine polypropylene and residual polymers from catalytic hydrocracking.

being the most effective catalyst for depolymerisation.

4. Conclusions

The recently developed MWAC method is effective in modifying FAU Y for hierarchical mesoporosity with a wide range of chelating agents such as oxalic and citric acids (Table S4), and is particularly effective with multidentate *clathro* chelators, such as EDTA. Importantly, it is a generic method which is applicable to systems involving different types of zeolites, such as zeolite beta (with citric acid, Table S5). Although post-synthetic dealumination and desilication have been used as in-dustrial methods for producing practical Y zeolites with the improved mesoporosity and stability, the process-efficiency of state-of-the-art methods has not yet been assessed comprehensively. The MWAC method is highly energy-efficient, exemplified by the preliminary comparison between the MWAC-Y-0.1-1-100 and HT-Y-0.1-360-100 zeolites. Specifically, regarding the production of 1 g hierarchical zeolite Y at the laboratory scale (SI), the MWAC method showed about 21-fold decrease in energy consumption (i.e. ~0.02 kW h g^{-1}) compared with that for the conventional hydrothermal method at ~0.42 kW h g^{-1}. Regarding the external surface area of hierarchical zeolite Y, the MWAC method only requires 6.04×10^{-5} kW h to create 1 m^2 external surface area, while the conventional method needs significantly more energy at 3.07×10^{-3} kW h (about 50 times as much as that by the MWAC). Therefore, the generic microwave promoted complexation effect high-lights the possibility of developing transformative technologies for making hierarchical zeolites with great energy efficiency, as well as the industrial relevance.

CRediT authorship contribution statement

Samer Abdulridha: Data curation, Writing - original draft. **Rongxin Zhang:** Data curation, Writing - original draft. **Shaojun Xu:** Data curation. **Aleksander Tedstone:** Data curation, Writing - original draft. **Xiaoxia Ou:** Data curation. **Jiacheng Gong:** Data curation, Writing - original draft. **Boyang Mao:** Data curation. **Mark Frogley:** Data curation, Writing - review & editing. **Zhaoxia Zhou:** Data curation, Writing - review & editing. **Xinran Zhang:** Data curation. **Sarayute Chansai:** Data curation. **Stuart M. Holmes:** Writing - review & editing. **Christopher Hardacre:** Writing - review & editing. **Arthur A. Garforth:** Writing - review & editing. **Sihai Yang:** Conceptualization, Methodology, Writing - review & editing. **Yilai Jiao:** Conceptualization, Methodology. **Xiaolei Fan:** Conceptualization, Writing - review & editing, Supervision.

Appendix A. Supplementary data

References

[1] D.M.U.S. Flanagan, Geological Survey Minerals Yearbook 2018: Zeolites, February 2019.

[2] Global Synthetic Zeolites Market Forecast to 2023: Opportunities in Rising Demand for Adsorbents & Recovering Oil Prices, 2018 accessed, https://www.research andmarkets.com/research/hjtmwf/global_synthetic?w=5. (Accessed 7 March 2020).

[3] J. Weitkamp, Zeolites and catalysis, Solid State Ion 131 (2000) 175–188.

[4] L. Kunhao, V. Julia, G.M. Javier, Realizing the commercial potential of hierarchical zeolites: new opportunities in catalytic cracking, ChemCatChem 6 (2014) 46–66.

[5] P. Selvam, J. Sauer, B. Garrett, C. Campbell, R. van Santen, P. Davies, A.L. Miller, M. Bowker, G. Hutchings, D. Wotton, H.-J. Freund, M. Howard, M. Feaviour, R. Burch, A.M. Raspolli Galletti, E. Gross, F. Ivars Barcelo, A. Kotarba, S. Kondrat, B. Weckhuysen, B. Majumdar, A. Bruix, N. Fischer, B. Gates, J. Moulijn, A. Roldan, N. Novak Tusar, T. Jakubek, D. Willock, M. Craven, K. Sethu, R. Catlow, R. Madix, H. Manyar, C. Friend, A. Corma, P. Wells, W. Ueda, A. Trunschke, R. Palmer, Designing new catalysts: synthesis of new active structures: general discussion, Faraday Discuss 188 (2016) 131–159.

[6] D. Verboekend, N. Nuttens, R. Locus, J. Van Aelst, P. Verolme, J.C. Groen, J. Perez-Ramirez, B.F. Sels, Synthesis, characterisation, and catalytic evaluation of hierarchical faujasite zeolites: milestones, challenges, and future directions, Chem. Soc. Rev. 45 (2016) 3331–3352.

[7] A. Corma, M.J. Díaz-Cabanas,˜ J. Martínez-Triguero, F. Rey, J. Rius, A large-cavity zeolite with wide pore windows and potential as an oil refining catalyst, Nature 418 (2002) 514.

[8] A. Inayat, I. Knoke, E. Spiecker, W. Schwieger, Assemblies of mesoporous FAU-type zeolite nanosheets, Angew. Chem. Int. Ed. 51 (2012), 1962–1965.

[9] H. Awala, J.-P. Gilson, R. Retoux, P. Boullay, J.-M. Goupil, V. Valtchev, S. Mintova, Template-free nanosized faujasite-type zeolites, Nat. Mater. 14 (2015) 447.

[10] J. Garcia-Martinez, M. Johnson, J. Valla, K. Li, J.Y. Ying, Mesostructured zeolite Y-high hydrothermal stability and superior FCC catalytic performance, Catal. Sci. Technol. 2 (2012) 987–994.

[11] I. Schmidt, A. Boisen, E. Gustavsson, K. Ståhl, S. Pehrson, S. Dahl, A. Carlsson, C.J. H. Jacobsen, Carbon nanotube templated growth of mesoporous zeolite single crystals, Chem. Mater. 13 (2001) 4416–4418.

[12] S. Abdulridha, J. Jiang, S. Xu, Z. Zhou, H. Liang, B. Mao, Y. Zhou, A.A. Garforth, Y. Jiao, X. Fan, Cellulose nanocrystals (CNCs) as hard templates for preparing mesoporous zeolite Y assemblies with high catalytic activity, Green Chem. 22 (2020) 5115–5122.

[13] D. Verboekend, G. Vile,´ J. P´erez-Ramírez, Hierarchical Y and USY zeolites designed by post-synthetic strategies, Adv. Funct. Mater. 22 (2012) 916–928.

[14] D. Verboekend, T.C. Keller, S. Mitchell, J. P´erez-Ramírez, Hierarchical FAU- and LTA-type zeolites by post-synthetic design: a new generation of highly efficient base catalysts, Adv. Funct. Mater. 23 (2013), 1923–1934.

[15] Y. Jiao, L. Forster, S. Xu, H. Chen, J. Han, X. Liu, Y. Zhou, J. Liu, J. Zhang, J. Yu, C. D'Agostino, X. Fan, Creation of Al-enriched mesoporous ZSM-5 nanoboxes with high catalytic activity: converting tetrahedral extra-framework Al into framework sites via post treatment, Angew. Chem. Int. Ed. (2020), https://doi.org/10.1002/ anie.202002416.

[16] R. Chal, C. G´erardin, M. Bulut, S. van Donk, Overview and industrial assessment of synthesis strategies towards zeolites with mesopores, ChemCatChem 3 (2011) 67–81.

[17] R. Zhang, P. Zhong, H. Arandiyan, Y. Guan, J. Liu, N. Wang, Y. Jiao, X. Fan, Using ultrasound to improve the sequential post-synthesis modification method for making mesoporous Y zeolites, Front. Chem. Sci. Eng. 14 (2020) 275–287.

[18] U. Chatreewongsin, Metal extraction from soil samples by chelation in a microwave system, Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 2000, p. 137.

[19] S. Czarnecki, R.-A. Düring, Closed-vessel miniaturised microwave-assisted EDTA extraction to determine trace metals in plant materials, Int. J. Environ. Anal. Chem. 94 (2014) 801–811.

[20] X. Meng, F.-S. Xiao, Green routes for synthesis of zeolites, Chem. Rev. 114 (2014) 1521–1543.

[21] M.D. Gonzalez,´ Y. Cesteros, P. Salagre, F. Medina, J.E. Sueiras, Effect of microwaves in the dealumination of mordenite on its surface and acidic properties, Microporous Mesoporous Mater. 118 (2009) 341–347.

[22] M.D. Gonzalez,´ Y. Cesteros, P. Salagre, Effect of microwaves on the surface and acidic properties of dealuminated zeolites, Phys. Procedia 8 (2010) 104–108.

[23] B.M. Chandra Shekara, B.S. Jai Prakash, Y.S. Bhat, Dealumination of zeolite BEA under microwave irradiation, ACS Catal. 1 (2011) 193–199.

[24] M.D. Gonzalez,´ Y. Cesteros, P. Salagre, Comparison of dealumination of zeolites beta, mordenite and ZSM-5 by treatment with acid under microwave irradiation, Microporous Mesoporous Mater. 144 (2011) 162–170.

[25] C.C. Pavel, W. Schmidt, Generation of hierarchical pore systems in the titanosilicate ETS-10 by hydrogen peroxide treatment under microwave irradiation, Chem. Commun. (2006) 882–884.

[26] S. Abello, J. Perez-Ramirez, Accelerated generation of intracrystalline mesoporosity in zeolites by microwave-mediated desilication, Phys. Chem. Chem. Phys. 11 (2009) 2959–2963.

[27] V. Paixao,˜ R. Monteiro, M. Andrade, A. Fernandes, J. Rocha, A.P. Carvalho, A. Martins, Desilication of MOR zeolite: conventional versus microwave assisted heating, Appl. Catal., A 402 (2011) 59–68.

[28] Z. Hasan, J.W. Jun, C.-U. Kim, K.-E. Jeong, S.-Y. Jeong, S.H. Jhung, Desilication of ZSM-5 zeolites for mesoporosity development using microwave irradiation, Mater. Res. Bull. 61 (2015) 469–474.

[29] R. Zhang, D. Raja, Y. Zhang, Y. Yan, A.A. Garforth, Y. Jiao, X. Fan, Sequential microwave-assisted dealumination and hydrothermal alkaline treatments of Y zeolite for preparing hierarchical mesoporous zeolite catalysts, Top. Catal. 63 (2020) 340–350.

[30] S. Abdulridha, Y. Jiao, S. Xu, R. Zhang, A.A. Garforth, X. Fan, Mesoporous zeolitic materials (MZMs) derived from zeolite Y using a microwave method for catalysis, Front. Chem. 8 (2020) 482.

[31] Z. Yan, D. Ma, J. Zhuang, X. Liu, X. Liu, X. Han, X. Bao, F. Chang, L. Xu, Z. Liu, On the acid-dealumination of USY zeolite: a solid state NMR investigation, J. Mol. Catal. 194 (2003) 153–167.

[32] G.T. Kerr, Chemistry of crystalline aluminosilicates. V. Preparation of aluminum-deficient faujasites, J. Phys. Chem. 72 (1968) 2594–2596.