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## Mg<sup>2+</sup>-derived mesoporous ultra-high silica twelvemembered-ring basic zeolites: straightforward synthesis and catalytic performance<sup>†</sup>

Jingyan Xie, Haimeng Wen, Wei Zhang, Yu Zhou\* and Jun Wang\*

 $Mg^{2+}$ -derived mesoporous ultra-high silica twelve-membered-ring zeolites with multiple topologies (MOR, BEA and MTW) were straightforwardly synthesized by a one-pot route, where the crucial step was the co-hydrolysis/condensation of silica source and magnesium salt under moderate acidic conditions.  $SiO_2/Al_2O_3$  ratios can be adjusted from ~30 to as high as 410, thus generating superior basicity that was further improved by the incorporation of Mg species. A mesoporous structure was self-formed without the assistance of any template or special strategy. Catalysis tests showed high activity of these zeolites in a typical base reaction, Knoevenagel condensation, even for the bulky substrates due to the enhanced mass transfer arising from the mesopores. This methodology provides a promising approach towards target synthesis of valuable  $Mg^{2+}$ -derived mesoporous ultra-high silica zeolites with tunable acid/base properties, which can even act as an efficient mesoporous zeolitic solid base.

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## 1. Introduction

Zeolites are crystalline aluminosilicates with large surface areas, well-defined uniform micropores, and excellent stability. They have been extensively applied as adsorbents, ion exchangers and catalysts in numerous industrial processes, such as petroleum refining and production of fine chemicals.<sup>1–4</sup> The actual performance of zeolites lies in their topology, elemental composition, morphology, surface state, *etc.* In this regard, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio (SAR) is one of the most important parameters for the application of zeolites in industry, because it significantly affects their properties, especially the acid/base properties.<sup>5–7</sup> Therefore, it is always one major research context to control SAR over the required zeolitic topology and composition.

SAR of zeolites can be basically tailored in two ways: (i) during a straightforward synthesis and (ii) by post-synthesis treatment. Although the post-synthesis treatment is an efficient way of tailoring SAR,<sup>8,9</sup> the control of SAR in the straightforward synthesis is preferred because of the following advantages: (1) simplification of the preparation process;<sup>10</sup> (2) excellent preservation of the crystallinity and microporous channels;<sup>11,12</sup> (3) avoidance of the usage of

additional acid or base solution that may increase the waste release.<sup>10</sup> Various zeolites with different topologies and SAR have been straightforwardly synthesized by using organic structure-direct-agents,<sup>13,14</sup> seeded growth,<sup>15</sup> or fluoride growth media.<sup>16</sup> One typical example is the ten-memberedring MFI topological zeolite, which can be synthesized in a wide SAR range (up to pure silica, *i.e.* silicalite-1).<sup>17</sup> However, it is still a huge challenge for the direct synthesis of many kinds of zeolites with widely tunable SAR, especially with ultra-high SAR.<sup>18</sup> According to Lowenstein's rule,<sup>19</sup> SAR  $\geq 2$ is commonly seen in the synthesis of zeolites, but no SAR  $\geq$ 2 is achieved over LTA, except for the only one example of pure silica LTA reported by Corma et al.,<sup>20</sup> suggesting that it is hard to adjust the SAR of LTA zeolites. For another example, SAR of MOR zeolites was limited to lower than 74 from the direct synthesis process.<sup>21</sup> As a result, many efforts have been made to develop new synthetic routes to control the growth of zeolite crystals.<sup>22</sup> One effectual way is the introduction of metal ions in the zeolite synthesis. The germanosilicate molecular sieve is a successful example in this context,<sup>23,24</sup> which implies that some metal additives may favor the formation of ultra-high silica zeolites.

During zeolite syntheses, NaOH frequently acts as a mineralizer;<sup>25</sup> yet, the role of bivalent metallic cations is rarely studied and limited to several isolated reports. The pioneering work of an early patent described the introduction of magnesium ions into directly one-pot synthesized zeolites, which however involved no characterization proof and discussion.<sup>26</sup> Recently, alkaline earth metal ions have been incorporated into silicalite-1 by directly adding the corresponding

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University (formerly Nanjing University of Technology), Nanjing 210009, Jiangsu, PR China.

*E-mail: njutzhouyu@njtech.edu.cn, junwang@njtech.edu.cn; Tel: +86 25 83172264* † Electronic supplementary information (ESI) available: Fig. S1–S5. See DOI: 10.1039/c5ce02075a

metal ions into the initial synthetic gels, and the obtained zeolites have been systematically characterized and have exhibited superior base properties due to the existence of framework alkaline earth metal ions.<sup>27</sup> It implies that magnesium ions as the metal additive benefited the synthesis of high silica or pure silica zeolites and intrinsically altered the acid/base properties for the obtained zeolites. Further, as known, in order to improve the mass transfer in zeolitic micro-channels, numerous approaches were proposed to directly fabricate a mesoporous structure over different zeolites.<sup>28,29</sup> Nonetheless, these syntheses usually relied on additional soft or hard templates, and the thus obtained zeolites normally acted as solid acids rather than bases.<sup>30,31</sup>

In this work, we report the straightforward synthesis of Mg<sup>2+</sup>-derived mesoporous ultra-high silica zeolites with tunable SAR and multiple topologies for twelve-membered-ring zeolites, which are proved to be a new series of mesoporous zeolitic solid bases. The synthesis is achieved via the unconventional pre-co-hydrolysis/condensation of a silica precursor with Mg salt under acid conditions;<sup>32,33</sup> this crucial early gelation stage does not involve any other metal ions and the introduced Mg ions contribute indispensably to the formation of an ultra-high silica zeolitic framework. Zeolitic phases are facilely controlled by the pH values employed for the followed hydrothermal crystallization processes. Multiple Mg<sup>2+</sup>-derived mesoporous zeolites with MOR, MTW or BEA topologies are achieved with ultra-high SAR (up to 410). Abundant mesopores are self-formed during the synthesis without the aid of any mesopore-formation template.<sup>34</sup> Herein, it is the first occasion to directly generate mesoporous zeolitic solid bases. Systematical syntheses and characterization are performed, and the catalytic performance is assessed in Knoevenagel condensations, a series of typical base-catalyzed reactions.<sup>35</sup> High conversion is achieved over Mg<sup>2+</sup>-derived ultra-high silica zeolites. Catalysis tests over the substrates with different molecular sizes illustrate the promoted activity due to the enhanced mass transfer in mesopores.

## 2. Experimental section

#### 2.1 Materials synthesis

 $Mg^{2+}$ -derived mesoporous ultra-high silica zeolites were synthesized by an acidic co-hydrolysis route.<sup>36</sup> Reaction mixtures having batch molar compositions of 0.02MgO: $xAl_2O_3$ : SiO<sub>2</sub>: 0.35TEAOH:22.5H<sub>2</sub>O, where x = 0.01-0.0125, were prepared by either an acidic or a base co-hydrolysis route. For the preparation by the acidic co-hydrolysis route, a mixed aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99 wt%, Sinopharm Chem. Reagent Co., AR) and tetraethylorthosilicate (TEOS, 28.4 wt% SiO<sub>2</sub>, Sinopharm Chem. Reagent Co., AR) was hydrolyzed under moderately acidic conditions (pH ~ 1.0) by dropwise addition of hydrochloric acid (HCl) aqueous solution (0.30 M, Shanghai Chem. Reagent Co., AR) at 90 °C for 4 h. After that, tetraethylammonium hydroxide (TEAOH, 35 wt% aqueous solution, Jintan Huadong, AR) and sodium aluminate (NaAlO<sub>2</sub>, 41 wt% Al<sub>2</sub>O<sub>3</sub>, Shanghai Chem. Reagent Co., AR) were added into the above mixture one by one. HCl was neutralized by excessive TEAOH, varying the mixture from acidic to basic conditions. The obtained slurry was aged at room temperature under dynamic (stirring) conditions for 24 h. The final molar composition of the gel was 1 SiO<sub>2</sub>:*x*Al<sub>2</sub>O<sub>3</sub>:0.02MgO: 0.35TEAOH:22.5H<sub>2</sub>O. After agitation, the pH of the gel was adjusted by sodium hydroxide (NaOH, 99 wt%, Sinopharm Chem. Reagent Co., AR) to the required value and then transferred into a Teflon-lined stainless steel autoclave and heated statically at 140 °C. The solids were separated by centrifugation, washed with deionized water and dried at 100 °C for 12 h. Finally, they were calcined at 550 °C for 5 h in air to remove the structure directing agent.

For the preparation by base co-hydrolysis, TEOS was added into the deionized water and stirred uniformly, and then TEAOH was added dropwise and stirred for 10 min. Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added into the above mixture. Afterwards, a mixture of sodium aluminate and deionized water was added. The obtained slurry was aged at room temperature under dynamic (stirring) conditions for 12 h. The final molar composition of the gel was 1SiO<sub>2</sub>:xAl<sub>2</sub>O<sub>3</sub>:0.02MgO: 0.35TEAOH: 22.5H<sub>2</sub>O. The pH of the gel was also adjusted by sodium hydroxide (NaOH, 99 wt%, Sinopharm Chem. Reagent Co., AR) to the required value. Finally, the slurry was transferred into a Teflon-lined stainless steel autoclave and heated statically at 140 °C for 14 days. The product was separated by centrifugation, washed with deionized water and dried at 100 °C for 24 h. After that, they were calcined at 550 °C for 5 h in air.

#### 2.2 Characterization

The crystalline structures of the prepared samples were characterized by X-ray diffraction analysis (XRD) using a SmartLab diffractometer from Rigaku equipped with a 9 kW rotating anode Cu source at 45 kV and 100 mA, from 5° to  $50^{\circ}$  with a scan rate of  $0.2^{\circ}$  s<sup>-1</sup>. The morphologies of the samples were tested using a field-emission scanning electron microscope (SEM; HITACHI S-4800). The nitrogen sorption isotherms and pore-size distribution curves were measured at the temperature of liquid nitrogen (77 K) by using a BELSORP-MINI analyzer with the samples degassed at 300 °C for 3 h before analysis. Specific surface areas and pore volumes of the calcined samples were obtained from N2adsorption-desorption isotherms using multipoint BET and t-plot methods. The FTIR spectra were recorded on an Agilent Cary 660 FT-IR instrument (KBr disks) in the 4000-400 cm<sup>-1</sup> region. The solid UV-vis spectra were measured using a SHIMADZU UV-2600 spectrometer, and BaSO4 was used as an internal standard. Chemical compositions of zeolites were analyzed by using a Jarrell-Ash 1100 inductively coupled plasma (ICP) spectrometer. The acid and base sites were analyzed by using a Catalyst Analyzer BELCAT-B under NH<sub>3</sub> and CO<sub>2</sub> atmospheres, respectively. The samples are pre-treated at 550 °C. The X-ray photoelectron spectra (XPS) were conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer

equipped with Al K $\alpha$  radiation (1486.6 eV). The <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectra were recorded on a Bruker AVANCE III 600 spectrometer. The <sup>29</sup>Si MAS NMR spectra with high-power proton decoupling were recorded on a 4 mm probe with a spinning rate of 12 kHz, a  $\pi/4$  pulse length of 2.6  $\mu$ s, and a recycle delay of 80 s. The chemical shift of <sup>29</sup>Si was referenced to TMS.

#### 2.3 Catalysis test

A typical procedure for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate was performed as follows: benzaldehyde (10 mmol) and ethyl cyanoacetate (10 mmol) were added to a 25 mL round-bottomed-flask reactor at the predetermined reaction temperature. After addition of 0.1 g of catalyst, the reaction slurry was stirred under reflux for the required reaction time. After reaction, the internal standard *n*-dodecane was added, and the resulting mixture was diluted with ethanol. The reaction mixture was centrifuged to remove the solid catalyst, and the liquid was analyzed by GC using a gas chromatograph (GC SP-6890) equipped with a flame ionization detector and a capillary column (SE-54; 30 m × 0.32 mm × 0.25 mm).

After reaction, the catalyst was separated from the reacted mixture by filtration, washed, and calcined at 550 °C for 5 h. The recovered catalyst was then charged into the next run for reuse.

### 3. Results and discussion

# 3.1 Formation of Mg<sup>2+</sup>-derived ultra-high silica MOR, BEA and MTW zeolites

Scheme 1 shows the synthesis procedures for the Mg<sup>2+</sup>-derived ultra-high silica zeolites. Three twelve-membered-ring (12R) zeolitic topologies can be obtained by controlling the pH value before crystallization, as well as the related SAR in the initial gel (Fig. 1). Pure phase Mg<sup>2+</sup>-derived MOR zeolites are obtained by controlling the pH value at 13.0 ± 0.1 with the crystallization at 140 °C for 14 days (Fig. 1A). The obtained samples are denoted as Mg-MOR(*n*), in which *n* 



**Scheme 1** Synthesis procedures for ultra-high silica zeolites of MOR, BEA and MTW, *via* straightforward hydrothermal crystallization involving acidic pre-co-hydrolysis/condensation.



**Fig. 1** XRD patterns for as-calcined Mg<sup>2+</sup>-derived mesoporous ultrahigh silica zeolites synthesized by acidic pre-co-hydrolysis/condensation. (A) MOR; (B) BEA; (C) MTW.

stands for the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio (SAR) in the starting reaction mixture. Adjusting the value of *n* from 100 to 800 gives the actual SAR from 32 to 274 in the final solid product (Table 1). Further increasing the SAR in the gel only attains an amorphous product, and even by extending the crystallization time to 18 days, no crystal product is obtained. The SiO<sub>2</sub>/MgO ratio for all final solid samples is roughly ~100, which is higher than the ratio (50) in the initial gels.

Two other zeolite phases of BEA and MTW are obtained by keeping the pH value of crystallization at  $12.5 \pm 0.1$  (Fig. 1). The corresponding samples are named as Mg-BEA(n) and Mg-MTW(n), respectively (Table 1). BEA and MTW zeolites possess a very similar topology, in which their a-c projection is viewed along and perpendicular to the 12R straight channels.<sup>27,34</sup> Crystal phase transformation could occur between BEA and MTW, because BEA can provide a specific growth surface for the crystallization of the MTW phase through their structural similarity (see Fig. S5<sup>†</sup> and the related additional explanation text).<sup>29</sup> Fixing the crystallization time at 14 days and varying the SAR in the gel (n) cause a significant phase transfer from BEA to MTW: a pure BEA phase is formed with n from 100 to 250 (Fig. 1B); a mixed phase of BEA and MTW is obtained with a higher *n* value (300–550) (Fig. S1A<sup> $\dagger$ </sup>), and a pure MTW phase is obtained with a more higher n (600–800) (Fig. 1C). Further increasing the n value causes an amorphous structure. In addition, BEA-MTW inter-zeolite transformation occurs when the crystallization time is varied from 6 to 18 days (Fig. S1B<sup>†</sup>), suggesting that a higher crystallization time favors the formation of the BEA phase. Correspondingly, two Mg<sup>2+</sup>derived ultra-high silica BEA zeolites, Mg-BEA(300) and Mg-BEA(800), are synthesized by the 18 days crystallization, giving the final SAR of 128 and 253 for solid products, respectively. Similarly, elongating the crystallization time to 18 days but with an extremely high n value of 1000 produces a high-silica MTW zeolite with a much higher SAR of 410 for the obtained sample Mg-MTW(1000). An amorphous structure is obtained with n > 1000 no matter what the crystallization time is.

Several synthesis parameters are explored and compared to further understand the above synthesis. When the synthesis is conducted under basic conditions throughout, in which the silica precursor undergoes no acidic pre-co-hydrolysis/ condensation process but is directly hydrothermally

Table 1 Textural properties of the as-calcined Mg<sup>2+</sup>-derived mesoporous ultra-high silica zeolite samples synthesized by acidic pre-co-hydrolysis/ condensation

Samples	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	$SiO_2/MgO^a$	$S_{\text{BET}}\left(\text{m}^2\ \text{g}^{-1} ight)$	$V\left(\mathrm{cm}^{3}\mathrm{g}^{-1}\right)$	D (nm)
Mg-MOR(100)	32	102	291	0.23	2.91
Mg-MOR(200)	58	106	296	0.23	2.91
Mg-MOR(300)	70	111	304	0.24	2.90
Mg-MOR(600)	96	111	312	0.24	2.89
Mg-MOR(700)	160	105	317	0.24	2.90
Mg-MOR(800)	274	112	324	0.24	2.89
Mg-BEA(100)	31	128	333	0.36	2.83
Mg-BEA(200)	82	123	427	0.41	3.84
Mg-BEA $(300)^b$	128	118	343	0.47	4.59
Mg-BEA(800) <sup>b</sup>	253	125	356	0.53	6.23
Mg-MTW(600)	127	125	197	0.22	4.47
Mg-MTW(700)	160	111	211	0.59	11.3
Mg-MTW(800)	348	125	333	0.58	6.95
$Mg-MTW(1000)^b$	410	100	289	0.57	7.89

 $^{a}$  SiO<sub>2</sub>/MgO and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios for the final solid products determined by ICP.  $^{b}$  The crystallization time is 18 days, and the crystallization time for the other samples is 14 days.

crystallized under alkaline conditions, only an amorphous structure can be observed (Fig. S1C<sup>†</sup>). All samples have high crystallinity and reflect the prerequisite role of the initial acidic co-hydrolysis/condensation stage. The high crystallinity is obtained when high temperature (90 °C) acidic cohydrolysis of TEOS precedes other operations (cooling down to room temperature, addition of sodium aluminate and TEAOH, room-temperature aging and hydrothermal treatment of the aged reaction mixture). On the other hand, keeping the synthesis conditions unchanged, no solid (crystalline) product is formed when co-hydrolysis of TEOS is performed at room or low temperature. This clearly indicates that the (high) temperature of TEOS co-hydrolysis is crucial for the processes which occur during either room-temperature aging or hydrothermal treatment of the reaction mixture. Thus, the influence of the temperature of TEOS co-hydrolysis on the course of crystallization may be, at the first instance, explained as follows: fast and complete hydrolysis of TEOS at high temperature causes the formation of silica nanoparticles,<sup>37</sup> and then the formation of Al-enriched amorphous silica and further formation of various silicate and aluminosilicate nanosized species during either room-temperature aging and/or the initial stage of hydrothermal treatment of the reaction mixture, which are precursor species for nucleation and crystal growth of zeolites.38,39 Since the silica nanoparticles needed for the formation of silicate and aluminosilicate precursor species obviously do not form, or the rate of their formation is not appropriate, during room-temperature hydrolysis, a crystalline product cannot be obtained when hydrolysis of TEOS is conducted at room temperature. The detailed investigation on the initial pH value (Fig. S1C†) shows the formation of amorphous products with either high (>1.0)or low (<0.7) pH values, revealing that the gel state after that hydrolyzation should have affected the creation of the preliminary zeolite phase. The pH value just before the onset of hydrothermal crystallization is also studied from 12.1 to 13.4. No solid can be obtained at pH values of 12.1, 12.3 and 12.7, and a much lower crystallinity of MOR is obtained at 13.4, which indicates that the highly crystallized zeolite phases are very sensitive to the pH conditions for the crystallization. More importantly, Mg-free synthesis is performed for comparison by controlling the similar pH values at 13.0 and 12.5 for the crystallization. In the case of pH = 13.0, analcite is the main product in the absence of  $Mg^{2+}$  in the gel (Fig. S1D<sup>†</sup>), indicating that magnesium is indispensable for the formation of the MOR phase. When pH = 12.5, the BEA phase changes to MTW in the absence of Mg ions at n = 200 (Fig. S1D<sup>†</sup>), suggesting that Mg ions may contribute to the formation of the BEA phase at the relatively low SAR in the gel. The Mg-free system cannot produce any products at a high nvalue ( $\geq 600$ ). These results demonstrate that the synthesis of these 12R ultra-high silica zeolites relies on the presence of Mg ions. The reason may be due to that Mg ions function as co-structure-directing sites, as performed by various other metal ions in zeolite syntheses.

Under acidic conditions, silica species are the less condensed linear oligomers, while in alkaline solution the silica species are the more cross-linked clusters.40 If the reaction mixtures are adjusted to the alkaline system, hydrolysates obtained by acid hydrolysis are easier to dissolve under hydrothermal conditions theoretically. More active components can be formed to participate in the formation of the crystal nucleus and growth of zeolite crystals, resulting in higher utilization of Si, so as to improve SAR. Moreover, the acidic conditions for hydrolysis and condensation of silica precursors offer a lower rate than the basic one,<sup>41</sup> allowing more opportunities for isolation and dispersion of metal ions and thus promoting the bond formation between metal ions and silanol groups.<sup>32,33</sup> In this way, it is more likely to generate the desirable Si-O-Mg-O-Si linkage (known as the primary building blocks for further growth of the heteroatomic zeolite crystals) in the gel mixture, and such interaction is crucial for Mg ions to act as co-structure-directing agents for the formation of zeolites. On the contrary, hydroxide or oxide precipitates can be generated quickly through the basic hydrolysis route, inhibiting the above interaction to perform the function of Mg ions as co-structure-directing agents. This is why the acidic co-hydrolysis route benefits the synthesis of high or ultra-high silica zeolites (Fig. 2).

#### 3.2 Mesoporosity and other characterization

Porosities of the above obtained Mg<sup>2+</sup>-derived ultra-high silica zeolites are measured by nitrogen sorption experiments (Fig. 3 and S2<sup>†</sup>). The corresponding textural properties are listed in Table 1. The N<sub>2</sub> sorption isotherms of all the samples demonstrate a sharp uptake at low relative pressure  $(p/p_0)$ < 0.05), index of typical zeolitic microporosity. The continuous increase in N<sub>2</sub> sorption at a relatively high pressure  $(p/p_0)$ = 0.1-0.99) reveals the presence of mesopores, which is further reflected by the apparent pore size distribution. The isotherms for Mg-MOR(100-800) samples exhibit a similar shape with a type H2 hysteresis loop, suggesting that these samples possess similar mesopores and the variation of SAR rarely affects the mesoporous structure. For Mg-BEA(n) series, they display a type H4 hysteresis loop with a sharp step closure at a relative pressure of about 0.6, and the larger SAR of these BEA zeolites and the higher uptake at high relative pressure  $(p/p_0 > 0.6)$  suggested enhanced mesoporosity upon an increase in SAR. In previous work, the formation of mesopores on zeolites during a straightforward synthesis usually relies on the utilization of additional soft/hard templates except for the one example under dynamic crystallization;<sup>28,29,34</sup> here, mesoporous zeolites are obtained by using a special acidic co-hydrolysis route without using any mesopore-formation template. The present synthesis has the advantages of saving raw materials and simplifying preparation procedures; for example it requires no template removal process like a hardtemplate pathway.

Fig. 4 shows the SEM images of Mg-MOR(n) zeolites, demonstrating significant variation of morphologies for this series. Mg-MOR(100) is composed of isosceles trapezoid flake layers with the size of about several micrometers. As SAR increases, the morphology evolves into terrace-like layers for n



**Fig. 2** Ternary phase diagram of topological structures obtained from the straightforward synthetic system synthesized by acidic pre-cohydrolysis/condensation.



Fig. 3  $N_2$  adsorption-desorption isotherms (left) and the corresponding pore-size distributions (right) for Mg<sup>2+</sup>-derived mesoporous ultra-high silica zeolites synthesized by acidic pre-co-hydroly-sis/condensation: (A) MOR; (B) BEA; (C) MTW.

= 200, and their size is higher than ten micrometers, slightly larger than that of Mg-MOR(100). At higher SAR of n = 300, it emerges as irregular particles derived from the aggregation of small primary crystals rather than the terrace-like layers, and their size is further expanded to tens of micrometers. Further increasing the SAR to n = 600, the terrace-like layers disappear and the morphology changes to fluctuating particles with a smooth surface, and their sizes vary in a wide range from several to tens of micrometers. Increasing n to 700 and 800, all the particles evolve into irregular aggregations with a rough surface and wide size distributions. SEM images of all the samples of Mg-BEA and Mg-MTW are presented in Fig. 4 and S3.† Their morphologies are all irregular bulks composed of small crystals with the size of hundreds of nanometers. These SEM images reveal that the formation of mesopores over these ultra-high silica zeolites may be due to the small



Fig. 4 SEM images for as-calcined samples synthesized by acidic preco-hydrolysis/condensation: (A) Mg-MOR(100), (B) Mg-MOR(200), (C) Mg-MOR(300), (D) Mg-MOR(600), (E) Mg-MOR(700), (F) Mg-MOR(800), (G) Mg-BEA(100), and (H) Mg-MTW(800); (I) TEM image for as-calcined Mg-MTW(1000).

intracrystalline voids inside the polycrystalline aggregates. For Mg-MOR samples, they are in the form of single crystals at SAR = 100 (Fig. 4A). These single crystals become more and more irregular in shape as SAR increases (Fig. 4B–F), which contain a small amount of mesopores. On the other hand, Mg-BEA and Mg-MTW samples appear mainly in the form of polycrystalline aggregates (Fig. 4G–I and S3†)<sup>39,42,43</sup> and most of them exhibit mesoporosity. The TEM image of Mg-MTW(1000) with the highest SAR shows that the primary particles are highly crystallized nano-crystallites and denotes that the nano-crystallites pack each other by intergrowth during the crystallization process into bigger particles, forming mesopores (Fig. 4I).

For Mg-MTW(1000), we further carry out <sup>29</sup>Si and <sup>27</sup>Al MAS NMR analysis to study the chemical state of silica and aluminum. The <sup>29</sup>Si NMR spectrum (Fig. 5A) presents two strong signals at -103 and -111 ppm that can be assigned to the  $Si(OSi)_4$  (Q4) structure,<sup>44,45</sup> suggesting that the majority of the silicon atoms are located in four-connected sites as expected for a framework silicate. The broad signal at -103 ppm very likely contains not only Q4 species but also Si(OSi)<sub>3</sub>(OH) (i.e. Q3 typically appearing around -102 ppm) and maybe also another Q4 site Si(OSi)<sub>3</sub>(OMg). One additional peak emerges at -94 ppm mainly attributable to the Q3 structure for Mg-MTW(1000), which is derived from the formation of some defects or silicon atoms representing the terminal (surface) ones. Such signal may comprise Si(OSi)<sub>2</sub>(OH)<sub>2</sub> (Q2) as well as Si species bonded to OMg and OH at the same time. The <sup>27</sup>Al NMR spectrum (Fig. 5B) exhibits a single band at 54 ppm for the tetrahedral coordinated aluminum species, while no signal at 0 ppm for the extra-framework octahedral coordinated aluminium species is observed.<sup>46</sup> Such phenomenon demonstrates that the Al atoms are entirely incorporated into the crystalline framework. The above NMR analysis further reveals the highly crystalline structure even for the sample with extremely high SAR.

Fig. 6 presents the IR and UV-vis spectra of these zeolites. Several characteristic vibrations for the MOR structure are found in the IR spectra of Mg-MOR(n) samples (Fig. 6A). The band observed at 580 cm<sup>-1</sup> is characteristic of the stretching vibration of the double five-membered rings, typically due to the variation of the pentasil framework.<sup>47</sup> The offset for the peak at 1100 cm<sup>-1</sup> with the increase in SAR agrees with the



Fig. 5 (A) <sup>29</sup>Si and (B) <sup>27</sup>Al MAS NMR spectra for Mg-MTW(1000) synthesized by acidic pre-co-hydrolysis/condensation.



Fig. 6 IR spectra (A) and UV-vis spectra (B) for as-calcined MOR samples and (C) IR spectra and (D) UV-vis spectra for as-calcined BEA and MTW samples, with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios. All samples are synthesized by acidic pre-co-hydrolysis/condensation.

high framework SAR for these MOR zeolites. Typical vibrations for the Mg-BEA and Mg-MTW samples are seen in Fig. 6C. The UV-vis spectra are shown in Fig. 6B. No absorption in the 220–800 nm range is observed over the Mg-free sample, while all the Mg<sup>2+</sup>-derived zeolites exhibit a distinct absorption band at 260 nm, the same as the Mg<sup>2+</sup>-incorporated silicate-1 sample.<sup>27</sup> Such a signal can be assigned to the excitation of O atoms around the framework Mg species, which is highly distorted or possesses vacancies compared to the regular MgO topology.<sup>48</sup>

Fig. 7 shows the XPS core-level spectra O 1s, Si 2p, and Mg 2p, for the selected ultra-high silica zeolites Mg-BEA(800), Mg-MTW(1000) and Mg-MOR(800). In the O 1s spectra, the peak shifts to higher binding energies with the increase in SAR (Fig. 7), due to reduction of the fraction of chemical oxygen environments bonded to aluminum (Al–O).<sup>49</sup> Mg-free sample MTW(200) exhibits a signal at 534.3 eV, compared to which, the peaks for Mg-BEA(800), Mg-MTW(1000) and Mg-



**Fig. 7** XPS O1s, Si 2p, and Mg 2p spectra for samples Mg-BEA(800), Mg-MTW(1000) and Mg-MOR(800). The samples are synthesized by acidic pre-co-hydrolysis/condensation.

MOR(800) all shift to lower binding energies. This is attributable to the introduction of the magnesium ions with weak electronegativity that increases the electron density in the O atom.<sup>50</sup> The observed similar shifts towards higher binding energies of Si 2p with the increase in SAR can be assigned to the change in the polarizability of oxygen, indicating the formation of a more stoichiometric SiO<sub>2</sub> phase.<sup>51-53</sup> Similar to the variation in the O 1s spectra, the Si 2p signals in these three Mg containing samples all shift to a lower binding energy than that (105.2 eV) for Mg-free MTW(200). Finally, the binding energy of Mg 2p for Mg-BEA(800) is 51.5 eV and shifts to 52.23 eV and 52.28 eV for Mg-MOR(800) and Mg-MTW(1000), respectively. These signals shift to a higher binding energy compared to the peak position of MgO (49.8 eV) and Mg(OH)<sub>2</sub> (49.7 eV),<sup>50</sup> reflecting a strong binding of Mg ions to the zeolitic framework, different from the Mg state in MgO or Mg(OH)<sub>2</sub>.<sup>54</sup>

Temperature-programmed desorption (TPD) of  $CO_2$  and  $NH_3$  is utilized to gain insight into the basic and acidic properties of these  $Mg^{2+}$ -derived ultra-high silica zeolites. Fig. 8A and C show their  $CO_2$ -TPD profiles. All the samples give only one peak ranging 100–200 °C, which is ascribed to  $CO_2$  desorption from weak/medium base sites. As SAR increases, no matter what the zeolite topology is, this peak shifts to higher temperature accompanied by the enlargement of the peak area, revealing the enhanced base intensity and increased concentration of basic sites. Fig. 8B and D are the  $NH_3$ -TPD profiles. All the samples show one  $NH_3$  desorption peak at 150 °C, which is attributable to weak acidic sites. As SAR increases, this peak shifts to lower temperature with the peak area dramatically decreasing, index of decreased acidity. The above  $CO_2$ - and  $NH_3$ -TPD analyses indicate that



Fig. 8 (A) CO<sub>2</sub>-TPD and (B) NH<sub>3</sub>-TPD curves for as-calcined ultra-high silica MOR samples synthesized by acidic pre-co-hydrolysis/condensation and (C) CO<sub>2</sub>-TPD and (D) NH<sub>3</sub>-TPD curves for as-calcined ultra-high silica BEA and MTW samples, with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios.

these  $Mg^{2+}$ -derived ultra-high silica zeolites possess enhanced basic sites, and the higher SAR, the more enhanced the basic properties are with correspondingly decreased acidity. In other words, with the increase in SAR, these samples demonstrate an enhanced  $CO_2$  desorption amount but a decreased  $NH_3$  desorption amount, index of increased basicity and decreased acidity. For example, the Mg-MOR(800) sample exhibits the largest  $CO_2$  desorption peak but the weakest  $NH_3$ desorption peak, suggesting that it possesses superior basicity but inferior acidity. By contrast, Mg-MOR(100) exhibits the largest  $NH_3$  but the weakest  $CO_2$  desorption, showing its superior acidity but inferior basicity.

The mediate sample such as Mg-MOR(600) demonstrates moderate  $CO_2$  and  $NH_3$  desorption, index of moderate acidity and basicity. For more comparison, Fig. 8(C) and (D) are  $CO_2$ -TPD and  $NH_3$ -TPD profiles for Mg-BEA(40) with a relatively much lower SAR of 30 for the final solid product and the Mg-free sample MTW(200), showing that their base intensity are obviously weaker, which accounts that both higher SAR and existence of magnesium ions are responsible for the enhanced base properties of our  $Mg^{2+}$ -derived high-silica zeolites.

#### 3.3 Catalytic performance

Catalytic performances are assessed in Knoevenagel condensation, a typical probe reaction for evaluating base catalysts. Knoevenagel reaction of aldehydes with compounds containing activated methylene groups has been widely employed in the synthesis of many fine chemicals including heterocyclic compounds of biological significance.<sup>55</sup> Fig. 9 shows the results of all the obtained Mg-MOR, Mg-BEA and Mg-MTW zeolites for catalysing Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. The conversion of ethyl cyanoacetate is 38% (selectivity >99.9%) over the catalyst Mg-MOR(100). With the increase in SAR, the conversion continuously increases and reaches the high level of 94% for Mg-



Fig. 9 Change in reactivity for Knoevenagel condensation over  $Mg^{2+}$ -derived mesoporous ultra-high silica zeolites with the increase in SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios in final solids. (A) Mg-MOR, (B) Mg-BEA (blue) and Mg-MTW (red). Reaction conditions: 0.1 g of zeolite catalyst, 10 mmol of benzaldehyde, 10 mmol of ethyl cyanoacetate, 5 mL of C<sub>2</sub>H<sub>5</sub>OH as solvent, 70 °C, 4 h.

MOR(800) (Fig. 9A). Parallel variation is observed over Mg-BEA and Mg-MTW samples (Fig. 9B). A high conversion of 96% is achieved over Mg-MTW(1000). The results demonstrate that SAR is the key factor for these zeolites, which significantly affects their activity for this reaction: the higher SAR, the better the performance. Such variation is well in accordance with the TPD results of Mg-zeolites, verifying that they do act as solid base catalysts. Nevertheless, zeolites having similar Mg content and SAR value but with different topologies do not give a similar catalytic performance. For example, Mg-MOR always presents the highest conversion, while Mg-BEA gives the lowest one, in the case of the same SAR. Such a phenomenon suggests that the microenvironment on the surface of zeolitic channels, closely related to the topology, affects the actual performance of the basic sites over these zeolites. Mg-MTW(1000) shows the highest conversion due to its highest SAR. After reaction, these zeolites can be directly separated by filtration and reused in the next run. Recycling tests are carried out over the selected ultra-high silica zeolites Mg-MOR(800), Mg-BEA(800) and Mg-MTW(1000) due to their superior activities (Fig. S4<sup>†</sup>). After the five-run recycles, still considerably high conversions of ethyl cyanoacetate are observed over these repeatedly used catalysts, more stable than the previously reported zeolitic solid bases.52

For further understanding the catalytic behavior, two control samples, Mg-BEA(40) with a relatively low actual SAR of 30 and Mg-free high silica ZSM-12 (SAR = 96), are catalytically assessed and compared in Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. Our  $Mg^{2+}$ -derived ultrahigh silica zeolites all show much higher catalytic conversions than that of Mg-beta (the conversion is 40%), indicating that higher values of SAR favor the displaying of  $Mg^{2+}$ -derived basicity and thus promotes the catalytic activity. Meanwhile, high silica ZSM-12 has a much lower conversion of 51%, due to the absence of the magnesium-derived basic sites.

Fig. 10 shows the conversion vs. reaction time in the condensation between ethyl cyanoacetate and benzaldehyde, 1-naphthaldehyde, 2-hydroxy-1-naphthaldehyde, or 9-anthraldehyde with different molecular sizes, catalyzed by Mg-MOR(800) and Mg-MTW(1000). A parallel test is also conducted on MgO, a commercially available solid base having plenty of weak base sites as well as certain medium and strong ones. Mg-MTW(1000) demonstrates the highest conversion due to its abundant mesopores, while MgO shows the lowest one, which is mainly attributed to its nonporous structure with a very small surface area of 7 m<sup>2</sup> g<sup>-1</sup>. When benzaldehyde is reacted with ethyl cyanoacetate, a high conversion of 96% is observed at 4 h over Mg-MTW(1000), higher than 94% over Mg-MOR(800) and 76% over MgO, although the conversions all reach 100% after 5 h. This implies that the existence of abundant mesopores favors a faster reaction rate due to the enhanced mass transfer in the mesopores. For the larger-sized 1-naphthaldehyde, the conversion over MgO is only 45% at 1 h; in contrast, a much higher conversion of



Fig. 10 Comparison of activity for Knoevenagel condensation of ethyl cyanoacetate with (A) benzaldehyde, (B) 1-naphthaldehyde, (C) 2-hydroxy-1-naphthaldehyde, and (D) 9-anthraldehyde, as a function of reaction time.

77% is achieved over Mg-MTW(1000) within the same reaction time, mostly also due to the enhanced mass transfer derived from the mesopores. A more apparent tendency can be observed over the condensation with the much larger substrates of 2-hydroxy-1-naphthaldehyde and 9-anthraldehyde. Mg-MTW(1000) with the most abundant mesopores can efficiently convert the bulky substrates with a more rapid reaction rate than Mg-MOR(800) with less mesopores, and the latter mesoporous zeolite once more reacts more rapidly than the nonporous MgO, further confirming the mesoporeresulted enhanced mass transfer.<sup>56–59</sup> This feature strongly reveals the positive function of the mesoporous zeolites in enhancing mass transfer for the liquid–solid heterogeneous Knoevenagel condensations.

## 4 Conclusions

 $Mg^{2+}$ -derived mesoporous ultra-high silica zeolites are directly synthesized by a one-pot acidic co-hydrolysis route, wherein the introduced  $Mg^{2+}$  is indispensible for achieving the ultra-high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio (SAR). Zeolite phases can be controlled to be MOR, BEA and MTW by finely adjusting the crystallization pH value, and SAR can be enhanced up to 410. Abundant mesopores are self-formed over these zeolites without using an additional mesopore-formation template. The ultra-high silica framework favors stronger basicity, which is further improved by the introduction of Mg ions. The obtained zeolites exhibit superior activity in the typical base reaction, Knoevenagel condensation, and can efficiently convert various bulky substrates due to the enhanced mass transfer arising from the mesopores. This

work reports the straightforward synthesis of ultra-high silica zeolites containing mesopores and Mg species, thus providing a new series of mesoporous zeolitic solid bases.

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### Notes and references

- 1 P. Guo, A. G. Greenaway, H. J. Choi, P. A. Wright and X. D. Zou, *Nature*, 2015, 524, 74–78.
- 2 M. Dusselier, P. V. Wouwe, A. Dewaele, P. A. Jacobs and B. F. Sels, *Science*, 2015, 349, 78–80.
- 3 M. Maria, M. Sharon, C. Paolo, C. David and P. R. Javier, *Nat. Commun.*, 2015, 5, 3922–3931.
- 4 M. Yang, S. Li, J. A. Herron, M. Mavrikakis and M. F. Stephanopoulos, *Science*, 2015, 346, 1498–1501.
- 5 T. C. Keller, E. G. Rodrigues and P. R. Javier, *ChemSusChem*, 2014, 7, 1729–1738.
- 6 T. C. Keller, S. Isabettini, D. Verboekend, E. G. Rodrigues and P. R. Javier, *Chem. Sci.*, 2014, 5, 677–684.
- 7 T. Sonoda, T. Maruo, Y. Yamasaki, N. Tsunoji and T. Sano, J. Mater. Chem. A, 2015, 3, 857–865.
- 8 S. Schallmoser, T. Ikuno, M. F. Wagenhofer, R. Kolvenbach, G. L. Haller, M. S. Sanchez and J. A. Lercher, *J. Catal.*, 2014, 316, 93–102.
- 9 M. M. Antunes, S. Lima, P. A. Urakawa and A. A. Valentea, J. Catal., 2015, 329, 522–537.
- 10 Z. P. Ma, J. Y. Xie, J. L. Zhang, W. Zhang, Y. Zhou and J. Wang, *Microporous Mesoporous Mater.*, 2016, 224, 17–25.
- 11 X. Qi, S. Li, Z. Wang, X. Liu and B. Lin, *Chin. J. Catal.*, 2003, 7, 535–538.
- 12 J. Wang, X. Cheng, J. Guo, X. Xu and Y. Long, *Microporous Mesoporous Mater.*, 2006, 96, 307–313.
- 13 M. B. Park, Y. Lee, A. M. Zheng, F. S. Xiao, C. P. Nicholas, G. J. Lewis and S. B. Hong, *J. Am. Chem. Soc.*, 2013, 135, 2248–2255.
- 14 G. T. Kerr and G. T. Kokotail, J. Am. Chem. Soc., 1961, 83, 4675.
- 15 Y. Bouizi, J. L. Paillaud, L. Simon and V. Valtchev, *Chem. Mater.*, 2007, **19**, 652–654.
- 16 J. E. Schmidt, D. Xie and M. E. Davis, J. Mater. Chem. A, 2015, 3, 12890–12897.
- 17 E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner and J. V. Smith, *Nature*, 1978, 271, 512–516.
- 18 R. G. Bell, R. A. Jackson and C. R. A. Catlow, Zeolites, 1992, 12, 870–871.
- 19 W. Lowenstein, Am. Mineral., 1954, 39, 92-96.

- 20 A. Corma, F. Rey, J. Rius, M. J. Sabater and S. Valencia, *Nature*, 2004, 431, 287–290.
- 21 A. L. Lv, H. Xu, H. H. Wu, Y. M. Liu and P. Wu, *Microporous Mesoporous Mater.*, 2011, 145, 80–86.
- 22 M. Yang, P. Tian, L. Liu and Z. M. Liu, *CrystEngComm*, 2015, 17, 8555-8561.
- 23 A. Corma, M. J. D. Cabanas, J. L. Jorda, C. Martinez and M. Moliner, *Nature*, 2006, 443, 842–845.
- 24 M. V. Shamzhy, O. V. Shvets, M. V. Opanasenko and M. Hartmann, *J. Mater. Chem.*, 2012, 22, 15793–15803.
- 25 D. H. Yuan, D. W. He, Z. M. Liu and Y. P. Xu, *Microporous Mesoporous Mater.*, 2015, 204, 1–7.
- 26 J. M. Garces, US4732747 A, 1988.
- 27 Y. Zhou, Y. H. Jin, M. Wang, W. Zhang, J. Y. Xie, J. Wang and L. M. Peng, *Chem. – Eur. J.*, 2015, 21, 1–10.
- 28 F. S. Xiao, L. F. Wang, T. Yokoi and T. Tatsumi, *Angew. Chem.*, *Int. Ed.*, 2006, 45, 3090–3093.
- 29 M. A. Camblor, A. Corma and S. Valencia, *Microporous Mesoporous Mater.*, 1998, 25, 59–74.
- 30 A. Ishihara, K. Inui, T. Hashimoto and H. Nasu, J. Catal., 2012, 295, 81–90.
- 31 M. Choi, K. Na, J. Kim, Y. Sakamoto and R. Ryoo, *Nature*, 2009, 461, 246–250.
- 32 J. Gu, Y. H. Jin, Y. Zhou, M. J. Zhang, Y. J. Wu and J. Wang, J. Mater. Chem. A, 2013, 1, 2453–2460.
- 33 Y. J. Wu, J. Wang, P. Liu and X. J. Wang, J. Am. Chem. Soc., 2010, 132, 17989–17991.
- 34 K. Na, M. Choi and R. Ryoo, *J. Mater. Chem.*, 2009, **19**, 6713–6719.
- 35 X. C. Wang, Y. Zhou, G. J. Chen and J. Wang, ACS Sustainable Chem. Eng., 2014, 2, 1918–1927.
- 36 J. L. Zhang, Y. M. Mao, J. Li and J. Wang, Chem. Eng. Sci., 2015, 138, 473-481.
- 37 C. Kosanovic, K. Havenscak, B. Subotic, V. Svetličić, T. Mišić, A. Cziraki and G. A. Huhn, *Microporous Mesoporous Mater.*, 2009, 123, 150–159.
- 38 N. Ren, S. Bosnar, J. Bronić, M. Dutour Sikirić, T. Mišić, V. Svetličić, J.-J. Mao, T. Antonić Jelić, M. Hadžija and B. Subotić, *Langmuir*, 2014, 30, 8570–8579.
- 39 N. Ren, B. Subotić, J. Bronić, Y. Tang, M. Dutour Sikirić, T. Mišić, V. Svetličić, S. Bosnar and T. Antonić Jelić, *Chem. Mater.*, 2012, 24, 1726–1737.
- 40 X. Zhang, T. T. Trinh, R. A. van Santen and A. P. J. Jansen, J. Am. Chem. Soc., 2011, 133, 6613–6625.
- 41 H. P. Lin and C. Y. Mou, Acc. Chem. Res., 2002, 35, 927–935.
- 42 P. Sharma, J.-G. Yeo, M. H. Han and C. H. Cho, J. Mater. Chem. A, 2013, 1, 2602–2612.
- 43 M. Kumar, H. Luo, Y. Roman-Leshkov and J. D. Rimer, J. Am. Chem. Soc., 2015, 137, 13007–13017.
- 44 K. U. Gore, A. Anuji, S. G. Hegde, R. Kumar, J. P. Amoureux and S. Ganapathy, *J. Phys. Chem. B*, 2002, 106, 6115–6120.
- 45 E. A. Eilertsen, M. Haouas, A. B. Pinar, N. D. Hould, R. F. Lobo, K. P. Lillerud and F. Taulelle, *Chem. Mater.*, 2012, 24, 571–578.

- 46 J. A. Bokhoven, D. C. Koningsberger, P. Kunkeler, H. Bekkum and A. P. M. Kentgens, J. Am. Chem. Soc., 2000, 122, 12842–12847.
- 47 Y. T. Meng, H. C. Genuino, H. Huang, L. C. Zhang and S. L. Suib, J. Am. Chem. Soc., 2013, 135, 8594–8605.
- 48 M. M. Forde, R. D. Armstrong, C. J. Kiely and G. J. Hutchings, J. Am. Chem. Soc., 2013, 135, 11087–11099.
- 49 T. F. Chaves, H. O. Pastore, P. Hammer and D. Cardoso, *Microporous Mesoporous Mater.*, 2015, 202, 198–207.
- 50 C. D. Wanger, W. M. Riggs, L. E. Davis and J. F. Muilenberg, *Handbook of X-ray photoelectron Spectroscopy*, Perkin-Elmer Corporation, America, 1979.
- 51 Y. Okamoto, M. Ogawa, A. Maezawa and T. Imanaka, *J. Catal.*, 1988, 112, 427–436.

- 52 T. L. Barr and M. A. Lishka, J. Am. Chem. Soc., 1986, 108, 3178-3186.
- 53 M. Huang, A. Adnot and S. Kaliaguine, J. Am. Chem. Soc., 1992, 114, 10005–10010.
- 54 J. A. Tossell, J. Am. Chem. Soc., 1975, 97, 4840-4844.
- 55 F. Freeman, Chem. Rev., 1980, 80, 329–350.
- 56 H. K. Min, S. H. Cha and S. B. Hong, *Chem. Commun.*, 2013, 49, 1115–1117.
- 57 B. Singh and A. K. Sinha, J. Mater. Chem. A, 2014, 2, 1930–1939.
- 58 S. A. Saba, M. P. S. Mousavi, P. Bühlmann and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2015, 137, 8896–8899.
- 59 H. B. Zhang, Z. J. Hu, L. Huang, H. L. Xu and Y. Tang, ACS Catal., 2015, 5, 2548–2558.