Synthesis and application of hierarchical zeolites prepared using amino-acid mesoporogens

M Hong1,3, Z W Chen1, J Zhang1, L Dong1, Y D Wang1, C Chen1, W Qian1, S W Wang2, Z A Huang2 and X N Yuan2

1 Guangdong Provincial Key Laboratory of Nano-Micro Materials Research, School of Chemical Biology & Biotechnology, Peking University Shenzhen Graduate School, Shenzhen 518055, China;
2 Ambulanc (Shenzhen) Tech., Co., LTD, 8/F, Building C, Chuangwei Innovation Valley, Tangtou 1st Road, Shiyan, Baoan District, Shenzhen 518108, China.
3 E-mail: hongmei@pkusz.edu.cn

Abstract. Amino-acid-templating is a newly developed versatile synthetic strategy for the effective construction of hierarchically porous architectures in zeolites. Although the role of amino acid polymerization on dealuminated zeolites has been well perceived in biochemical evolution as possible origin of life, the use of amino acids to tailor pore architectures in zeolites has merely merged. The present work provides an overview from the early studies on aluminosilicate surfaces as promoters in probiotic chemistry to our recent endeavours on designing hierarchically porous zeolites using various amino acids. The power of amino acids is depicted through assessing their multi-functional roles and the differences to that of surfactant templates. The key advantages using amino acids as mesoporogens include wide availability and rich diversity offering cost efficiency and unparalleled control of zeolite architecture, minimal interference on the 3D continuous zeolite crystallization, easy removal through washing with water, and amino acid recyclability. Finally, the application of amino-acid-mediated hierarchical zeolites and potential industrial usage are highlighted.

1. Introduction

Bernal’s hypothesis stated that mineral surfaces played a key role for prebiotic adsorption and generation of replicating biopolymers [1]. The minerals, according to Smith’s proposal, are dealuminated zeolites having adjacent organophilic and catalytic regions that could organize organic species into specific polymers [2], indicating that there is unique interaction between biologically important amino acids and mineral aluminosilicates. However, this evolutionally optimized peculiar interaction between biologically important amino acids and mineral aluminosilicates, has seldom been employed to tailor crystalline aluminosilicates or zeolites. The reason might be surprisingly simple. The current bottom-up templating techniques to synthesize hierarchical zeolitic structures typically utilize mesoscale sized template for generating mesopores [3], while amino acids are too small building blocks and only proteins that contain hundreds of amino acids could reach the size > 2 nm.

On the other hand, the synthesis of hierarchical zeolites has attracted tremedous interest [4]. The construction of secondary pore system, especially mesopores, overcomes the diffusion limitation of solely microporous zeolites, averts the low stability and acidity of purely mesoporous aluminosilicates, and preserves the desired shape selectivity [5, 6]. Various methods have been developed for creating...
mesoporosity in zeolites, including removal of framework atoms [7], hard templating [8], and soft templating [9-11]. Soft templates typically include surfactants [12] or soft polymers [13] which have relatively flexible structure. In 2006, significant breakthrough was achieved in the synthesis of mesoporous zeolites in both surfactant templating using ingeniously designed organosilane [14] and polymer templating using exquisitely chosen cationic polymers [15]. Their glory continued by the successful utilization of polyquaternary ammonium surfactants [10] and bifunctional polymers [16]. However, in all these approaches, supramolecular or mesoscale templates were used, which tend to be expensive [17] and are usually encapsulated within the zeolite during the synthesis and removed afterwards by calcination to release the mesoporosity [18].

Herein, we discovered that amino acids (AA) are powerful small molecules that could generate intracrystalline mesopores while keeping the long-range ordering of zeolite framework structure. The mesoporogens of amino acids, as small molecules, possess a high degree of structure flexibility and tunable interactions with the inorganic species, similar to that of surfactants. However, unlike the bulkier mesoscale polymer or supramolecular surfactant based approaches, the gentle chimie douce approaches features minimal interference on the zeolite crystallization. Their stability and solubility ensured easy removal after the hydrothermal synthesis by a simple washing step, eliminating energy-intensive calcination process and allowing for template recovery, and thus amino-acid-mediated process is a greener alternative to the mesoscale-templating route mediated by surfactants or polymers. The low cost and high structure diversity of amino acids and their biocompatibility open door to easy access to a variety of hierarchical zeolites for industrially important applications as adsorbents, ion exchangers, and catalysts.

2. Methodology

In contrast to the aforementioned mesoscale hard or soft templating approaches, amino-acid-oriented strategies present a much higher degree of structure flexibility, and permit to achieve tailored textural properties through one-pot incorporation of soluble amino acids in zeolite synthesis gel as the mesopore generating agents, or mesoporogens. The zeolite framework investigated include mesoporous LTA zeolite (MLTA) [19] synthesized from a molar composition of 1Al₂O₃: 2SiO₂: 2Na₂O: 130H₂O: 1 AA and mesoporous FAU zeolite (MFAU) [20, 21] synthesized from a molar composition of 1Al₂O₃: 5SiO₂: 2.5Na₂O: 150H₂O: 1AA or 1Al₂O₃: 10SiO₂: 8Na₂O: 500H₂O: 10alcohol: 2AA when co-modulated with mono-alcohols. The structures of the utilized amino acids are drawn in Scheme 1 with their names and abbreviations listed.

![Scheme 1 Chemical structure, name and abbreviation of the nine natural amino acids used in this study.](image-url)
3. Results and discussion

Thanks to the knowledge gained regarding bio-polymerization on family of zeolitic and related silica-rich species [22], a handful of zeolite structures could be investigated by amino acid approach for conceiving mesoporosity. These approaches are particularly stimulated by the goal to tailor mesoporosity in zeolites as well as to understand the role of inorganic framework flexibility induced by small biomolecules. These strategies will be highlighted in the following sections for the synthesis of mesoporous NaA and NaY zeolites with LTA and FAU topologies respectively.

3.1. Synthesis of mesoporous zeolites with permanent zwitterionic amino acids

Carnitine, or L-carnitine (abbreviated as LC), is an important amino acid manufactured in the body from the essential amino acids of lysine and methionine. It is a natural zwitterionic molecule. When used as additive in the NaA synthesis prepared from a starting silica-to-alumina ratio (SAR_{NaA}) of 2, it generated mesoporous LTA zeolites (MLTA-LC) [19] with Si/Al ratio of 1:11. The powder X-ray patterns of the MLTA-LC samples (Figure 1a) exhibited peaks that can be indexed to a cubic unit cell of the LTA zeolite framework structure with no discernible impurity and similar crystallinity compared to conventional LTA (CLTA). There are no obvious change of peak intensity and no distinct broadening of peak width, indicating the absence of nanocrystal aggregates, unlike surfactant mediated mesoporous LTA zeolites. SEM images clearly revealed that the MLTA-LC samples (Figure 1b) preserved a cubic-shaped crystal outline with truncated edges typical of crystalline LTA, with uniform particle sizes ~1.1–1.4 μm. MLTA-LC samples exhibit obviously rugged surfaces indicating the existence of mesopores within the particles. Mesopores with average pore sizes of 22.0 ± 4.5 nm measured from TEM images were located within the MLTA-LC crystallites. These mesopores were disordered as illustrated by the high-resolution TEM images (Figure 1c), which also show uniformly orientated lattice fringes over the entire image regions confirming the single crystalline nature of the MLTA zeolites. The mesopores created are thus confined within LTA crystallites with high crystallinity. The N_{2} adsorption-desorption isotherms exhibited no N_{2} uptake for the conventional CLTA samples because of the narrow micropore apertures. The mesoporous MLTA samples, on the other hand, showed a type IV N_{2} adsorption isotherm (Figure 1d) with a steep step at P/P_{0} in the range of 0.6–0.99 and an H_{3} hysteresis loop without any limiting adsorption at high relative pressure, confirming the additional mesopores which induced capillary condensation of N_{2} gases. Therefore, while the CLTA samples exhibited marginal BET surface area of 3.5 m^{2}/g, the mesoporous MLTA-LC possessed high BET surface area of 90 m^{2}/g. The mesopores were between 10 to 50 nm in diameter from BJH mesopore size distribution (Figure 1e), with a distribution peak centered at 15–20 nm, consistent with the observations from TEM images. These mesopores generated by amino acids are obviously larger than the 6–10 nm mesopores mediated by amphiphilic organosilane surfactants [14].

When the L-carnitine mesoporogen was applied to zeolite Y with FAU topology prepared from a starting silica-to-alumina ratio (SAR_{FAU}) of 5, it created mesoporous zeolite Y (MFAU-LC) [20] with core–shell structure containing ant-nest like hollow interior and Si/Al ratio of 2. The core–shell zeolite Y crystals were a highly developed zeolite framework showing 20% higher crystallinity (Figure 2a) than conventional zeolite Y (CFAU) synthesized in an organic-free approach. They were also mechanically strong and could not be crushed even after cryogenically frozen in liquid nitrogen. Therefore, to investigate the core structure, the sample was micromotized to 80 nm thickness using a diamond blade for transmission electron imaging. The TEM image of the ultrathin section of an entire crystal (Figure 2b) revealed extensive channel-shaped mesopores and chamber-like voids in the core surrounded by a 165 nm non-mesoporous shell. These channels were long and tortuous which could extend over 1 μm but narrow in width between 2 and 50 nm. High-resolution TEM of the core revealed that the high density of channel-shaped pores were interconnected and each was connected to several chambers (Figure 2c), structurally comparable to the architecture of an ant nest. Around these secondary mesopores were of high periodic encircling zeolite walls exhibiting clearly visible parallel lattice fringes of (111) planes with a d spacing of 1.42 nm over the entire image region that are only interrupted by intracrystalline mesopore channels. The N_{2} physisorption results (Figure 2d) showed
clear type IV N₂ adsorption isotherm and an H₄ hysteresis loop without any limiting adsorption at high relative pressure, confirming the additional mesopores and the induced capillary condensation of N₂ gas. The BJH mesopore distribution were mostly between 10 to 50 nm in diameter, with a distribution peak centered at ~25 nm, consistent with the observations from TEM images, and also similar to those generated in MLTA-LC zeolites.

Figure 1. Texture properties of NaA zeolite synthesized with L-carnitine (MLTA-LC) in comparison with conventional LTA (CLTA). [19] (a) powder XRD patterns, (b) SEM image, (c) high resolution TEM image with red marks as visual guide to the intracrystalline mesopore areas. Inset is the corresponding FFT diffractogram, (d) N₂ adsorption–desorption isotherms, and (e) the BJH mesopore size distribution corresponding to the desorption branch.

When the L-carnitine mesoporogen was applied to zeolite Y synthesis from a starting silica-to-alumina ratio (SAR(lig)) of 10, it created hidden defects [21]. Mono-alcoholic crystal modifier of tert-butanol (TB) generated zeolite NaY microspheres (MFAU-TB). When LC was used for co-modulation, it decreased 25% of the relative (111)/(220) peak intensity to 3.73 (Figure 3a). As the inherent three-dimensional micropores in zeolite Y particles with FAU topology are oriented along the [110] direction, the decrease in the relative (111)/(220) peak intensity means more alleviated transport resistance. The LC co-modulation also caused remarkable differences in samples post-treated with tartaric acid (LT). While LT treatment on MFAU-TB microspheres only generated deep gaps in the surface, the same post-treatment on MFAU-TBLC microspheres created perpendicular mesochannels 30 nm in width penetrating from the surface to core (Figure 3b,c). Clearly discernible parallel lattice fringes of (111) planes with a d spacing of 1.4 nm could be observed over the entire image area disconnected only by the intracrystalline mesopore channels (Figure 3d). In addition, LC co-modulation enhanced Si/Al ratio, and increased mesopore volume after LT treatment. Determined by SEM-EDX, the Si/Al ratio for CFAU-LT, MFAU-TB-LT, and MFAU-TBLC-LT samples was 1.92, 2.01, and 2.10 respectively. Determined from N₂ adsorption-desorption isotherms (Figure 3e) by
subtracting \( t \)-plot micropore volume from total pore volume calculated at \( P/P_0 = 0.98 \), the mesopore volume for CFAU-LT, MFAU-TB-LT, and MFAU-TBLC-LT samples was 0.07, 0.10, and 0.13 cm\(^3\)/g respectively. The strengthened dealumination on MFAU-TBLC to create radially aligned mesochannels indicated that there should be altered local framework environment that caused framework dissolution to propagate along localized radii. The \( ^{27} \text{Al} \) MAS NMR spectra (Figure 3f) of MFAU-TB and MFAU-TBLC samples almost overlapped, indicating an almost identical aluminium state. Only one peak at \( \delta \sim 63 \text{ ppm} \) appeared and no signal could be found around 0 ppm confirmed that all aluminium atoms are entirely incorporated in a tetrahedral environment within the FAU framework. [23] However, a mild LT-treated revealed the subtle difference, The change in chemical shift to lower magnetic fields was more noticeable in MFAU-TBLC after post treatment. The chemical shift moved to a lower magnetic field of 63.5 ppm for MFAU-TB-LT, and even lower to 63.8 ppm for MFAU-TBLC-LT, meaning that the zeolite framework in LC co-modified microspheres was slightly more prone to structural distortion by post-treatment to form decreased T-O-T angles. Therefore, the differences due to LC co-modulation was small and can be viewed as subtle structural “hidden defects”, which did not affect the overall mechanical strength. The measured microhardness was high for MFAU-TBLC reaching breakdown point close to 1.0 mN, much higher than that of \(~0.5\) mN for MFAU-TB.

![Figure 2](image)

**Figure 2.** Texture properties of NaY zeolite synthesized with L-carnitine mesoporogen (MFAU-LC). [20] (a) powder XRD patterns, (b) TEM image, (c) TEM image at 49k magnification of the core showing ramified channels and uniformly oriented lattice fringes disconnected only at the mesopores. Inset is the HRTEM at 245k magnification showing 1.42 nm lattice fringes expected for FAU-type zeolites. (d) \( \text{N}_2 \) adsorption–desorption isotherms and (e) the BJH mesopore size distribution corresponding to the desorption branch.
Figure 3. Texture properties of NaY zeolite synthesized with tert-butanol modulation (MFAU-TB) and L-carnitine mesoporogen co-modulation (MFAU-TBLC). [21] (a) XRD patterns, I(111)/(220) is the intensity of (111) face diffraction at 2θ of 6.24°)/(intensity of (220) face diffraction at 2θ = 10.03°) from XRD patterns; (b) SEM images of cracked MFAU-TBLC-LT microsphere samples which show the wheel-like mesoporous channels; (c) Low-resolution TEM image of MFAU-TBLC-LT cross-section; (d) HRTEM image showing uniformly oriented (111) lattice fringes disconnected only at the mesoporous channels, red lines were used as a visual guide to the intracrystalline mesochannel in FAU crystallites; (e) N2 adsorption–desorption isotherms with inset showing the BJH mesopore size distribution corresponding to the desorption branch; (f) 27Al MAS NMR spectra of MFAU-TB and MFAU-TBLC and their corresponding post-treated samples, * refers to spinning sidebands. The red line for MFAU-TBLC overlaps the black one for MFAU-TB.

3.2. Synthesis of mesoporous zeolites with standard proteinogenic amino acids
Over 300 amino acids have been discovered in nature, and among them, 22 are the primary building blocks of proteins [24]. These proteinogenic amino acids can be divided into four categories according to their side chain groups into polar basic, polar acidic, polar non-ionizable, non-polar non-ionizable. We have chosen two amino acids from each category, that is, totally 8 different amino acids, as additives in NaA synthesis. They are alanine (A), aspartic acid (D), glutamic acid (E), histidine (H), proline (P), serine (S), threonine (T), and arginine (R), representing the overall amino acid categories.
All these amino acids generated mesopores in the LTA zeolite crystals when introduced in the synthesis media, thus the scope of the amino acids as mesoporogens for zeolites can include not only permanent zwitterionic amino acids, but also standard amino acids with amphiprotic properties. For example, the threonine-mediated mesoporous A-type zeolite MLTA-T took crystal outlines in between cubes and spheres with particle size of 1.31±0.24 μm, having rounded edges, apexes and dented surfaces (Figure 4a). The BET surface area derived from N2 adsorption-desorption isotherms was 75 m2/g and the mesopore size distribution curve showed average pore size centered at 19 nm. To probe the internal structure and properties, MLTA-T crystals were ultramicrotomed to a thickness of 80 nm for cross-sectional TEM images and selected area electron diffraction (SAED) study (Figure 4b).
Abundant mesopores were uniformly distributed throughout the whole crystal from surface to the interior. They are probably single crystalline, as shown by the uniformly oriented lattice fringes with spacing of 1.23 nm expected for (200) planes of LTA-type zeolites and the discrete diffraction spots in the SAED pattern.

![Figure 4](image1.png)

**Figure 4.** (a) SEM image of an intact MLTA-T crystal and (b) cross-sectional TEM image of an ultramicrotomed MLTA-T crystal with the corresponding selected area diffraction pattern. [25]

![Figure 5](image2.png)

**Figure 5.** Effect of physical properties of amino acids on the texture properties of MLTA-X zeolites (X is the single-letter code of amino acid) synthesized with different amino acids [25]: (a) FAU content in MLTA as a function of amino acid isoelectric point, and (b) average mesopore size of MLTA as a function of amino acid hydropathy index. The size of the bubble represents (a) average mesopore size of, and (b) FAU content in MLTA respectively. * represents zero.

The effect of macroscopic properties of the different amino acid on hierarchical zeolite mesopore formation have been studied in detail. The isoelectric point of amino acids significantly affected the amount of impurity phase (Figure 5a) almost linearly from 0 to 5.6 wt% FAU. Using hydropathy index (H) values to predict the tendency of an amino acid to seek a hydrophobic (H>1) or an aqueous (H<1) environment [24], Figure 5b shows that the average mesopore size generally decreased when the hydropathy index (H) values increased. This means that hydrophilic amino acids generated larger mesopores compared to hydrophobic ones. This trend is opposite to the role of hydrophobic moieties in organosilane surfactant mesoporogens [26, 27]. As LTA zeolite with Si/Al ratio of 1 is the most hydrophilic zeolite [28], amino acids with higher H values are expected to interact less strongly with the negative zeolite framework by taking less room for the self-assembly process, and thus yielded smaller mesopores. On the other hand, the surfactant route generated mesopores small than 10 nm, which could be further expanded to beyond 10 nm by adding polymeric [26] or linear hydrocarbon swelling agents [29] that permeate into the hydrophobic core of surfactant micelles which in turn expand mesopores in the zeolite. For amino acid mediated route, the created mesopores are orders of
magnitude larger than the molecule size of itself, and the tendency of mesopore size on hydrophobicity is contrary to surfactant-route suggesting a different mesopore formation pathway from that of surfactant-templating. Detailed mechanism investigation and preferably molecular-level simulation study are needed to fully understand these behaviours.

4. Applications of amino-acid-mediated mesoporous zeolites
Mesoporous zeolites possess improved mass transfer efficiency and alleviated diffusion limitations. The creation of pore hierarchy in zeolites confer them great new values, an example would be of mesoporous type Y zeolite which has been commercialized as industrial catalyst. Hierarchical zeolites are widely used for catalysis, adsorption and separation, energy and biomedical applications since they provide large surface areas for reaction, high dispersion of active sites at multilevel pores, shortened mass diffusion paths or minimized diffusion barriers.

4.1. Immobilization of enzyme macromolecules
The creation of hierarchical structures containing >10 nm mesopores in a biologically compatible way can be a remarkable benefit for immobilization and encapsulation of biomacromolecules, which could not enter the small micropores in conventional zeolite. Therefore, immobilization of relatively large enzymes was tested. The bovine liver catalase enzyme, a glycoprotein containing four polypeptide chains, each over 500 amino acids long, has a molecular size of ~10 nm and is widely used in industry for catalyzing the degradation of hydrogen peroxide into water and oxygen. The mesoporous MLTA samples all exhibited a much higher catalase enzyme adsorption capacity (e.g., 264 mg/g for MLTA-LCLT), more than doubled than that of conventional LTA (Figure 6a). As zeolite LTA with low Si/Al ratio is famous for its extreme hydrophilicity, such a high enzyme immobilization capacity could be ascribed to the enhanced electrostatic interaction and hydrogen bonding. The absence of hydrophobic effect could better protect the enzymes from denaturation induced by conformation change to expose their hydrophobic residues which are normally buried within the enzyme molecule. As a result, the catalase enzyme immobilized on all MLTA samples retained more than 90% enzymatic activity of the equivalent free catalase molecules (Figure 6b), much higher than the <20% reported for functionalized carbon nanotubes, [30] or <3% for the metal−organic framework ZIF-90 [31]. This suggests that the hydrophilic MLTA mesopore surfaces induced almost no structural change of catalase during adsorption process. The conventional LTA exhibited 82% retained catalase enzyme activity, ~10% lower than the hierarchical MLTA samples, probably due to the mass transport limitations or the non-optimized interface between LTA and catalase.

![Figure 6](image_url)

**Figure 6.** Catalase adsorption on water-washed MLTA zeolites synthesized with different amino acids and CLTA [19]. (a) kinetics and (b) relative activity.
4.2. Improved catalyst for acid-catalysed reaction

The mesoporous zeolite Y of MFAU-LC samples are promising acid catalyst for chemical transformation. This was demonstrated in the Friedel-Crafts benzylation of toluene at 110 °C for 30 h (Table 1). The conversion with MFAU-LC catalyst reached 84%, nearly twice the conversion obtained over conventional CFAU. The performance of the MFAU-LC hollow core-shell zeolite Y catalysts is much better than that of the previously reported FAU nanosheets exhibiting highest conversion of 75% although mesopore volume of nanosheets, 0.25 cm³/g, was much higher. [32] This can be directly attributed to the well-defined hierarchical structure with interconnected mesopore channels and strong acidities of their highly crystalline zeolitic frameworks, considering the similarities of MFAU-LC to conventional Y zeolite in terms of Si/Al ratios of 2 and aluminum distribution, as well as the relatively larger particle size of MFAU-LC to that of CFAU. The product selectivity towards monosubstituted toluene of up to 93% with similar distributions of o-, m-, p-benzyltoluene confirmed the preserved shape selectivity of zeolite framework. The core-shell zeolite Y MFAU-LC sample exhibited high acid resistance. The side product of hydrochloric acid did not affect zeolite crystallinity and morphology, evidenced by the high intensity of diffraction peaks and unaltered crystal shape of MFAU-LC samples collected after several catalytic reaction cycles. The nearly micron-range crystal size as well as the high mechanical stability resistant to crushing also ensured easy handling for industrial applications.

Table 1. Catalytic performances of the MFAU-LC samples in comparison to conventional CFAU and LC-post-treated Y CFAU-TD for the benzylation of toluene with benzylchloride. [20]

| Catalyst | Conversion (%) | Selectivity (%) | Isomer m- (%) | o- (%) | p- (%) |
|----------|----------------|----------------|---------------|--------|--------|
| MFAU-LC  | 84.17          | 93.46          | 6.12          | 34.5   | 52.84  |
| CFAU     | 43.34          | 94.02          | 6.33          | 35.76  | 51.93  |
| CFAU-TD  | 47.55          | 91.75          | 6.67          | 32.65  | 52.43  |

4.3. Improved nanoreactor after transition metal incorporation

As the MFAU-TBLC-LT zeolitic structure combined wheel-like axial channels and mesopores hierarchically interconnected within one microsphere with high crystallinity and strength, it was thus presumed to be an ideal framework for various functionality incorporation owing to the decreased internal path length for sorbate and reactant diffusion. To proof this concept, we prepared different Ag@Y microspheres for surface-enhanced Raman scattering (SERS) sensing. The Ag@Y microsphere reporters are advantageous for SERS application as the spherical form would exhibit enhanced molecular binding sites, fast binding speed, improved selectivity and sensitivity, whereas the negatively charged inorganic zeolite framework would confer improved selective adsorption as well as thermal, chemical, and mechanical stability. Monodisperse Ag nanoparticles with average size ~8.5 nm were evenly encapsulated in the interior after a simple ion exchange and reduction step on MFAU-TBLC-LT microspheres (abbreviated as Ag@MY) evidenced by TEM images (Figure 7a,b) and EDX-mapping. The hybrid nanostructure composed of well-controlled mesoporous zeolite microspheres and plasmonic metal led to enhanced sensitivity as demonstrated in improved detection limit orders of magnitude higher for p-nitrobenzene thiophenol (PNTP) and p-aminobenzenethiophenol (PATP), compared to that by conventional FAU-LT counterparts (abbreviated as Ag@CY). When Ag@MY was added into the PNTP or PATP solution, strong Raman signals immediately appeared at as low concentration as 10⁻¹⁰ M (Figure 7c,d). On the contrary, Ag@CY exhibited almost no Raman signal even at 10⁻⁷ M. The enhanced sensing capacity would partly relied on the patterned mesopore channels and adsorption capacity of zeolite, which allows bulky PNTP or PATP molecules to diffuse to the close proximity of the integrated Ag nanoparticles for fast in situ transformation into p,p'-dimercaptoazobenzene (DMAB). The simple Ag@MY microspheres with better than literature reported Raman sensing capacity might find wide applications in low abundance food residue and environmental pollutant detection [33].
Figure 7. Mesoporous zeolite Y microspheres for enhanced SERS sensing. [21] (a) SEM image and (b) cross-sectional TEM image of sample Ag@MY, inset curve shows particle size distribution of encapsulated Ag nanoparticles. (c-d) SERS of (c) PATP and (d) PNTP solution using Ag@MY in comparison with Ag@CY, inset in (c) represents the SERS detection reaction involved.

5. Conclusions
An amino-acid-mediated technique has emerged in the past few years for designing complex mesoporous architecture within zeolites. The as-synthesized materials exhibited advantages of easy access and enhanced transport ascribed to the effective construction of hierarchical mesoporosity, while the synthesis process showed advantages of template recyclability through water washing. Many differences were found between the amino-acid-based and the surfactant-based mesopore generating strategy. The mesopores generated by amino acids were larger than 10 nm, orders of magnitude higher than their molecular sizes, while those by surfactants were smaller than 10 nm. With the increase of hydrophobicity, the surfactant-mediated mesopores increased in size, while for amino acids, the increase of hydropathy index decreased the mesopores. The amino acid mesoporogens can be easily removed from the zeolite framework by washing with water, while the surfactant mesoporogens need to be removed by post calcination or solvent extraction. All these differences suggest that the mesopore generation mechanism should be different with these two different mesoporogens. However, the development of mesoporous zeolites using amino acids is still at an early stage, questions remain open for the synthesis mechanism, control over hierarchical pore geometries, and the impact of the secondary porosity in the mass transport properties of the zeolites. These challenges are expected to be tackled in the near future for better tailoring external and internal architecture in zeolites as well in other materials, which will open door to a wide number of applications.
Acknowledgements
This work was supported by National Natural Science Foundation of China (21671010), Guangdong Science and Technology Program (2017B030314002), and Shenzhen Government (JCYJ20170818085754055).

References
[1] Bernal J 1951 *The Physical Basis of Life* London, England: Routledge and Kegan Paul
[2] Smith JV 1998 *Proc Natl Acad Sci U S A* 95(7) 3370-3375
[3] Nima M, GN Rémy, K Freddy 2018 *Adv Mater* 30(16) 1704439
[4] Valtchev V, S Mintova 2016 *MRS Bull* 41(9) 689-693
[5] Hartmann M, AG Machoke, W Schwieger 2016 *Chem Soc Rev* 45(12) 3313-3330
[7] Valtchev V, et al 2013 *Chem Soc Rev* 42(1) 263-290
[8] White RJ, et al 2014 *J Am Chem Soc* 136(7) 2715-2718
[9] Pal N, A Bhaumik 2013 *Adv Colloid Interface* 189–190(0) 21-41
[10] Na K, et al 2011 *Science* 333(6040) 328-332
[11] Xu DD, et al 2014 *Nat Commun* 5 4262
[12] Sachse A, J García-Martínez 2017 *Chem Mat* 29(9) 3827-3853
[13] Serrano DP, JM Escola, P Pizarro 2013 *Chem Soc Rev* 42(9) 4004-4035
[14] Choi M, et al 2006 *Nature Mater* 5(9) 718-723
[15] Xiao FS, et al 2006 *Angew Chem, Int Ed* 45(19) 3090-3093
[16] Tian QW, et al 2016 *Adv Funct Mater* 26(12) 1881-1891
[17] Wei Y, et al 2015 *Chem Soc Rev* 44(20) 7234-7261
[18] Prasomsri T, et al 2015 *Chem Commun* 51(43) 8900-11
[19] Chen Z, et al 2016 *J Mater Chem A* 4(6) 2305-2313
[20] Zhang J, et al 2017 *J Mater Chem A* 5(39) 20757-20764
[21] Chen Z, et al 2018 *J Mater Chem A* 6(15) 6273-6281
[22] Orgel LE 1998 *Origins Life Evol Biosphere* 28(3) 227-234
[23] Van Aelst J, et al 2015 *Adv Funct Mater.* 25(46) 7130-7144
[24] Bischoff R, H Schlüter 2012 *J Proteomics* 75(8) 2275-2296
[25] Zhang J, et al 2017 *Microporous Mesoporous Mat* 252 79-89
[26] Cho K, et al 2009 *Chem Mater* 21(23) 5664-5673
[27] Zhafteng X, et al 2012 *J Mater Chem* 22(6) 2532-2538
[28] Rangnekar N, et al 2015 *Chem Soc Rev* 44(20) 7128-7154
[29] Hasan F, R Singh,PA Webley 2012 *Microporous Mesoporous Mat* 160 75-84
[30] Zhang C, S Luo, W Chen 2013 *Talanta* 113 142-147
[31] Shieh FK, et al 2015 *J Am Chem Soc* 137(13) 4276-4279
[32] Yutthalekha T, et al 2017 *J Cleaner Prod* 142, Part 3 1244-1251
[33] Li Y, et al 2016 *Talanta* 147 493-500