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ARTICLE TYPE

Hierarchical bulky ZSM-5 zeolite synthesized *via* glycerol-mediated crystallization using a mesoporous steam-treated dry gel as precursor

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Glycerol-mediated crystallization transforms a steam-treated dry gel as mesoporous precursor into hierarchical ZSM-5 zeolite. The hierarchical ZSM-5 with auxiliary mesoporosity and acidity exhibits higher activity in the aldol condensation of benzaldehyde with n-butyl alcohol reaction.

Zeolites with micropores (< 2.0 nm) and cavities have achieved considerable success in catalysis, adsorption and ion-exchange [1,2]. However, the conventional zeolites, possessing only small-sized micropores, can not afford easy transference of large molecules within the intrazeolitic space, and thereby catalysis occurs only on the limited external surface sites [3]. Hierarchical zeolites with auxiliary meso- or macro- pores or nanosized zeolites can overcome such accessibility limitations [4]. Diverse synthetic methods have been established to charge mesopores over zeolites, for instance, postsynthetic treatments (dealumination and desilication) [5, 6] can create intra-crystalline mesopores through partial dissolution of the zeolite components. On the other hand, it is common to employ nanoscale materials, including carbon materials [7, 8], polymers [9-11] and surfactants [12, 13], as sacrificial mesoscopic templates to generate mesopores in zeolite, which work cooperatively with molecular zeolite structure-directing agent (SDA) and can be facilely removed by combustion.

From economic and synthetic viewpoint, it is demanding to just use common SDA to synthesize hierarchical zeolites that are always in the form of nanozeolite aggregates [4]. The mesotemplate-free synthesis of such hierarchical zeolites can be realized by hydrothermal synthesis (HTS) method[14, 15] and steam-assisted crystallization (SAC) method [16-18], where massive nucleation plays an important role. Bein et al. [16] converted concentrated gels into nanosized Beta zeolite assemblies by a SAC method. The substantial mesoporosity is stimulated by the occurrence of burst nucleation under SAC treatment. Similarly, the crystal nuclei in the dry gel also largely promote the steam-assisted crystallization of hierarchically nanosized ZSM-5[17]. However, SAC method is sometimes difficult to preserve the mesoporosity without the aid of mesotemplate, as shown by the large loss of mesoporosity in the self-bonded silica pellets after SAC process [18].

To effectively preserve mesoporous structure, Su et al. [19, 20] used glycerol medium to transform self-formed hierarchically meso-macroporous aluminosilicalites impregnated by SDAs into hierarchical MFI and *BEA-type zeolites. The mesoporosity of precursor was well maintained thanks to the quasi-solid-state conditions created by glycerol medium. However, this method involves complex manipulations in acquiring mesoporous precursors.

In our previous report [21], we found that mesoporosity can be generated after 3 h SAC treatment of a dry gel even without adding organosilane. This finding inspires us to use such an easily available pre-crystallized dry gel as mesoporous precursor to generate hierarchical zeolite with the assistance of glycerol, which has been found to be effective to inhibit the fusion of zeolitic crystals by Su and co-workers [19]. Before the glycerol-mediated crystallization, it is necessary to find the pre-crystallized dry gel with optimal mesopore volume and surface area, and therefore we have synthesized a series of pre-crystallized dry gel with varied steaming durations. The obtained samples are denoted as DG (0), DG (W2) and DG (W3), respectively, where W represents water and the numbers indicate the duration of steaming at 170 °C under SAC conditions.

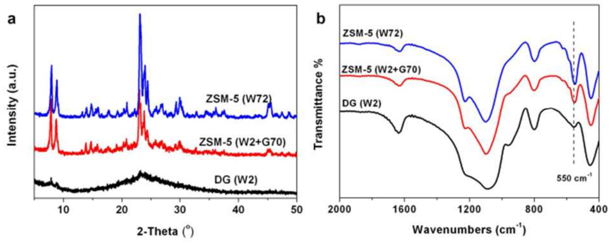

Fig. 1 (a) XRD patterns and (b) FT-IR spectra of DG (W2), ZSM-5 (W2+G70) and ZSM-5 (W72).

During the short time SAC treatment (0 - 3 h), the material exhibits a trend of increase in intensities of XRD peaks of ZSM-5 zeolite (Fig. S1a), but its mesoporosity increases initially and then decreases (Fig. S1b). After prolonged steaming time, e.g., 72 h, the obtained material ZSM-5 (W72) has good crystallinity (Fig. 1a or S1a) but poor mesoporosity (Fig. S1b) [21]. As shown in Table S1, DG (W2) at 2 h has a higher mesoporosity (0.84 cm^3/g) than DG (W3) at 3 h (0.62 cm^3/g). Besides, the semi-crystalline DG (W2) exhibits a narrow pore size distribution (PSD) centered at *ca.* 18 nm (Fig. S1b). Compared with DG (0) (Fig. S1c), DG (W2) has a rough surface for the bulky matrix, which also shows the presence of mesopores (Fig. S1d). Therefore, uncalcined DG (W2) is more potential to be selected as the precursor for the subsequent glycerol-mediated crystallization. From a point of view of experimental design, the selection of DG (W2) with substantial amorphous phase helps to attribute the crystallinity of the final zeolite to the promotional effect of glycerol on crystallization.

The pre-crystallized DG(W2) was subjected to solvothermal treatment in glycerol media for 70 h, the produced solid powder was collected and labeled as ZSM-5 (W2+G70) (G represents glycerol). As shown in Fig. 1a, ZSM-5 (W2+G70) exhibits typical strong MFI reflections, more crystalline than DG (W2), but slight amorphous background is still detectable. Comparatively, ZSM-5 (W72) after 72 h of steaming has stronger peak intensity than ZSM-5 (W2+G70) and shows no amorphous halo (Fig. 1a). In the FT-IR spectra (Fig. 1b), the framework vibration at 550 cm^{-1} (double five rings) is the characteristic of MFI zeolite. The optical density ratios (ODRs) of the 550 cm^{-1} to 450 cm^{-1} bands (I_{550}/I_{450}) are 0.401, 0.594 and 0.773 for DG (W2), ZSM-5 (W2+G70) and ZSM-5 (W72), respectively, which confirms that the framework is made up of pentasil rings [22]. Although ZSM-5 (W2+G70) has enhanced crystallization compared with DG (W2), the ODR value is still below 0.7, implying the presence of amorphous phase that is also indicated by XRD data [22]. However, the increased proportion of MFI structure units compared with that in DG (W2) indicates the excellent promotional effect of glycerol on the ZSM-5 crystallization. Moreover, the incompletely crystallized ZSM-5 zeolite still has potential catalytic advantage [23]. Comparatively, when we directly mixed DG (0) with glycerol to age at 170 °C for 72 h, the obtained ZSM-5 (G72) is far from well-crystallized (Fig. S2), though having also provided the evidence of glycerol promoted crystallization.

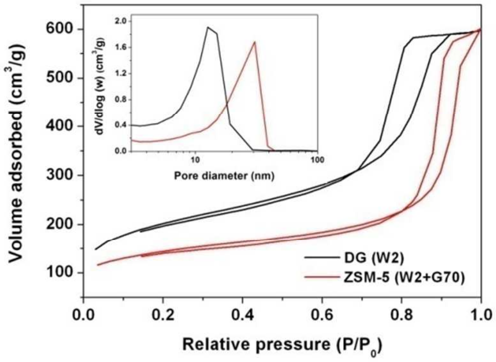

Fig. 2 N_2 adsorption-desorption isotherms and the corresponding pore size distribution (inset) of DG (W2) (extracted from Fig. S1a) and ZSM-5 (W2+G70).

It is interesting to explain the difference between crystallization feasibilities of ZSM-5 (W2+G70) and ZSM-5 (G72). In the crystallization of ZSM-5 (G72), the very low mesoporosity of DG (0) does not allow glycerol to penetrate into the inner space and thus can only transform the external aluminosilicalite species into zeolite. Comparatively, the successful crystallization of ZSM-5 (W2+G70) is not only due to the high mesoporosity of DG (W2), which was similarly implied in Su's work[19], but also benefits from the elimination of the maximum crystallization barrier for ZSM-5 crystallization caused by initially formed nuclei [17]. However, it has been reported that when the highly ordered mesoporous MCM-41 silica was used as the mesoporous precursor, glycerol can only help to create protozeolitic ZSM-5 (invisible by XRD) containing mesoporous materials [24]. The unsatisfactory crystallization is probably due to the unique nature of the selected MCM-41[25] and the low crystallization temperature. In our case, however, the precrystallized dry gel can be facilely transformed to zeolite, and the role of glycerol is to limit the growth of nanocrystal to its full size and enlarge the spacing between zeolitic crystals.

In addition, it is also necessary to evaluate the effect of glycerol on the preservation of mesoporosity. It is encouraging that ZSM-5 (W2+G70) has the same mesopore volume (0.84 cm^3/g, Table S1) with DG (W2), proving that the mesoporosity is almost fully preserved. Besides, the BET surface area reduces from 714 to 501 m^2/g (Table S1). In spite of the highly preserved mesoporosity, the isotherms have experienced some variations from that of DG (W2), namely the transformation from type IV to a mixture of I and IV (Fig. 2). Correspondingly, there is a shift in the most probable mesopore size from about 20 to 40 nm (Fig. 2 inset). Therefore, it is reasonable to say that the relatively mild glycerol system slows down the crystal growth and prevents the collapse of mesoporous structure within DG (W2) [19].

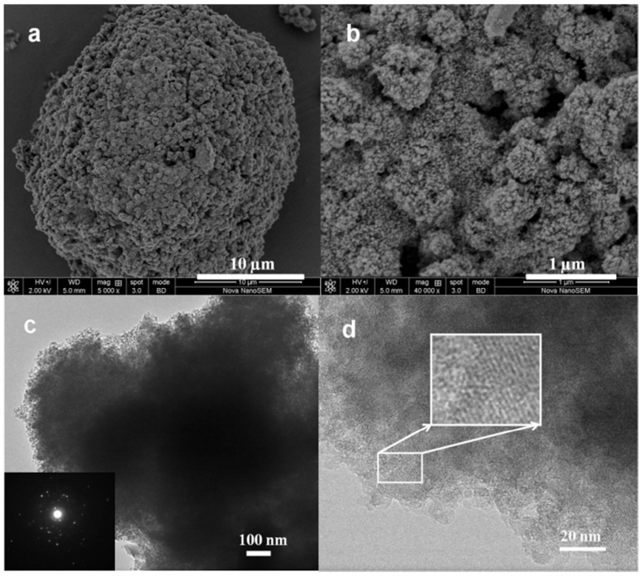

Fig. 3 (a and b) SEM and (c and d) TEM images of ZSM-5 (W2+G70).

Fig. 3a shows that ZSM-5 (W2+G70) exhibits as a bulky matrix in the range of tens of several micrometers, which was largely retained from the DG (W2). The morphology is different from the well-separated aggregates of ZSM-5 (W72) by SAC treatment (Fig. S3) [21], indicating that the absence of moisture in the glycerol-mediated crystallization helps to efficiently suppress the mobility of aluminosilicalite species. The rough surface of the matrix is agglomerated by many nanoparticles (Fig. 3b and c). The absence of polycrystalline-like ring forms in SAED pattern suggests that those nanoparticles may take orientation to some extent (Fig. 3c). Fig. 3d also exhibits lattice fringe for the nanoparticles.

After 50 h treatment of ZSM-5 (W2+G70) in boiling water for 50 h [23], the material shows similar an XRD pattern (Fig. S4) and N_2 isotherms (Fig. S5) and suffers only a slight loss of BET surface area, micro- and mesopore volumes (Table S1), indicating the good hydrothermal stability.

To reveal the chemical environment of Al, ^{27}Al MAS NMR spectra of DG (W2), ZSM-5 (W2+G70) and ZSM-5 (W72) have been collected, as shown in Fig. 4a. All the three materials display a strong peak at 55 ppm assigning to tetrahedrally coordinated aluminium and a weak peak at 0 ppm assigning to octahedrally coordinated aluminium. Besides, DG (W2) shows a signal at 13 ppm ascribed to hexa-coordinated extra-framework aluminium species [26, 27]. Moreover, the desired coordination for ZSM-5 (W2+G70) proves that moisture-free condition created by glycerol is also able to incorporate Al atoms into the zeolite framework.

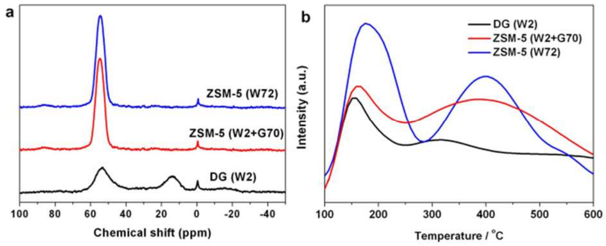

Fig. 4 (a) ^{27}Al MAS NMR spectra and (b) NH_3-TPD profiles of DG (W2), ZSM-5 (W2+G70) and ZSM-5 (W72).

NH_3-TPD profiles of the materials are shown in Fig. 4b. The weak acid sites according to peak at 180 °C are commonly possessed by the three samples. In the higher temperature range, NH_3 also desorbs at around 310 °C for DG (W2), revealing the amorphous nature [11]. After SAC treatment, ZSM-5 (W72) has strong acidic sites according to the peak at 400 °C. Importantly, the NH_3-TPD profile of ZSM-5 (W2+G70) shows that glycerol-mediated crystallization also transforms the medium acid sites (310 °C) to strong ones (400 °C), although the transformation is not complete. The acidity is consistent with the degree of zeolite crystallization by glycerol (Fig. 1). Besides, the concentration of acid sites follows the order of ZSM-5 (W72) > ZSM-5 (W2+G70) > DG (W2).

Table 1 Catalytic performance of various catalysts.

Sample	Si/Al[a]	catalytic conversion[b]
DG (W2)	41.2	31.2%
ZSM-5 (W72)	40.3	23.4%
ZSM-5(W2+G70)	40.7	51.9%

[a] The numbers indicate Si/Al ratio obtained by ICP-OES analysis. [b] Catalytic activity is indicated by benzaldehyde conversion and the selectivity to the target product molecule is close to 100%.

To unravel the catalytic properties and accessibility of acid sites for ZSM-5 (W2+G70), aldol condensation of benzaldehyde with n-butyl alcohol was selected as a liquid-phase probe reaction (Table. 1). The highly mesoporous ZSM-5 (W2+G70) has the higher activity (51.9 %) than ZSM-5 (W72) (23.4 %), indicating that the enhanced accessibility of acid sites helps to improve the catalytic performance. With the similar mesoporosity, ZSM-5 (W2+G70) has higher activity than DG (W2) (31.2 %), which is benefited from its higher concentration/strength. It proves that although ZSM-5 (W2+G70) is not highly crystalline, it is still a promising catalyst [23].

In this work, semi-crystalline materials DG (W2) obtained through steaming dry gel at 170 °C for 2 h shows abundant mesoporosity. The subsequent glycerol-mediated crystallization for 70 h can convert DG (W2) into bulky hierarchical ZSM-5 zeolite (ZSM-5 (W2+G70)) with obviously enhanced crystallinity and well-preserved mesoporosity. Catalytic test indicates that ZSM-5 (W2+G70) has favourable catalytic performance in the aldol condensation of benzaldehyde with n-butyl alcohol reaction because of the high mesoporosity and relatively strong acidity.

Experimental

(1) Synthesis of steam-treated dry gel with high mesoporosity.
According to the procedure in our previous work [21], tetraethylorthosilicate (TEOS), aluminum isopropoxide (AIP), tetraethylammonium hydroxide solution (TPAOH, 25 wt % aqueous solution) and ethanol were mixed to achieve the following composition: 0.025AIP: 1TEOS: 0.15TPAOH: 5.6H_2O: 40EtOH. The solution was stirred at room temperature for 3 h and then dispersed in a Petri dish to undergo solvent evaporation.

The obtained dry-gel DG (0) was transferred to a 10 ml Teflon beaker, placed in a Teflon-lined autoclave (100 mL) with 10 g water at the bottom of the liner. The dry gel was steamed at 170 °C for 2 h (or 3 h) and then dried at 80 °C for 3 h. The obtained material was calcined at 550 °C for 6 h for porosity measurement. Both uncalcined and calcined materials are denoted as DG (W2) (or DG (W3)), where W represents water.

(2) Synthesis of hierarchical ZSM-5 zeolites by using glycerol as medium.

The uncalcined DG (W2) was mixed with 3 g glycerol, transferred to a Teflon-lined autoclave, and aged at 170 °C for 70 h. After aging, the products were washed, dried and calcined at 550 °C for 6 h. The sample is denoted as ZSM-5 (W2+G70), where G represents glycerol. Besides, ZSM-5 (G72) was prepared by aging DG (0) in 3 g glycerol at 170 °C for 72 h and ZSM-5 (W72) was synthesized by steaming DG (0) at 170 °C for 72 h.

(3) Characterization and catalytic test

X-ray diffraction (XRD) patterns were recorded with a Rigaku D/Max2550V diffractometer, with CuKα Radiation at 40 kV and 100 mA. The Fourier transform infrared spectra (Nicolet 6700 FTIR) of the samples were recorded in the range of 400~4000 cm^{-1} with a resolution of 2 cm^{-1}. Nitrogen adsorption–desorption isotherms were measured at 77 K on an ASAP 2010 (Micromeritics, USA) analyzer. Morphology of the samples were observed by both scanning electron microscopy (Hitachi 3400N) and transmission electron microscopy (JEM-2100f). Solid state ^{27}Al MAS NMR spectra were recorded with an AVANCE 500 NMR spectrometer at a spinning frequency of 130.3 MHz. A 1.0 M solution of aluminum nitrate with a chemical shift 0.0 ppm was used as an external reference. Surface acidities were measured by NH_3-temperature program desorption (NH_3-TPD) on an apparatus TP-5080 (Tianjin Xianquan Technology Development Co., Ltd.). Aldol condensation of benzaldehyde with n-butyl alcohol was carried out at 80 °C for 8 h under N_2 in a three-necked flask equipped with a reflux condenser and a magnetic stirrer. The details of the NH_3-TPD and catalytic reaction have been described elsewhere [10]. Elemental analysis for the Si/Al ratio was performed with inductively coupled plasma optical emission spectroscopy (ICP-OES) using a SPECTRO ARCOS ICP Spectrometer.

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Notes and references

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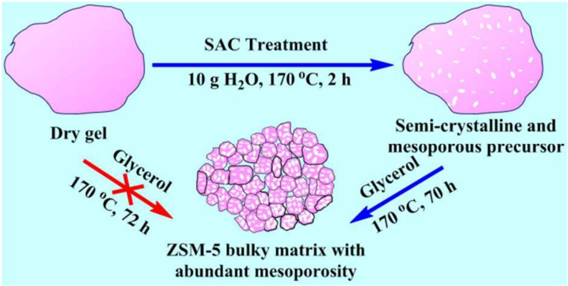

The mesoporous precursor obtained by steaming the dry gel can be transformed into a hierarchical ZSM-5 zeolite by using glycerol as crystallization medium.