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Solventless green synthesis of sodalite zeolite using diatomite as silica source by a microwave heating technique

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ABSTRACT

Microporous zeolite sodalite can be simply synthesized by mixing, grinding and microwave heating the solid mixture of raw natural clay and pseudoboehmite without solvent. The sample obtained by microwave-assisted solventless route exhibits good crystallinity and high yield. This method is very efficient, rapid, economic, and environment friendly for the synthesis of sodalite.

Zeolites have attracted great interest and have been widely applied in the fields of catalysis, ion exchange, separation and adsorption owing to their high surface areas, uniform micropores and excellent thermal stability [1–2]. Sodalite is a type of zeolite having ultra-micropore size and is commonly used as a heterogeneous basic catalyst in specialty and fine chemical production, which is generally prepared by hydrothermal synthesis under autogenous pressure [3–6]. However, this hydrothermal route has several disadvantages. A large amount of water necessitates the use of a large reactor resulted in reduction of synthesis efficiency, and accordingly, losses of the nutrients of aluminosilicates dissolved in the waste water. As a result, the zeolite yield is significantly reduced as well as massive amounts of polluted wastewater are produced. In order to reduce the water content in the synthesis mixture, a solvent-free route was developed for zeolite synthesis with improvement of product yields and decreased wastes [7]. Moreover, the rapid increase in consumption of zeolites calls for using low cost raw materials for the preparation of zeolites, since they are much less expensive than the chemical or reagent grade.

In the last decades, the use of natural clay such as kaolin [8], rectorite [9], diatomite [10–12], *etc.* has been increasing for preparation of zeolites or its composites [13,14]. Diatomite, known as a type of siliceous biologic sedimentary rock, is an attractive raw material with high silica contents and available in bulk quantities at low cost. Being advantages of amorphous silica skeletons and silica rich over other materials, diatomite is available for zeolite synthesis without purification such as thermal treatment. Until now, FAU [15], MFI [16], GIS [17] and SOD type zeolite [10], *etc.* have been hydrothermally synthesized using diatomite as precursors. However, all these synthetic procedures require a long synthesis period.

Additionally, microwave-assisted hydrothermal process was effective for zeolite synthesis from freshly prepared sodium aluminosilicate gel precursor owing to shortening reaction time and saving energy [18–21]. Recently, our group developed a novel green procedure for preparing low silica zeolites under solventless microwave radiation [22]. This means that a very significant reduction in the water and less energy and time consumption could be attained, which is a very important achievement for a future up-scaled.

Herein, we report a rapid, convenient, economic and environment friendly route for the fabrication of zeolite sodalite *via* a *in-situ* crystallization technique using natural clay as sole silica source for minimizing pollution and reducing cost. It is facile and appropriate for large-scale synthesis of sodalite using natural materials by a microwave solventless technique.

The sample obtained by microwave-assisted solventless route designed as MS-sodalite (pure sodalite) or MS-SOD/Dt$_n$ (composite), where n denotes the proportion of diatomite in composites (The origin of all reagents were provided in the Supplementary Material). MS-sodalite was successfully prepared in the absence of water using diatomite as sole silica source *via* microwave heating. The XRD pattern of the initial diatomite revealed the main phase consists mainly of the cristobalite

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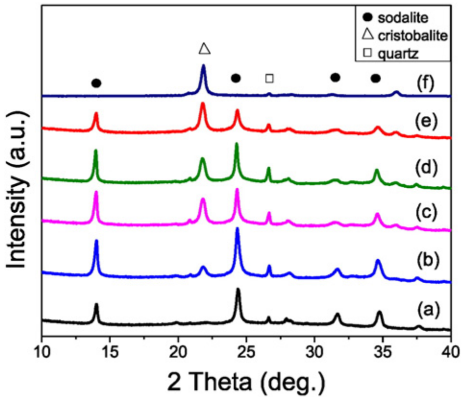

Fig. 1. XRD patterns of diatomite and as-synthesized samples in microwave solventless route. (a) MS-sodalite, (b) MS-SOD/$Dt_{0.12,}$ (c) MS-SOD/$Dt_{0.25,}$ (d) MS-SOD/$Dt_{0.3,}$ (e)MS-SOD/$Dt_{0.4}$ (f) diatomite.

silica form with the characteristic peak centered at 21.8° (2θ) mixed with a small amount of quartz (Fig. 1f). This result was consistent with previous observations of diatomite [14]. Fig. 1 shows the XRD patterns of as-synthesized samples with varying experiment parameters (Table S1) through a microwave solventless route. The prominent peaks at 14.0°, 24.4°, 31.7°, 34.8°, 37.7° (2θ) are found to match with the characteristic peaks of sodalite octahydrate zeolite (JCPDS Card no. #11-0401), indicating sodalite was successfully synthesized. Moreover, the reflection peak at 26.7° (2θ) indicates the presence of a minority amount of quartz in sodalite, this result is attributed to tiny quartz remains from natural raw diatomite (Fig. 1f). Additionally, a series of composites of diatomite and sodalite (12–40 wt%, calculated by weight of diatomite) were produced when the molar ratio of Na_2O/SiO_2 less than 1 in the reaction mixture *via* the microwave solventless route (Fig. b–e). It is worth mentioning that we cannot obtain zeolite products if it is absent of NaOH. Therefore, the amount of NaOH is a critical parameter influencing the transformation of the diatomite and lower Na_2O/SiO_2 ratios resulted in incomplete dissolution of entire raw diatomite and caused incomplete reaction [13].

Fig. 2 represents the nitrogen adsorption-desorption isotherms of initial diatomite and zeolite samples prepared by the microwave solventless route. The MS-sodalite exhibits a type II isotherm ($S_{BET} = 17.8\ m^2/g$) with a H1 hysteresis loop above 0.8 (P/P_o) associated with the filling and emptying of the mesopores by capillary condensation, which implies the existence of a small amount of mesopores (*ca.* 50 nm, $V_{meso} = 0.11\ m^3/g$). Such a feature is associated with voids formed by the close packing of nano particles derived from process of transformation of diatomite. Remarkably, compared with the surface area of 0.12 m^2/g initial diatomite had (Fig. 2e), the Brunauer–Emmett–Teller (BET) surface area of composites enhanced with increasing the amounts of sodalite in the composites (0.8, 2.66, 5.22 m^2/g for MS-SOD/$Dt_{0.4}$, MS-SOD/$Dt_{0.25}$, MS-SOD/$Dt_{0.12}$ respectively, (Fig. 2 b–d)). Additionally, the comparison of detailed data of the products prepared by microwave-assisted solventless method and conventional methods are summarized in Table S2.

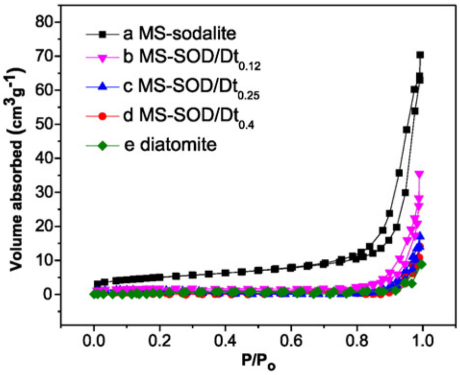

Fig. 2. N_2 adsorption-desorption isotherms of diatomite and prepared samples (a) MS-sodalite, (b) MS-SOD/$Dt_{0.12}$ (c) MS-SOD/$Dt_{0.25}$, (d) MS-SOD/$Dt_{0.4}$, (e) diatomite.

Fig. 3 presents the SEM images of diatomite, MS-sodalite and its composites (MS-SOD/Dt). The MS-sodalite crystals exhibited thread-ball-like spheres with diameter of *ca.* 2.5 μm (Fig. 3a), and clearly indicating that no bulk diatomite particles were existed in the product (Fig. 3f), this is agreement with XRD results (Fig. 1a). As shown in Fig. 3, a few fragments of diatomite were still present in the composite samples (Fig. 3e), which clearly indicates that alkalinity was insufficient to digest the entire raw materials and cause incomplete reaction. All MS-SOD/Dt composites displayed the similar spherical morphology evolved from irregularly shaped diatomite, of which exhibited thread-ball-like spheres with small deformed cristobalite derived from unreacted raw diatomite, clearly illustrated in Fig. 3e, and the corresponding particle sizes (2–5 μm) had no obvious changes with increasing diatomite amount from 0.6 to 2.2 g (Fig. b–e).

For comparison, we prepared sodalite from similar chemical composition by thermal treatment *via* a solventless route (Table S1). However, some differences in appearance were observed depending on the selected heating mode. Monolith was formed for oven heating and the microwave method provided packless bulk material (Figs. S1, S2). XRD pattern revealed characteristic peaks of obtained sample associated to SOD type topology with a small amount of quartz, which is consistent with that of microwave heating (Fig. S3). However, the morphology of S-sodalite displayed spheres with corrugated surface rather than thread-ball-like spheres (Fig. 4). The same sizes (*ca.* 2.5 nm) of the spherical products as the sample prepared by microwave heating (Fig. 4). Therefore, the difference in shape of sodalite can be probably ascribed to different heating method.

In conclusion, we performed a series of experiments to synthesize sodalite zeolite with thread-ball-like morphology using natural clay diatomite as sole silica source through mixing, grinding and microwave heating of the solid raw materials. At the same time, it is accompanied by the generation of composites SOD/Dt with varying ratio of diatomite through adjusting initial chemical composition. We expect this eco-friendly method will expend to LTA, FAU and MFI type zeolite synthesis, so as to provide a cost-effective approach for industrial production of zeolites at large scale in the future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2016.06.013.