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Journal Name

COMMUNICATION

## Facile and green aerosol-assisted synthesis of zeolites

Zhendong Guo, Guang Xiong\*, Liping liu, Jinpeng Yin, Ruixue Zhao, and Shiqiang Yu

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

**Here we report a facile and green aerosol-assisted method to synthesize zeolites. Compared with conventional hydrothermal route, the new method is simpler and less polluted, and requires lower template amount, reaction volume, and crystallization temperature.**

Zeolites are widely used as catalysts in industrial chemical processes due to their large porosity, uniform channels, and excellently thermal and hydrothermal stabilities.<sup>1-4</sup> These materials are typically synthesized under solvo/hydrothermal conditions which usually require a large amount of solvent and relatively high crystallization temperature. The solvents normally results in the discharge of polluted water, and lower synthesis efficiency owing to the occupation of the autoclave space by the solvent.<sup>2,5</sup> In 1990, a dry gel method was proposed by Xu et al. to reduce pollution and enhance the yield of the products.<sup>6,7</sup> However, the method is difficult to scale up due to the complicated procedure. Recently, Xiao et al. presented solvent-free synthesis of various zeolites. The method is very simple and less polluted, but mainly focused on the synthesis of micro-size zeolites.<sup>2,5</sup> The findings from the above methods, which have their own merits and weaknesses, are able to guide further research.

As a green, adaptable and scalable route, aerosol method has been widely used to synthesize mesoporous and macroporous molecular sieves.<sup>8-15</sup> Heteroatoms can be finely dispersed in the silica or silica–alumina matrix by the method.<sup>8,15</sup> Nevertheless, to the best of our knowledge, aerosol method has not been employed for synthesis of microporous silica-alumina or transition metal substituted zeolites.

In this communication we show a generalized aerosol-assisted method for the synthesis of various zeolites (TS-1, silicalite-1, Beta, ZSM-5, Zn-ZSM-5, Fe-ZSM-5). The detailed synthesis methods and

characterizations of the above mentioned zeolites are shown supporting information. The method includes two steps: (1) The precursor solutions were prepared by mixing raw materials. By an aerosol-dry apparatus (Figure S6), the precursor solutions were quickly transformed into amorphous powder. (2) The amorphous powder and a given amount of template agent were loaded into Teflon-lined autoclave and crystallized under autogenous pressure. No extra water is added, which maintains a high concentration of template agent. Here, as a model study, the synthesis of TS-1 by aerosol-assisted method is presented.

Among zeolites reported to date, TS-1 has received great attention due to its excellent catalytic properties in a series of selective oxidation reactions with hydrogen peroxide under mild conditions.<sup>16-19</sup> It has been successful used as an industrial catalyst in the processes of propylene epoxidation, cyclohexanone ammoximation, and phenol hydroxylation.<sup>16, 20, 21</sup> However, there are still some problems limiting the practical applications of the conventional hydrothermal synthesis of TS-1:

i) A relatively high cost of TS-1 due to the use of the expensive template: TS-1 was firstly synthesized by using tetrapropylammonium hydroxide (TPAOH) as a template.<sup>22</sup> However, the industrial application of TS-1 is limited by a relatively high price of TPAOH.<sup>16, 17, 23</sup> Although other inexpensive organic amines were used to synthesize low-cost TS-1, their performances are not as good as that of the classical TS-1.<sup>16, 24</sup>

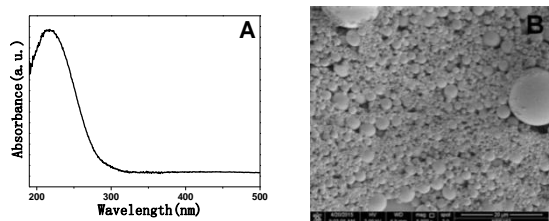
ii) The synthesis procedure is relatively complicated and time-consuming. The catalytic performance of TS-1 zeolite greatly depends on the coordination state of the titanium species.<sup>16, 25</sup> However, the hydrolysis of Ti alkoxide is so fast, which easily leads to the formation of the TiO<sub>2</sub> precipitates. To avoid the problem, the Ti alkoxide is hydrolyzed following some strict procedures: dripping TPAOH slowly at 0 °C, dissolving TBOT in isopropyl alcohol, operating under a CO<sub>2</sub> free atmosphere.<sup>26-29</sup>

The above problems can be resolved by the aerosol-assisted method. Figure 1A shows the UV-vis spectrum and SEM (scanning electron microscopy) image of SiO<sub>2</sub>-TiO<sub>2</sub> amorphous powder, which was obtained in the first step. The UV-vis spectrum exhibits a strong absorption at 218 nm, which is assigned to the isolated tetrahedral

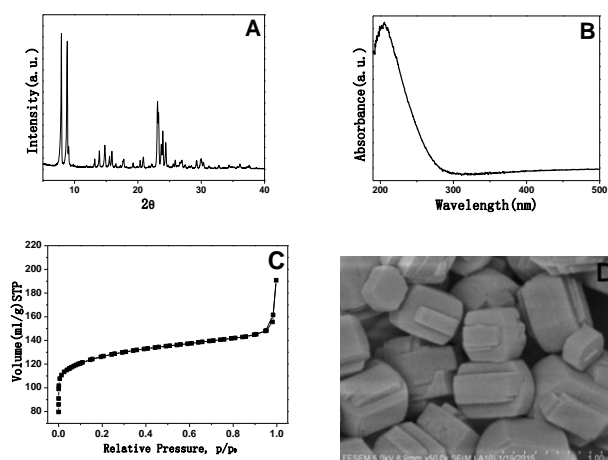
State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China Fax: (+86) -411-84986340 E-mail: gxiong@dlut.edu.cn

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

titanium species.<sup>23, 25, 30</sup> This indicates that titanium ions are already well dispersed in the SiO<sub>2</sub>-TiO<sub>2</sub> amorphous powder. The magnification image (Figure 1B) shows that the SiO<sub>2</sub>-TiO<sub>2</sub> amorphous powder has a spherical morphology. The particle size ranges from 50 nm to 10 μm.



**Figure 1.** A) UV-vis spectrum of the SiO<sub>2</sub>-TiO<sub>2</sub> amorphous powder, B) SEM image of the SiO<sub>2</sub>-TiO<sub>2</sub> amorphous powder.



**Figure 2.** Analytical data for the TS-1-0.05. A) XRD patterns, B) UV-vis spectrum, C) N<sub>2</sub> sorption isotherms, D) SEM image.

Figure 2 shows X-ray diffraction (XRD) pattern, UV-vis spectrum, N<sub>2</sub> sorption isotherm and SEM images of the final product, TS-1-0.05 sample (TPAOH/Si=0.05). The XRD pattern of TS-1-0.05 (Figure 2A) shows the characteristic peaks at  $2\theta = 7.8, 8.8, 23.0, 23.9$  and  $24.4^\circ$ , which are typical for MFI topology.<sup>31, 32</sup> The UV-vis spectrum of the TS-1 zeolite shows a strong band at 213 nm, indicating the presence of the framework Ti species. The amorphous Ti species and anatase TiO<sub>2</sub>, corresponding to the absorptions at 270 nm and 320 nm, are not observed.<sup>30</sup> This suggests that titanium ions are well dispersed in the framework of TS-1-0.05 sample. Figure S7 exhibits the Raman spectrum of TS-1-0.05 excited with the 244 nm laser line. The Raman peaks at 490, 530, and 1125 cm<sup>-1</sup> are associated with the framework titanium species.<sup>33</sup> Figure S8 shows Raman spectrum of TS-1 collected with the 325 nm laser line which is sensitive to anatase TiO<sub>2</sub>. The peaks at 144, 390, 515 and 637 cm<sup>-1</sup> are not observed, indicating the absence of anatase TiO<sub>2</sub>. The X-ray fluorescence spectroscopy indicates that the SiO<sub>2</sub>/TiO<sub>2</sub> ratio of the TS-1 is 63.6, which is close to the mole ratio (60) of the starting precursor solution. N<sub>2</sub> adsorption-desorption isotherms of the TS-1-0.05 sample (Figure 2C) shows a sharp increase at a relative pressure below 0.02, indicating the presence of micropores. A small hysteresis loop and a steep increase at a relative pressure of  $0.9 < P/P_0 < 1$  can be observed, which is due to the intercrystal pore.

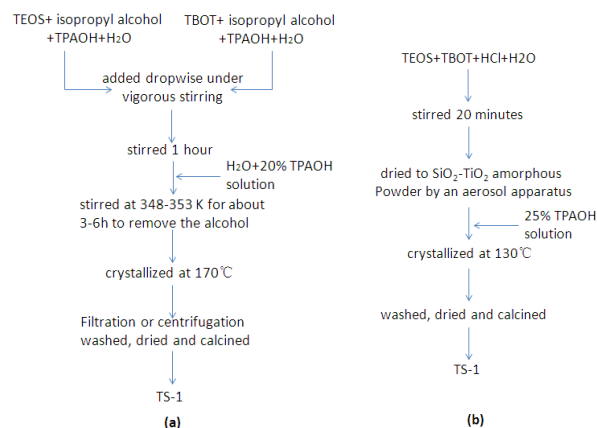
The BET surface area and pore volume are 466 m<sup>2</sup>/g and 0.3 cm<sup>3</sup>/g, respectively. The magnification image (Figure 2D) shows that TS-1-0.05 sample has crystal morphology with diameters of 350-800 nm. However, if the crystallization process is conducted at 110°C for 48h, the crystal size of TS-1 is reduced to 150-400 nm (Figure S9), indicating that the crystal size can be adjusted by the synthesis conditions.

**Table 1.** Catalytic performance of calcined TS-1 for the epoxidation of propylene

Cat.	X <sub>H<sub>2</sub>O<sub>2</sub></sub> /%	S <sub>PO</sub> /%	U <sub>H<sub>2</sub>O<sub>2</sub></sub> /%	Y <sub>PO</sub> /%
TS-1(aerosol)	96.0	90.1	97.5	84.3
TS-1(convention)	95.1	90.6	93.5	80.6

[a] Reaction conditions: catalyst 0.2 g, methanol 34 mL, H<sub>2</sub>O<sub>2</sub> 1 mol/L, propylene pressure 0.4 MPa, 333 K, 1 h.

Table 1 shows the catalytic performance of the calcined TS-1 in propylene epoxidation. The TS-1, which was prepared according to the improved conventional method, was used as a reference.<sup>29</sup> X-ray diffraction (XRD) pattern, UV-vis spectrum, and scanning electron microscopy (SEM) of the TS-1 (convention) are shown in Figure S10. The results suggest that both H<sub>2</sub>O<sub>2</sub> conversion and selectivity of propylene oxide are almost the same for the two samples. However, the utilization of H<sub>2</sub>O<sub>2</sub> for the TS-1-0.05 (aerosol) is higher than that of the TS-1 (convention).



**Figure 3.** The typical processes of TS-1 synthesized by conventional hydrothermal method (a) and aerosol-assisted method (b).

The typical processes of conventional hydrothermal method and aerosol-assisted method are shown in Figure 3. Compared with conventional hydrothermal synthesis, the aerosol-assisted method has the following obvious features: 1) A simpler synthetic process. The aerosol-dry process makes titanium ions highly distributed without complex operations to avoid the formation of TiO<sub>2</sub> precipitates. As shown in Figures 2 and S11, the extra-framework titanium species are absent when the SiO<sub>2</sub>/TiO<sub>2</sub> ratio ranges from 40 to 60. Furthermore, due to the presence of HCl, TEOS can hydrolyze completely at room temperature in a short time (< 5 minutes). By the aerosol-dry process, HCl and ethyl alcohol were removed in a short time. Therefore, the time-consuming process of evaporating alcohol can be avoided. 2) The template amount is ultralow. TS-1 can be completely crystallized at the ratio

TPAOH/SiO<sub>2</sub> = 0.04 (Figure S12), which is much lower than that for the conventional hydrothermal method. 3) Less pollution. The only water comes from the template agent (25 % TPAOH solution). During crystallization processes, the TPAOH aqueous solution is absorbed due to the relatively high porosity of the MFI structure. As a result, almost no waste solution is discharged. 4) Low pressure. In conventional hydrothermal synthesis, a large amount of Ti species will be lost at low crystallization temperature. Therefore, TS-1 is usually crystallized at 170 °C.<sup>17, 19, 23, 26, 31</sup> In this work, most of Ti species can be successfully incorporated into the framework of TS-1 at 130 °C. The saturated vapor pressure of water is 270.02 kPa at 130 °C and 791.47 kPa at 170 °C. Hence the decreased pressure reduces the equipment requirements. 5) Better utilization of autoclaves. During the hydrothermal crystallization process, H<sub>2</sub>O occupies most space of autoclaves in the conventional synthesis. However, in an aerosol-assisted method, only a small space is required for crystallization. For example, in a 3 ml autoclave, 1.4 g TS-1 can be obtained by the aerosol-assisted method, which is about 8 times of that for a typical hydrothermal synthesis (0.173 g).<sup>3,5</sup>

In conclusion, various zeolites have been successfully synthesized by an aerosol-assisted method. Compared with conventional route, the new method is simpler and less polluted, requires lower template amount, reaction volume and crystallization temperature. This method is particularly useful for the synthesis of transition metal substituted zeolites, in which heteroatoms are required to be finely dispersed in silica matrix. As a model case, TS-1 exhibits good catalytic performance in epoxidation of propylene. This green aerogel route can be extended to the synthesis of other zeolites and has potential application to the synthesis of industrial zeolites in the future.

### Acknowledgements

This work was financially supported by the National Science Foundation of China (NSFC, Grant 21473016, 21206017, 20603004, 20773019).

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