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Template-free synthesis of cost-efficient nano-sized titanium silicalite-1

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Highlights

- Novel cost-efficient nano-TS-1 (UTS-1) was synthesized by template-free method.
- As-synthesized Silicalite-1 (S-1) rather than calcined S-1 was employed as the seed.
- Only uncalcined S-1 seed rather than calcined S-1 seed could successfully achieve TS-1.
- TPA^+ occluded in the micropores helps incorporate tetra-coordinated Ti into framework.

1. Introduction

Titanium silicalite-1 (TS-1) with unique micropores of ca. 0.5nm has been extensively studied as promising industrial catalysts for selective epoxidation reactions. Earlier work on the synthesis of TS-1 normally used expensive tetrapropylammonium cation (TPA) template for the formation of the zeolite structural sub-units, which hinders the industrialization process. Herein, we report a cost-efficient and energy-saving approach to synthesize novel TS-1(UTS-1) in the absence of expensive TPA templates, in which uncalcined Silicalite-1 (S-1) seeds play similar roles of the templates. Notably, calcined S-1 seed and calcined S-1 seed with small amount of TPAOH template lead to formation of slicalite-1 and TS-1 with poor titanium species, respectively. Only uncalcined S-1 seed with tiny amount of the residuary TPA template occluded inside the micropores results in perfect TS-1 with isolated titanium species. The effect of uncalcined S-1 seeds on the physico-chemical properties of TS-1 is further investigated. The results provided in this work are of referential importance to the design of highly efficient and environmental friendly TS-1 catalysts.

2. Methods

TS-1 was synthesized by using colloidal silica and tetrabutyl titanate as silicon and titanium source, respectively. N-butylamine was used as the base to regulate the basicity of the gel. Uncalcined S-1 zeolite or calcined S-1 zeolite was used as crystal seeds in the synthesis of TS-1. Traditional TS-1 and TS-1 samples using uncalcined S-1 zeolite and calcined S-1 zeolite as seeds are denoted as TS-1-0, UTS-1 and CTS-1, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns, FT-IR spectra and UV-vis spectra of UTS-1, CTS-1 and TS-1-0 samples. The results indicate that besides conventional TS-1, only UTS-1 which using uncalcined S-1 zeolite as seeds shows framework isolated titanium species (tetracoordinated Ti). This result is also confirmed by elemental analyses (ICP), which shows that the framework n(Si/Ti) of UTS-1 and CTS-1 are 35 and 200, respectively, when the Si and Ti compositions during the synthesis are the same. Moreover, together with TEM-Mapping, N_2 physisorption and TG characterizations found that uncalcined seeds with the residuary TPA^+ occluded in the microporous channels plays the indispensable role in incorporating tetra-coordinated titanium into the framework. And the schematic diagram of crystallization process is shown in fig. 2.

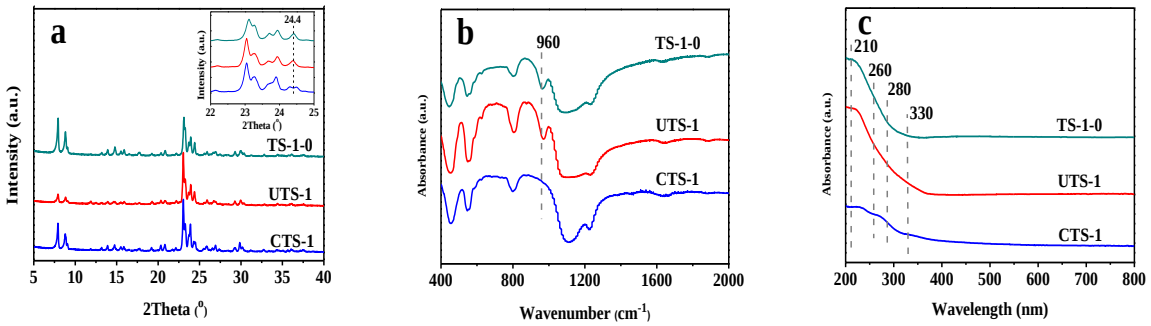

Figure 1. XRD (a), FT-IR spectra (b) and UV-vis spectra (c) of UTS-1, CTS-1 and TS-1-0 samples .

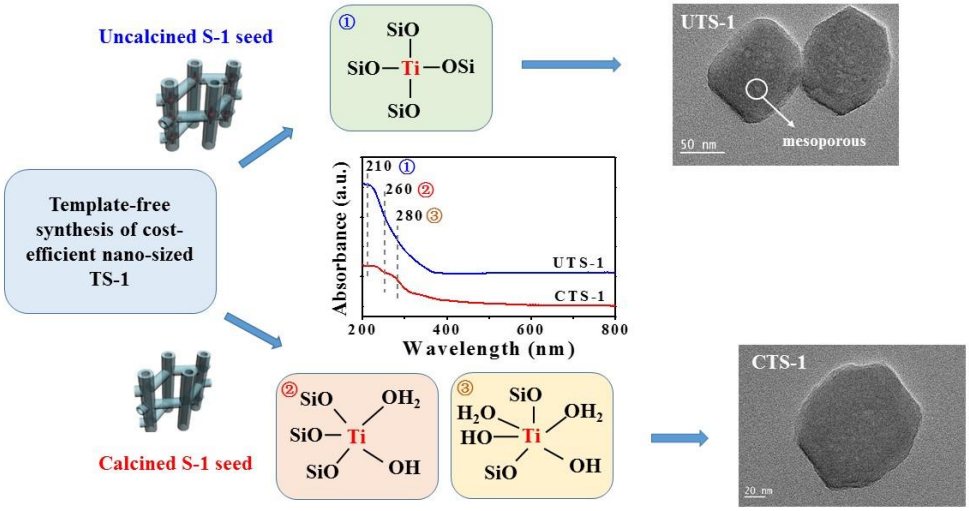

Figure 2. Schematic diagram of crystallization process

4. Conclusions

In conclusion, TS-1 sample with high relative crystallinity have been synthesized using uncalcined S-1 seed in an organic templates free hydrothermal system. The crystal size of UTS-1 sample obtained by using uncalcined nanosized S-1 seed (100 nm) is significantly smaller than that of the conventional TS-1(300 nm). The uncalcined S-1 seed plays a structure directing role in place of an organic template, enhancing the nucleation and formation of small crystal TS-1 zeolite. Interestingly, uncalcined S-1 seed is better than calcined S-1 seed in promoting isolated tetracoordinated Ti species incorporate into the MFI framework. The detailed reason is further investigated by multi-techniques such as UV-vis, FT-IR, N_2 physisorption, AAS, TGA, etc. This work not only significantly reduces consumption of the synthetic cost to produce high-performance TS-1 but also elucidates the unique role of uncalcined S-1 seed. The novel UTS-1 support is promising for industrial application.

References

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Keywords
TS-1; template-free; cost-efficient.