Colloidal suspensions of template-removed zeolite nanocrystals†

Huanting Wang, Zhengbao Wang and Yushan Yan*

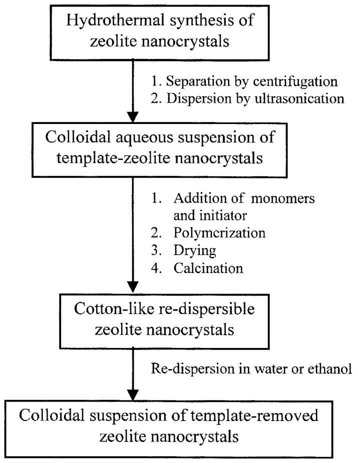
Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA.
E-mail: yushan.yan@ucr.edu

Received (in Irvine, CA, USA) 1st August 2000, Accepted 13th October 2000
First published as an Advance Article on the web 10th November 2000

Colloidal suspensions of template-removed zeolite nanocrystals were prepared by using an organic polymer network as a temporary barrier during calcination to prevent zeolite nanocrystal aggregation.

There is considerable interest in the synthesis of colloidal zeolite nanocrystals because they can serve as model systems for the fundamental study of zeolite crystal growth.[1–5] Colloidal suspensions of zeolite nanocrystals have also been used to deposit seed layers for preparation of zeolite membranes.[6,7] Very recently, construction of hierarchically porous crystalline structures through templated self-assembly of colloidal zeolite nanocrystals has also been reported.[8,9] Colloidal suspensions of zeolite nanocrystals are usually synthesized *via* hydrothermal procedures using clear aqueous solutions.[1–9] In most of these syntheses, organic templates (or structure-directing agents) are used, and the colloidal crystals so obtained contain organic template in their void spaces. We are interested in using colloidal suspensions of organic-functionalized zeolite nanocrystals as building blocks to construct hierarchical porous inorganic–organic hybrid materials that have potential applications in separation, catalysis, and microelectronics.[10–13] For this purpose, suspensions of template-free nanocrystals are required. Thus far, the most commonly used method for template removal is through high temperature calcination in air or oxygen. This method, however, has proved unsuitable for colloidal nanocrystals because it leads to significant irreversible aggregation.[8,9]

Here we report a novel approach to prepare colloidal suspensions of template-free zeolite nanocrystals by using an organic polymer network as a temporary barrier to isolate as-synthesized nanocrystals during template removal. Scheme 1 shows a flowchart of the preparation process. This approach appears general for all zeolites, however, only the preparation of a colloidal suspensions of template-free silicalite nanocrystals is reported here as an example. To the best of our knowledge, this is the first report on colloidal suspensions of calcined zeolite nanocrystals.



Scheme 1 Preparation protocol for colloidal suspensions of template removed zeolite nanocrystals.

An aqueous colloidal suspension of template-containing silicalite nanocrystals was synthesized as follows.[8] A clear synthesis solution was prepared by dropwise addition of tetrapropylammonium hydroxide solution (TPAOH, Aldrich) into tetraethyl orthosilicate (TEOS, Aldrich) with strong agitation followed by 1–3 days of aging at 30 °C under stirring. The final solution molar composition was 1 TPAOH : 2.8 SiO_2 : 11.2 EtOH : 40 H_2O. Crystallization was carried out at 80 °C for 3 days with constant stirring at 250 rpm. A stable aqueous suspension of silicalite nanocrystals was obtained by repeated cycles of centrifugation at 15 000 rpm, decanting, and ultrasonic redispersion in pure water until pH < 8. Other dispersants such as ethanol could also be used if desired.

The water soluble organic monomers acrylamide $CH_2{=}CHCONH_2$ (AM, Aldrich), and *N*,*N*′-methylenebisacrylamide, $(CH_2{=}CHCONH_2)_2CH_2$ (MBAM, Aldrich), and the initiator $(NH_4)_2S_2O_8$ (Aldrich) were used to prepare the polymer network. Typically, 1.0 g AM, 0.1 mg MBAM and 25 mg $(NH_4)_2S_2O_8$ were added under stirring into 10 g of a silicalite colloidal suspension with 5 wt% solid loading. After the monomers were dissolved, the mixture was ultrasonicated for 15 min to ensure complete dispersion of the silicalite nanocrystals. The aqueous solution containing the monomers has a fairly low viscosity and could readily be polymerized and crosslinked *via* a free-radical mechanism into an elastic hydrogel once the temperature was increased to 50 °C or a catalyst [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED)] was added at room temperature.[14] Polyacrylamide hydrogels have been commonly used as binders in ceramic forming processes[14] and are expected to be compatible with silicalite nanocrystals whose surface silanol groups interact favorably with $-NH_2$ groups. The solid polymer–silicalite composite was dried at 80–100 °C overnight before it was carbonized under nitrogen at 550 °C for 2 h (heating rate 2 °C min^{-1}) and then calcined at 550 °C for 3 h under air (Scheme 1).

TGA was used to monitor the thermal decomposition of dried polymer–silicalite composite under N_2 and air (ESI†). Under N_2 a weight loss of *ca*. 18% was recorded between room temperature and 280 °C, due to desorption of water and TPAOH. A weight loss of *ca*. 42% occurred between 280 and 600 °C as a result of decomposition of occluded TPA and carbonization of the polymer network. Based on a theoretical value of 11.7% weight loss for TPA decomposition (four TPA^+ cations per silicalite unit cell),[9] the weight loss during carbonization was estimated to be 28 wt%. The residual silicalite was 16 wt% after heating under air at 550 °C which removes carbon completely, and thus the carbon is calculated to be 24 wt%. TG analysis of a sample without incorporation of the polymer network shows that template TPAOH can be removed completely through this procedure.

Fig. 1 shows SEM images of silicalite nanocrystals after direct drying and calcination in the absence of a polymer network barrier. Clearly, direct drying of an as-synthesized silicalite suspension by evaporation leads to densely packed crystals [Fig. 1(a)], which upon calcination aggregate irreversi-

---

† Electronic supplementary information (ESI) available: Suppl. Figs. 1–3: TGA curves, XRD patterns and IR spectra. See http://www.rsc.org/suppdata/cc/b0/b006518h/

DOI: 10.1039/b006518h

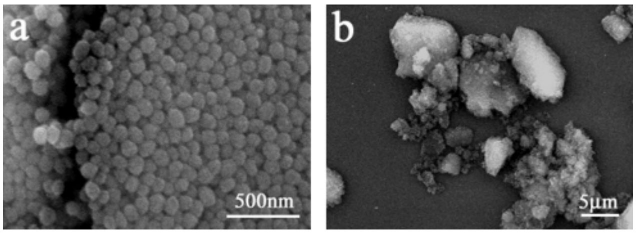


Fig. 1 SEM images of silicalite nanocrystals prepared without polymer network barrier: (a) after drying, (b) after calcination.

bly into large solid particles and grinding using a mortar and pestle for 2 h did not appear to improve its re-dispersibility. These particles cannot be re-dispersed into a suspension, and precipitated quickly after mild shaking [Fig. 1(b)].

The aggregation of zeolite nanocrystals is a result of condensation reactions between surface silanol groups of zeolite nanocrystals.[8,9] For condensation reactions to occur, close packing of the nanocrystals is required [Fig. 1(a)].[8,9] The function of the polymer network used here is to keep the nanocrystals separated during carbonization and calcination. Fig. 2 shows SEM images of the composite after drying, carbonization and calcination. After drying, the silicalite nanocrystals are uniformly distributed and well separated in the polymer network [Fig. 2(a)]. Carbonization at 550 °C generated large voids in the composite owing to production of gaseous products [Fig. 2(b)].[15] SEM examination of the carbon skeleton shows that zeolite nanocrystals are uniformly distributed and well separated within the carbon matrix [Fig. 2(c)]. Final calcination removes the carbon barrier and leads to a loose cotton-like white powder [Fig. 2(d)]. We have carried out extensive SEM studies on suspensions with various solid loading and aging times (*e.g.*, 3–4 months) by dip-coating the nanocrystals onto silicon wafers. The substrate withdrawal rate was 1 cm s^{-1} and clean-room-grade wafers were cut into 2 × 2 cm square pieces and used without further cleaning. Our SEM results suggest that the calcined nanocrystal powders can be easily dispersed in water and many other dispersants such as ethanol to form stable suspensions. Uniform films can be formed using suspensions of template-removed silicalite nanocrystals with an appropriate solid loading, and this indicates that the processed nanocrystals have good film-forming properties. Fig. 2(e) shows an example of such a film (*ca*. 0.3 μm thick).

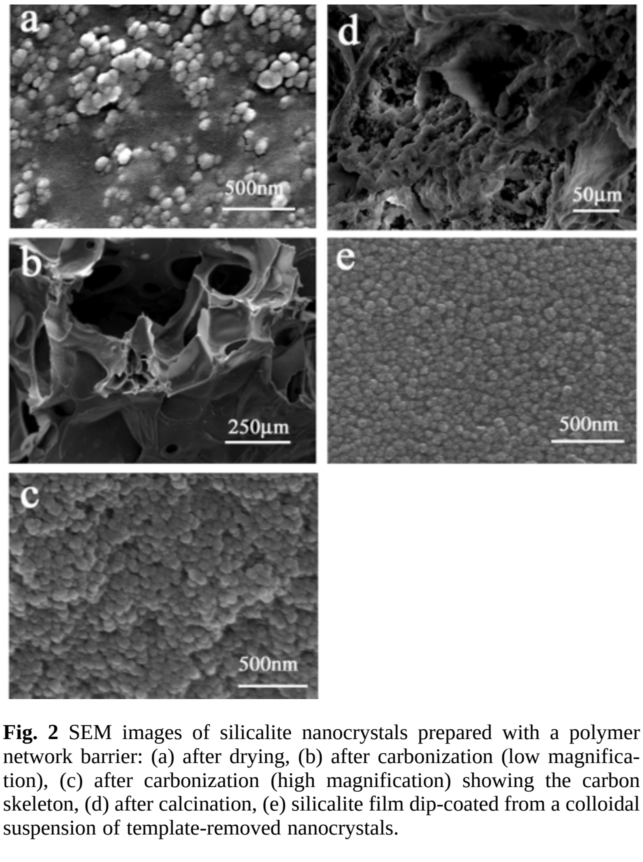


Fig. 2 SEM images of silicalite nanocrystals prepared with a polymer network barrier: (a) after drying, (b) after carbonization (low magnification), (c) after carbonization (high magnification) showing the carbon skeleton, (d) after calcination, (e) silicalite film dip-coated from a colloidal suspension of template-removed nanocrystals.

The powder X-ray diffraction (PXRD) pattern of a re-dispersible white powder sample matches that of a typical 100% crystalline nanoslicalite sample (ESI†).[8,9] FTIR spectra show the nanopowder has an MFI type structure (band at 550 cm^{-1}, with *ca*. 97% crystallinity) and a high concentration of terminal Si–OH groups (band at 972 cm^{-1}) (ESI†).[8,9] N_2 adsorption measurements show that the BET surface area and pore volume for the cotton-like sample are 355 $m^2\ g^{-1}$ and 0.18 $cm^3\ g^{-1}$, respectively. These data show that the polymerization, carbonization and calcination processing has no influence on crystallinity and porosity of the nanocrystals.

The weight ratio of polymer to nanocrystals appears important in determining the re-dispersibiltiy of the nanocrystals. We have examined several polymer/zeolite weight ratios and a ratio around 2.0 sufficiently separates nanocrystals. It is recognized that the nanocrystals do move closer and may even contact one another during the final burn-off of carbon. SEM images clearly show that the contact areas among nanocrystals are rather small within the cotton-like nanopowder. It is also possible that during the early stage of calcination some reactive silanol groups on isolated (by carbon) nanocrystals condensed among themselves, and this in turn should reduce the amount of surface silanol groups and the probability of aggregation.

In conclusion, we have demonstrated that colloidal suspensions of template-free zeolite nanocrystals can be prepared by using an organic polymer network as a temporary barrier to avoid nanocrystal aggregation during calcination. Work is under way on organic functionalization of zeolite nanocrystals and construction of hierarchical inorganic–organic hybrid materials using zeolite nanocrystals as building blocks. It is noted here that this approach is not zeolite specific, and thus could become a general strategy for retrieving various nanoparticles from synthetic solutions without aggregation.

This work is partly supported by CE-CERT of UC-Riverside, UC-SMART, UC-TSR&TP, UC-EI, and a UC Regents Faculty Fellowship to Y. Y. We thank Dr. Re Lai and Mr. Piboon Pantu of Caltech for N_2 adsorption measurements.

Notes and references

1 S. Mintova, N. H. Olson, V. Valtechev and T. Bein, *Science*, 1999, **283**, 958.
2 B. J. Schoeman, J. Sterte and J. E. Otterstedt, *Zeolites*, 1994, **14**, 110.
3 G. S. Zhu, S. L. Qiu, J. H. Yu, Y. Sakamoto, F. S. Xiao, R. R. Xu and O. Terasaki, *Chem. Mater.*, 1998, **10**, 1483.
4 M. A. Camblor, A. Mifsud and J. Perez-Pariente, *Zeolites*, 1991, **11**, 792.
5 N. B. Castagnola and P. K. Dutta, *J. Phys. Chem. B*, 1998, **102**, 1696.
6 L. C. Boudreau, J. A. Kuck and M. Tsapatsis, *J. Membr. Sci.*, 1999, **152**, 41.
7 M. C. Lovallo and M. Tsapatsis, *AIChE J.*, 1996, **42**, 3020.
8 L. M. Huang, Z. B. Wang, J. Y. Sun, L. Miao, Q. Z. Li, Y. Yan and D. Y. Zhao, *J. Am. Chem. Soc.*, 2000, **122**, 3530.
9 B. J. Zhao, S. A. Davis, N. H. Mendelson and S. Mann, *Chem. Commun.*, 2000, 781.
10 M. J. MacLachlan, I. Manners and G. A. Ozin, *Adv. Mater.*, 2000, **12**, 675.
11 M. H. Lim, C. F. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467.
12 C. J. Jones, K. Tsuji and M. E. Davis, *Nature*, 1998, **393**, 52.
13 T. Asefa, M. J. MacLachlan, N. Coombs and G. A. Ozin, *Nature*, 1999, **402**, 867.
14 H. T. Wang, X. Q. Liu and G. Y. Meng, *Mater. Res. Bull.*, 1997, **32**, 1705.
15 Y. Yan, M. E. Davis and G. R. Gavalas, *J. Membr. Sci.*, 1997, **126**, 53.