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Synthesis of KIT-6 type mesoporous silicas with tunable pore sizes, wall thickness and particle sizes via the partitioned cooperative self-assembly process

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ABSTRACT

With bi-continuous cubic mesostructures of *Ia3d* symmetry and interpenetrating cylindrical pore system, KIT-6 type mesoporous silica has attracted a great deal of interest for its application in various areas. Unfortunately, so far the reports on the tuning of mesostructures or other physical properties are rather limited due to the restrictions on synthetic conditions. In this work, one previously reported partitioned cooperative self-assembly (PCSA) process was applied for the synthesis of KIT-6s with good meso-orderings, allowing facile manipulation over mesostructures, e.g. the mesopore size, pore wall thickness and particle sizes. By simply partitioning the addition of tetraethoxysilane (TEOS), the mesopore sizes of KIT-6s can be varied between around 8 and 10 nm (KJS). For a given addition combination (1st part of 7.0 g and 2nd part of 3.0 g in total 10.0 g TEOS), the meso-orderings show some improvement with the increase in the interval time from 1 to 5 h. In combination with hydrothermal treatment at high temperatures (e.g. 140 °C), the PCSA process, though not yielding larger mesopore sizes, favors the formation of KIT-6 with higher meso-orderings than that of conventional method derived KIT-6. Moreover, the particle sizes of KIT-6s can be significantly reduced from sub-millimeter to several microns via the PCSA process. The PCSA process thus represents a simple but effective way to manipulate the mesostructures and particle sizes of KIT-6s.

1. Introduction

Ordered mesoporous silicas, since their discovery in 1990s [1], have drawn enormous attention due to their ordered mesopore arrangement at mesoscopic scale, high surface area and mesopore volume. As shown in many reviews [2–10], in order to better suit versatile demands in various application, to controllably engineer the mesoporous structures and particle morphologies and so on is the research target of materials scientists in this area. Among the mesoporous silicas developed so far, KIT-6 possesses a bicontinuous cubic structure of *Ia3d* symmetry and interpenetrating cylindrical pore system [11,12], similar to those observed in the MCM-48 structure [13] but with larger mesopores. Such unique 3-D channel network is thought to be able to provide a highly opened porous host with easy and direct access for guest species, thus facilitating the inclusion or diffusion throughout the pore channels with mitigated pore blockage. In many works, KIT-6 has been studied for various application as catalyst supports [14,15], nano-containers [16,17] and ideal nanocasting template for non-silica mesoporous materials, including mesoporous carbons [18–20], metal [21], metal oxides [22–28] and ceramics [29].

In the typical synthesis of KIT-6 under moderately acidic conditions, Pluronic surfactant P123 and n-butanol were used as template and co-surfactant, respectively [11,12]. As a result, mesopore sizes in the range of 7–9 nm were normally obtained by varying the synthetic compositions or conditions, while larger pore sizes up to 12 nm can only be achieved with hydrothermal treatment at temperature as high as 130 °C in the synthesis [11,12]. So far, the reports on the tuning of mesostructures and other physical properties of the KIT-6 are extremely limited [30], largely because the synthesis process of KIT-6 needs to be strictly controlled to guarantee the formation of *Ia3d*-type cubic mesostructures rather than *p6 mm* (e.g. SBA-15) or mixed mesophases of *Ia3d* & *p6mm* [12]. As reported, at a fixed amount of TEOS, increasing the amount of butanol results in a transition from a

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p6mm to *Ia3d* cubic mesophase and then to a distorted phase eventually. In addition, at fixed butanol and TEOS concentrations, an increase in the acid amount leads to a transition from cubic to hexagonal phase [12]. Apparently, the *Ia3d* cubic phase only forms at a certain range of butanol concentration and a certain low acid concentration as well, relative to the amount of TEOS. Therefore, there is no much room left for alterations to the TEOS/P123/butanol/HCl(aq.) quaternary templating system to tune the mesostructures or particle morphologies of KIT-6s without compromising the *Ia3d* mesostructures.

As demonstrated by Ruthstein et al. [31], in the formation of *Ia3d* cubic mesophase, butanol molecules interpenetrated in the P123 micelles and their migration from the corona/PPO-core interfaces to water/corona interfaces decrease the hydrophilic volumes (V_H) relative to the hydrophobic volumes (V_L) and therefore induce the transformation of the mesostructures from *p6mm* symmetry to *Ia3d* cubic mesophase. Interestingly, in our recently reported works on the SBA-15 with hexagonal mesophases, the hydrophilic volume can actually be varied by a so-called partitioned cooperative self-assembly (PCSA) process, which enables the tuning of the mesopore sizes and other mesostructural properties [32], so do for the SBA-15s with plugs or constrictions in the mesochannels [33]. In such PCSA process, the addition of silica precursor was partitioned into two parts, with the 2nd part added some interval time after the 1st one, while the other synthesis procedures were actually the same as those for the conventional synthesis procedure. Such 'simple' modification to the synthesis procedure conveyed interesting mesostructural and morphological features to the resultant SBA-15 products [32,33]. Here comes the question: in view of the synthesis of KIT-6, whether or not the structures can be manipulated based on the same strategy via the PCSA process by tuning the V_H?

Herein, the syntheses of KIT-6 type mesoporous silica are conducted via the previously reported PCSA process, including the detailed study on the synthetic parameters, e.g. the interval time, addition combinations and hydrothermal temperatures. Various characterization techniques were employed to examine the mesostructures and particle morphologies. As will be demonstrated, KIT-6s with tunable pore sizes, wall thickness and particle sizes can be obtained via the PCSA process in a much simple and direct way. The PCSA process is therefore believed to open a new pathway to the facile tuning of the KIT-6 structures.

2. Experimental

2.1. Materials

The concentrated HCl (37 wt%, denoted as conc. HCl), n-butanol and tetraethoxysilane (TEOS, AR) were purchased from the Sinopharm Chemical Reagent Co., Ltd. Pluronic PEO_{20}–PPO_{70}–PEO_{20} (P123 with Mw = 5800) was purchased from Aldrich. All the chemicals were used as received.

2.2. Preparation of KIT-6 via the PCSA process

Typically: 4.65 g P123 was dissolved in 167.4 g doubly deionized (DI, conductivity ~1 μS/cm) water and 9.2 g conc. HCl under stirring (800 rpm) at 35 °C to form a clear solution, into which 4.65 g n-butanol was added. After stirring for 1 h, 2.0 g TEOS (1st part) was dropped into above synthesis mixture. After an interval time of 1 h, the rest of 8.0 g TEOS (2nd part) was then added in the same way. Upon the completion of addition of TEOS, the mixture was stirred at the same speed for 24 h at 35 °C and then transferred to an autoclave for hydrothermal treatment (HTT) at 100 °C for another 24 h statically. The molar composition of the synthesis mixture of TEOS:P123:HCl:H_2O:n-BuOH equals 1:0.017:1.93:195:1.31. The white product was collected by filtration, washing (Though often omitted in preparations of KIT-6s [11,12], washing step that was applied in this work to eliminate residue HCl to avoid corrosion to equipment was found not to prevent the formation of *Ia3d* mesostructures) and then drying at 50 °C overnight, followed by calcinations at 550 °C for 4 h with the heating ramp of 1.5 °C/min in a chamber muffle furnace in open air. The samples after calcination were kept in sealed plastic bags in a desiccator. The final calcined sample was designated as 2-1 h-8, where the numbers of '2' and '8' stand for the masses/mass ratios of TEOS added in the 1st and 2nd part, respectively, '1 h' denotes for the interval time. Unless indicated otherwise, the HTT temperature was always 100 °C. Other KIT-6s, e.g. 7-1h-3, prepared with HTT at 140 °C is denoted as 7-1h-3@140. Other namings can be deduced by analogy.

2.3. Conventional synthesis of KIT-6s

As a control, KIT-6 was also synthesized via conventional method using TEOS as precursor. Typically, 10.0 g TEOS was continuously added to the acidified P123 solution at 35 °C as described above. The stirring time is 24 h before being transferred to an autoclave for HTT. The following steps are the same as those for the PCSA process using TEOS as silica precursor. The sample is denoted as 10-0.

2.4. Characterization

All the low-angle powder XRD patterns at 2θ angles from 0.6° to 3° were recorded at an interval of 0.01° on a Bruker D8 diffractometer using Cu Kr radiation (40 kV, 120 mA). Low-angle diffraction peaks were used to determine the d-spacings according to the normal Bragg relationship. The unit cell parameter (a) for the *Ia3d* cubic mesophase is calculated from $d(211)$, where $d(211)$ is obtained from the 2θ value of the main peak in the XRD pattern from $d(100) = \lambda/(2\sin(\theta))$, where $\lambda = 0.15417$ nm for the Cu Ka line. Transmission electron microscopy was performed using a FEI Tecnai G2 F20 instrument operated at 200 kV. The samples were prepared by dispersing a small amount of powders in ethanol and placing drops of the suspension on carbon-coated copper grid, followed by evaporation. FE-SEM images were recorded using Field-emission Scanning Electron Microscope (Hitachi S4800).

Nitrogen adsorption isotherms were measured at -196 °C using Tristar 3020 volumetric adsorption analyzers manufactured by Micromeritics (Norcross, GA). Before adsorption measurements, the samples were out-gassed under vacuum for at least two hours at 200 °C. The specific surface area of the samples was calculated using the BET method within the relative pressure range of 0.04–0.2. The pore size distributions were determined using the BJH method calibrated for cylindrical pores according to the KJS method [34]. The mesopore size distributions (PSDs) were calculated on the basis of adsorption branches of nitrogen isotherms. The primary mesopore size, w_{KJS}, was defined as a maximum on the PSDs. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.995. The primary mesopore volume, V_p, and micropore volume, V_{mi}, were respectively evaluated using the α_s-plot method with the relationship of α_s with relative pressure p/p^0 defined by the equation: $\alpha_s = 0.1385(60.65/(0.03071\text{-}\ln(p/p^0)))$^0.3968 [Refs. 34,35]. The V_{mi} was calculated using the standard reduced adsorption, α_s, interval from about 0.8 to 1.2 and from about 1.8 to 2.2 for the calculation of V_{mi+me}. The primary mesopore volume (V_p) was estimated as a difference between V_{mi+me} and the V_{mi}.