

Process Factors on Sol-Gel Synthesis of Ti-Doped Mesoporous Silica

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SiO₂-TiO₂ mesoporous materials were synthesized from tetraethylorthosilicate (TEOS) and tetraethylorthotitanate (TEOT) by a sol-gel method using the self-assembly of stearyltrimethylammonium chloride (C₁₈TAC) under acidic condition of pH=2 (HCl). To obtain a SiO₂-TiO₂ product with controllable mesoporous properties, the present work was focused on the process factors. In the beginning, one-step (TEOS and TEOT were added together) and two-step process (TEOT was added after TEOS had been pre-hydrolyzed for a certain time) were compared. Products synthesized by either process possessed large specific surface area above 1000m²/g. However, the one by the two-step showed two times higher acidity than the one by the other, which was due to inhomogeneity of Ti-loading. Further investigation of the two-step process revealed that the pore sizes were enlarged by the increase of H₂O-quantity, while narrowed by the increase of Ti-quantity. Acidity was controlled by Ti-quantity. Its maximum value appeared at TiO₂/SiO₂ was 0.02:1 in mol. Surfactant was removed by calcination rather than acidic extraction.

Key word: sol-gel, process factors, mesoporous materials, acidity, surfactant

1. INTRODUCTION

Although silica-based mesoporous materials by the cooperative assembly of organic surfactant have been studied, the focus was mainly put on the selection of organic "template"^[1,2]. However, many interdependent factors are involved beginning with precursors to the final surfactant-removal stage, such as the precursors used, the temperature, the solvents effect, the pH condition and the relative concentration of different materials in the solution etc. So, much work still exists on the preparation of materials with controllable properties using sol-gel process. The aim of this work is to give a comprehensive overview of a better-controlled synthesis. Present work focused on reaction factors under acidic condition upon the mesostructured adsorptive properties and acidity, a detailed description of the Ti-doped mesoporous silica materials synthesized with self-assembly of stearyltrimethylammonium chloride (C₁₈TAC) as template has been given.

2. EXPERIMENT

Precursors were Si(OC₂H₅)₄(TEOS) and Ti(OC₂H₅)₄ (TEOT). C_nH_{2n+1}(CH₃)₃NCl (C_nTAC, n=18) was used as

a surfactant. The solution was adjusted at pH=2 with HCl. Composition of the solution was mainly set at TEOS: TEOT: H₂O: C_nTAC =1: 0.01: 20: 0.2 in mol and synthesis temperature was kept at 50°C through the process.

1) One-step hydrolysis

Surfactant was firstly dissolved in H₂O (pH2, HCl) and stirred for 30min, then TEOS and TEOT diluted with ethanol was added together into the solution. The white precipitation formed instaneously if TEOT was added directly. In the preliminary study, we found when TEOT was added after diluted with ethanol to above 20 times, no precipitation but light-yellow translucent solution appeared. So, TEOT was diluted before added into the solution to postpone its fast hydrolysis ratio.

2) Two-step hydrolysis

After TEOS was partially hydrolyzed by distilled H₂O (pH2, HCl) for 30 min, C₁₈TAC was dissolved directly into the solution. Then TEOT diluted with ethanol was added.

After gelation, all samples were calcined in air at 600 °C to remove the structurally incorporated surfactant template except the gels for the study of other

extract method. Pure SiO_2 and TiO_2 were also synthesized under the same conditions for comparison.

The specific surface area and average pore size of calcined gels were determined by BET method of nitrogen adsorption isotherm using ASAP-2000. Plots of the derivative of the pore volume per unit weight with respect to the pore diameter (dV/dD) were used to show the pore distribution. And desorption branch is often used for the assessment of the distribution of pore sizes. The acidity of calcined gels was measured by the amine titration in benzene using *p*-dimethylaminoazobenzene ($\text{pK}_a=+3.3$) as an indicator, and acidic strength of products was determined using the following indicators: methyl red ($\text{pK}_a=+4.8$), *p*-dimethylaminoazobenzene (+3.3), benzeneazodiph-enylamine (+1.5), dicinnama-acetone (-3), benzalacetophenone (-5.6) and anthraquinone (-8.2), respectively. SEM-EDX (scanning electron microscope-energy dispersive X-ray spectroscopy) was used to give the information on the surface portion while XFD-EDX (X-ray fluorescence-energy dispersive X-ray spectroscopy) was used to give averaged information from the samples, since the difference in the penetration abilities of the electron beam (25kV) and X-ray (Rh-target, 50kV).

3. RESULTS AND DISCUSSION

3.1 One-step hydrolysis and two-step hydrolysis

In the sol-gel process, heteocondensation is possible when two kind of precursors are hydrolyzed, which results in chemical modification, resulting in M-O-M' bond formation^[3]. In the present work, the comparison of one-step and two-step hydrolysis process was performed. Results of the surface property were shown in Table I and pore distributions were shown in Figure 1. Products synthesized by either process possessed large specific surface area above $1000\text{m}^2/\text{g}$ with pore sizes on meso-scale, two-step one showed a larger pore size. In addition, a narrow and sharp pore distribution showed in Fig.1 suggests the mesopores are uniform. The appearance of two peaks in one-step hydrolysis curve suggests inhomogeneous distribution of pore size, which is caused by more reactive of TEOT than TEOS with about five orders of magnitude difference in the hydrolysis rate.

The acidities of products were also summarized in Table I. It is well known that both single oxides, SiO_2 and TiO_2 , possess little acidity. Here, addition of TiO_2 into the SiO_2 structure greatly increased surface acidity. The acidity of $\text{SiO}_2\text{-TiO}_2$ products by both processes was much larger than the sum of two single oxides (acidity of SiO_2 was of 4.5mmol/g and one of TiO_2 cannot be measured using this indicator due to its poor acidity.), which is considered being due to new acidity point provided by the formation of Si-O-Ti phase. In addition, the two-step product showed almost 3 times higher

acidity than the one by one-step process. From the comparison of two processes, the two-step hydrolysis will be employed to further investigating other factors. In addition, since no significant effect was shown when prehydrolysis time was changed during 30–100 min in our work, organic species C_{18}TAC will be added after TEOS was prehydrolysis for 30min.

Table I The surface properties with respect to two processes

	S_{BET} (m^2/g)	d_{BET} (nm)	Acidity (mmol/g)	Acidity/ S_{BET} ($\times 10^{-2}$)
one step	1203	2.6	8.1	0.66
two-step	1356	3.4	22.4	1.65

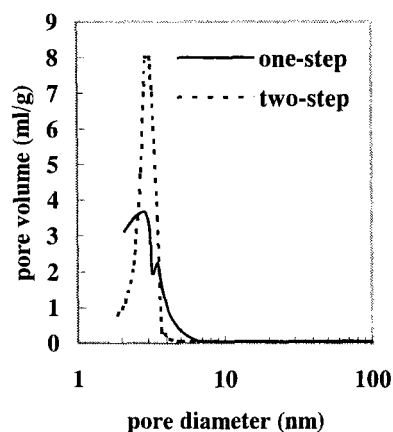


Fig.1 The pore distribution with respect to two processes

3.2 The effect of solvent and temperature:

In general, solvent (such as ethanol) is added to prevent liquid-liquid phase separation during the initial stages of the hydrolysis reaction. However, it should be noted that ethanol, which can be produced as by-product of the hydrolysis reaction, and which was added to dilute TEOT, also can alcoholize formed M-O-M (or M-O-M') bond, which is unfavorable to accomplishment of gel. So produced ethanol must be gradually removed by evaporation. The most notable influence as to temperature was reflected by reaction time. Gelation time shortened with increasing temperature, that is 18h at room temperature, 6h at 50°C (water bath), and even 3h at 110°C (silicon oil bath). The decreasing reaction time with increasing reaction temperature is caused by faster evaporation of solvents. Moderately higher temperature will promote the evaporation, however, unduly fast evaporation caused

uncompleted hydrolysis resulting in inhomogeneity. For all products to be described below, temperature was kept at 50°C all through the gelation.

3.3 The effect of surfactant quantity

The preparation of mesostructured materials from cooperative organization of inorganic species and surfactants is a current topic. In this new pathway, an effective “template” is one of important factor. To study the effect of surfactant quantity, s in TEOS : C₁₈TAC = 1 : s was changed as 0.1, 0.2 and 0.5 in mol. Products without surfactant was also synthesized. The porous properties of products were shown in Table II.

Table II The surface properties as a function of quantity of surfactant

s	S_{BET} (m^2/g)	d_{BET} (nm)	Acidity (mmol/g)	Acidity/ S_{BET} ($\times 10^{-2}$)
no surfactant	329	1.4	---	---
0.1	929	2.3	15.76	1.69
0.2	1356	3.4	22.4	1.65
0.5	1350	3.3	25.64	1.89

Comparing to product without surfactant, “template” functionally increases the surface area as 3–4 times as much and enlarges the pore sizes from micropore to mesopore range. In addition, similar surface area and pore size were shown when $s > 0.2$, which suggested $s = 0.2$ is enough to the process. On the other hand, although the acidity is various, the ratios of acidities to specific surface area were similar, which suggests that the amount of acidic point per unit surface area is similar, which also means that the similar Ti-O-Si state in products. So, although surfactant can functionally increased the surface area and pore size, the increasing quantity cannot change the formation of Ti-O-Si phase.

3.4 The effect of H₂O

The hydrolysis reaction was performed with TEOS : H₂O (pH2, HCl) = 1 : r , where $r = 2, 5, 10$ and 20 in mole. The BET results were listed in Table III, and the isotherm plots were illustrated in Fig.2. Products with $r = 2 \sim 20$ possessed large specific surface area above 1000 m^2/g . With increase of r , the average pore size increased from 1.8nm to 3.4nm, and the isotherm plot also change from type I, characteristic of a microporous solid ($r = 2$ and 5) according to IUPAC classification^[6], to type IV, typical of mesoporous solids.

It is known that the stoichiometric amount of water for hydrolysis is 2 moles if condensation goes to completion according to the schematic reaction, however excess H₂O is necessary from the results. The excess H₂O

Table III The surface properties as a function of quantity of H₂O

r	S_{BET} (m^2/g)	d_{BET} (nm)	Acidity (mmol/g)	Acidity/ S_{BET} ($\times 10^{-2}$)
2	1585	1.8	25.33	1.6
5	1371	2.4	22.74	1.66
10	1160	3.1	19.14	1.65
20	1356	3.4	22.4	1.65

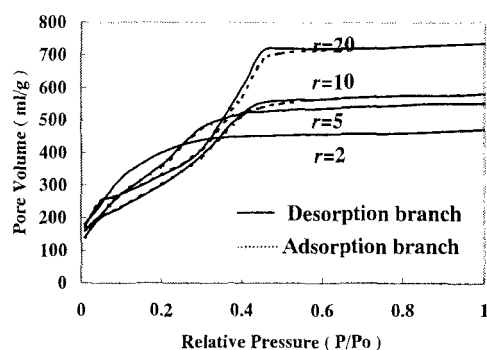


Fig.2 The isotherm plot as a function of quantity of H₂O

amount is considered linking with the dissolved surfactant state in the solution. Increasing H₂O amount is benefit the formation of micelle cooperated by both precursors and surfactant, subsequently results in larger pore size. In addition, the similar value of Acidity/ S_{BET} with respect to H₂O amount, which is consist with the results in section 3.1, also indicated that increasing H₂O amount only promoted the function of surfactant state employing as “template”, but not affect the Si-O-Ti state.

3.5 The effect of TEOT amount

The porous properties with different Ti/Si ratio were investigated through varying the amount of TEOT in solution. The molar ratio is set as TEOS: TEOT = 1 : x , $x = 0.01, 0.02, 0.1$ and 1, respectively. The BET results of products were shown in Table IV.

All were narrowed products possess larger surface area above 1000 m^2/g , while the pore sizes from 3.4 to 2.0nm by doped Ti phase. Acidic strength measured with indicators of different pK_a was summarized in Fig.3. Acidity increased initially with increasing Ti-quantity and at $x = 0.02$ the curves reached the maximum points. After maximum points, further increasing of Ti/Si ratio decreased the values of acidity. This trend indicated that acidity of products depended on x value, however, not

Table IV The BET results as a function of TEOT quantity

x	S_{BET} (m^2/g)	d_{BET} (nm)
0.01	1356	3.4
0.02	1130	3.1
0.1	1178	2.7
1	1096	2

the proportional one. Since Ti/Si in *mol.* both on the surface portion and in whole sample approximately equal to the nominal one determined by SEM-EDX and XFD-EDX, it is certain that all TEOT completely reacted. The acidity results suggests the surface acidity was enhanced in a certain range by the increasing number of acid points caused by new Si-O-Ti state, and a quantity limitation existed meanwhile, the reason is still not clear by now. In addition, the product with $x > 0.1$ showed weak acidity strength with $H_0 < -3.0$, while the ones synthesized with $x = 0.01$ and 0.02 showed the highest acidic strength above $H_0 > -5.6$ and even to $H_0 = -8.2$ (although acidity can not be calculated caused by difficulty of determining the end point of the titration from the acidic color (light yellow) to basic color (clear

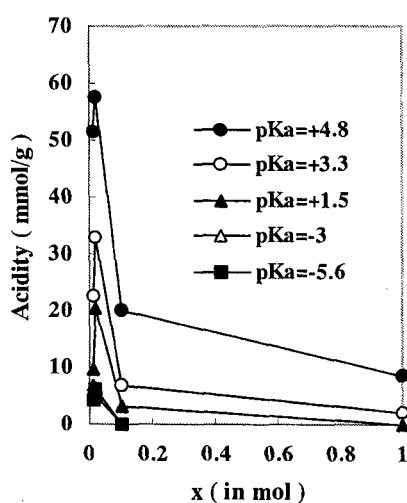


Fig.3 Acidic strength as a function of TEOT quantity

yellow).)

3.6 The extraction of organic surfactant "template"

In general, three kinds of method can be employed to

remove the surfactant, freeze-drying, acidic extraction and calcinations. However, freeze-drying does not permit the preparation of gels^[4]. In this work, the effects of acidic extraction and calcination were compared.

The acidic extraction technique to remove the surfactant from the as-synthesized materials was described as^[5]: extraction of the surfactant was performed by stirring the solid product with a 1M HCl solution in ethanol at 70 °C for about 30h. The solid-to-liquid ratio was 300ml/g. The extracted products was filtered, washed with ethanol and dried. Compared with acidic extraction method, the calcination is very simple that gels were calcined in air at 600°C. From the experiment, acidic extraction cannot completely remove the surfactant "template", that both specific surface area (748m²/g) and pore size (1.4nm) are lower than those (1356m²/g and 3.4nm, respectively) by calcination. On the other hand, using calcination to remove the organic surfactant is a very convenient.

4. SUMMARY

A two-step hydrolysis process was used to rectify the large difference in the hydrolysis rate between TEOS and TEOT. Above 1000m²/g surface area can be obtained using C₁₈TAC as "template". Moderately increasing quantity of H₂O can effectively promote the function of surfactant. The amount of TEOT can directly change the amount of Si-O-Ti state, resulting in varies of acidity and acidic strength. The maximum acidity appeared at TiO₂/SiO₂ was 0.02:1 in mol. The surfactant can be effectively removed by calcination.

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