Short Communication

An acid-free route for the facile synthesis of iron-functionalized mesoporous silicas: Transformation between hollow nanospheres and cage-like mesostructures

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ABSTRACT

Iron-substituted silicas with hollow nanospherical morphology and cage-like mesostructure have been synthesized using triblock copolymer F127 as surfactant and tetramethoxysilane (TMOS) as silica source with no necessary addition of mineral acids. Iron-functionalized hollow nanospheres were obtained using $\text{Fe}(\text{acac})_3$ as iron source. When $\text{Fe}(\text{NO}_3)_3$ was employed as iron source, iron-containing cage-like FDU-12 mesostructure and hollow nanospheres were formed with Fe/Si molar ratio lower than 0.008 and higher than 0.015, respectively. The formation of hollow spheres at high Fe/Si ratio can be regarded as gradually dissociation of nanocages from Fe-FDU-12. The structure of the iron centers was determined by spectroscopic methods (UV–vis and UV–Raman measurements) and by elemental analyses. The facile structural evolution between cage-like and nanospherical structures may be helpful for further understanding the formation mechanism of mesoporous silicas.

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1. Introduction

Mesoporous silicas have attracted much attention in last decades due to their wide applications in adsorption, catalysis, and drug delivery [1–4]. Metal-containing mesoporous silicas are of great interest because these functionalized silicas are extremely attractive as catalysts for acid–base, redox, and alkylation reactions [5–7]. One-pot hydrothermal synthesis is preferred for the preparation of metal-substituted mesoporous silicas in the presence of structure-directing agents under acidic [8], neutral [9], or basic [10] conditions.

For transition-metal substituted mesoporous silicas, it is apparent that the transition metal center and the porous structure both play important roles in obtaining desirable properties. Attributed to the development in the material science, the silicas with different morphology and mesostructure have been successfully synthesized [11,12]. However, only limited attention has been paid to the structure and morphology control of the transition-metal substituted mesoporous silicas, partly due to the unmatched conditions for the incorporation of transition metal ions and the formation of silicas with controlled morphology and mesostructure. For example, the nonionic-surfactants (such as P123, F127) have been

widely used as templates for the fabrication of mesostructured silicas normally in strongly acidic conditions [13]. However, the highly acidic media are not ideal for incorporation of transition-metal ions due to the high solubility of the Si–O–M species. The previous studies show that the mild reaction media may solve this problem [14–17], but the structural and morphological control of silicas in mild reaction medium is not well developed yet.

It is still a challenge to synthesize transition-metal functionalized mesoporous silicas with desirable active metal centers (such as highly isolated metal sites [18]) and architectures (such as spherical and cage-like pore structures). Among the silica fibers, spheres, rods and nanoparticles, the hollow nanospheres are very attractive, given that the hollow interior can encapsulate the guest molecules for wide application potentials [19–28]. The modification of the shell of the hollow nanospheres may further expand the application potentials of the hollow nanospheres [29–35]. The strategies for the synthesis of hollow silica-based nanospheres were already well reviewed [36,37], and can be categorized as: selective etching or dissolution, soft templating, self templating, galvanic replacement method, and Ostwald ripening method, etc. Based on the composition and structure, the obtained hollow nanospheres can be classified as pure siliceous nanospheres [38,39], phosphosilicate nanospheres [40], multi-shell silica nanospheres [32,41], organo-functionalized silica nanospheres [22,42], and yolk-shell nanoparticles [34,37], etc. Our group has developed an

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Fig. 1. TEM images of Fe-substituted hollow nanospheres: (a) NS-0.8 and (b) NS-1.5.

easy, convenient and efficient method for the green synthesis of hollow nanospheres in deionized water without any mineral acid addition [43]. The neutral synthesis medium may provide an opportunity for the effective incorporation of transition-metal ions in the shell of the hollow nanospheres.

To the best of our knowledge, the synthesis of transition metal ion-substituted hollow nanospheres *via* direct hydrothermal route has rarely been reported. In this study, based on our previous study [43], we report the facile synthesis of Fe-containing silica hollow nanospheres in acid-free neutral medium using F127 as the structure-directing agent. In addition, the evolution of hollow nanosphere to cage-like FDU-12 mesostructure was observed by simply varying the iron precursor and Fe/Si molar ratio.

2. Experimental sections

2.1. Reagents

All materials were of analytical grade and used as received without any further purification. Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) was purchased from Sigma–Aldrich Company Ltd. (USA). Tetramethoxysilane (TMOS), 1,3,5-trimethylbenzene (TMB), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{acac})_3$, and K_2SO_4 were obtained from Shanghai Chemical Reagent, Inc. of Chinese Medicine Group.

2.2. Synthesis

For the synthesis of Fe-substituted hollow nanospheres, F127 (1.00 g), TMB (1.00 g), and K_2SO_4 (3.49 g) were dissolved in water (60 mL), and the solution was stirred at 13.5 °C for 2 h. Desired amount of $\text{Fe}(\text{acac})_3$ dissolved in TMOS (3.04 g) was added to the above surfactant solution. After stirring at 13.5 °C for 24 h, the mixture was transferred into a Teflon-lined autoclave and aged at 100 °C for another 24 h. The precipitate was filtered off, rinsed repeatedly with water and dried at 100 °C. The as-synthesized sample was calcined in air at 550 °C for 10 h with a ramp of 1 °C min^{−1}. The calcined samples were denoted as NS-*n* (*n* = 0.8 or 1.5), where *n* is the mol% of Fe/Si in the initial mixture.

NO_3 -NS-*n* (*n* = 0.8, 1.5, and 2.3) samples were synthesized using a method similar to NS-*n* samples with slight variation. $\text{Fe}(\text{NO}_3)_3$ was used as iron source and the molar ratio of H_2O /F127 is 28000 (the H_2O /F127 molar ratio for NS-*n* is 42000). The calcined samples were denoted as NO_3 -NS-*n* (*n* = 0.8, 1.5, and 2.3), where *n* is the mol% of Fe/Si in the initial mixture.

In order to investigate the role of TMB in the synthesis process, NS*-0.8 and NO_3 -NS*-0.8 were synthesized with the same

procedures to NS-0.8 and NO_3 -NS-0.8, respectively, except for the addition of TMB.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu K α radiation of 0.15406 nm wavelength. The nitrogen sorption experiments were performed at −196 °C on a Micromeritics ASAP 2020 system. Prior to the measurement, the materials were out-gassed at 120 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) specific surface areas were calculated using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.25. Pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method based on the adsorption branch and Horvath–Kawazoe (HK) method. The total pore volumes were estimated from the amount adsorbed at a relative pressure P/P_0 of 0.99. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2000EX and a FEI Tecnai G² Spirit at an acceleration voltage of 120 kV. Field-emission scanning electron microscopy (FESEM) was undertaken on a HITACHI S-4800 microscope operating at an accelerating voltage of 1–30 kV. UV–vis diffuse reflectance spectra were recorded on a JASCO V-550 UV–vis spectrophotometer. The powder material was loaded into a quartz cell, and the spectra were collected in the range of 190–800 nm with BaSO_4 as the reference. UV resonance Raman spectra were measured at room temperature with a Jobin-Yvon T64000 triple-stage spectrograph with a spectral resolution of 2 cm^{−1} [44]. The 290 nm line from a Coherent Innova 300 Fred laser was used as an excitation source. The power of the 290 nm line at samples was below 1.0 mW. The Si content of the samples was determined by X-ray fluorescence spectrometer (XRF, Axios PW4400, Panalytical), and the Fe content was measured with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, IRIS Intrepid II XSP, Thermo Fisher) after the sample was dissolved in a mixture of HF and HNO_3 . The ammonia temperature-programmed desorption (NH_3 -TPD) was measured on a Micromeritics Autochem 2920 instrument. The catalyst (0.15 g) was charged in a U-shaped quartz cell and pretreated in Ar (20 mL min^{−1}) at 500 °C for 1 h (ramp rate 10 °C min^{−1}), then cooled down to 100 °C followed by changing the gas flow to a mixture of 10% NH_3 -90% Ar (40 mL min^{−1}) for 2 h. The sample was then purged with Ar (20 mL min^{−1}) at 100 °C for 2 h to remove free and weakly adsorbed ammonia. The NH_3 -TPD profile was obtained by rising the temperature up to 550 °C (ramp rate 10 °C min^{−1}), using a TCD detector.

3. Results and discussion

3.1. Synthesis

As reported elsewhere, we have previously found that hollow silica nanospheres could be synthesized using the combination of F127–TMOS–TMB– K_2SO_4 under neutral conditions [43]. In order to incorporate the iron species in the siliceous hollow nanospheres, $Fe(acac)_3$ was chosen as an iron source. The TEM images of NS- n ($n = 0.8$ and 1.5) samples are displayed in Fig. 1. Mono-dispersed hollow nanospheres with shell thickness of 4.0 nm and core diameter of 12.0 nm could be clearly observed in the TEM image of NS-0.8 sample. Similarly, NS-1.5 also has the hollow nanospherical morphology with the shell thickness of 4.4 nm and core diameter of 9.3 nm. Increasing of the concentration of iron in the synthesis gel resulted in a slight decrease in the core diameter. From the SEM images (Fig. 2), it can be seen that both NS-0.8 and NS-1.5 samples have spherical morphology, but it is difficult to determine the accurate size of the spheres due to the resolution of the images. Thus the loading of iron provides a facile way of finely tuning the core diameter (size of interior void) of hollow nanospheres. Nitrogen sorption isotherms and BJH pore size distributions of Fe-NS- n samples are depicted in Fig. 3A and B, respectively. Two capillary condensation steps (the first is from the interior core, and the second is from the interparticle void space) are present in all these isotherms, which is similar to the N_2 sorption isotherms of previously reported hollow nanospheres [20,43]. The core diameters of the hollow nanospheres are in the range of 11.3 and 8.8 nm for Fe-NS-0.8 and Fe-NS-1.5, respectively (Table 1), which are consistent to those estimated from TEM. The BET surface area and pore volume of NS-1.5 is slightly higher than that of NS-0.8. The Fe content in NS-0.8 and NS-1.5 is of 0.51 and 0.85 wt%, respectively (Table 1). In addition to the mesopores, the micropore size distribution from HK method indicates that NS-0.8 has micropores with diameter centered at ca. 0.5 nm, as shown in Fig. 3C. The micropores are likely originated from the shell of the hollow nanospheres, which are randomly interconnected to reach the inner cavity [20,43]. The above characterizations suggest that the Fe-substituted hollow nanospheres have been successfully synthesized in the neutral reaction medium.

A comparative sample synthesized in a similar condition to NS-0.8 but without using K_2SO_4 was obtained in very low yield. This indicates that K_2SO_4 plays a significant role in effective hydrolysis–polymerization of TMOS to form the spherical morphology in such an acid-free synthetic solution [16,45–47]. However, under strongly acidic conditions, it was reported that the F127–KCl–TMB system tends to form cage-like mesostructure [42,46,47]. Under neutral buffer solution (NaH_2PO_4 – Na_2HPO_4 , pH $\approx$ 7.0), the formation of nanospheres was investigated in details [48], where inorganic salt from buffer solution may play a similar role to K_2SO_4 in the present work. Given that the surfactant F127 may exist as

individual micelles in the current system, the hollow nanospheres could be formed by condensation of hydrolyzed TMOS species around these single F127 micelles [27,48]. In this case, $Fe(acac)_3$ is well dissolved in TMOS but not in water, so that Fe might be incorporated into the silica framework during the hydrolysis and condensation process of TMOS for the formation of Si–O–Si species.

The NO_3 -NS- n ($n = 0.8, 1.5$, and 2.3) samples were synthesized under similar conditions to NS- n samples but using $Fe(NO_3)_3$ as iron source and lower H_2O /F127 ratio (the H_2O /F127 molar ratio for NO_3 -NS- n and NS- n is 28,000 and 42,000, respectively). The XRD patterns of NO_3 -NS- n ($n = 0.8, 1.5$, and 2.3) samples show one prominent peak in the low-angle range, indicating the formation of mesoporous materials (Fig. 4). NO_3 -NS-2.3 has less ordering compared with NO_3 -NS-0.8 and NO_3 -NS-1.5. The TEM technique was used for further characterization of the structure of NO_3 -NS- n samples ($n = 0.8, 1.5$, and 2.3) (Fig. 5). The TEM image of NO_3 -NS-0.8 clearly shows that this sample has typical FDU-12 cage-like mesostructures. The ordered lattice array over large domains under the TEM observations suggests that the sample has a uniform, cubic mesostructure ($Fm-3m$) without intergrowth [46,47]. The diameter of the cages may be directly measured from the thin edge of the particle in Fig. 5a to be about 17.1 nm, in good accordance with the N_2 sorption results (see below). Moreover, large pores formed can be regarded as the linear combination of many spherical cages for NO_3 -NS-0.8. Increasing Fe/Si molar ratio to 0.015 leads to the aggregated hollow nanospheres with particle size of 25.2 nm and shell thickness of 5.1 nm, as can be clearly observed in the TEM image of NO_3 -NS-1.5 (Fig. 5b). When Fe/Si molar ratio reaches to 0.023, the co-existence of hollow nanospheres with particle size of 25.0 nm and shell thickness of 6.0 nm and broken hollow nanospheres was observed (Fig. 5c). The SEM images of NO_3 -NS- n samples are shown in Fig. 6. NO_3 -NS-0.8 is composed of microspheres with particle size of 1–2 μm . The microspheres which are composed of nanospheres were found in the SEM image of NO_3 -NS-1.5 (Fig. 6b). The nanospheres could be clearly observed in the SEM images of NO_3 -NS-2.3 sample. The above results further confirm that NO_3 -NS- n ($n = 1.5$ and 2.3) samples have nanospherical morphology.

The nitrogen sorption isotherms and BJH pore size distributions of NO_3 -NS- n ($n = 0.8, 1.5$, and 2.3) are displayed in Fig. 7. The textural parameters are compiled in Table 1. NO_3 -NS-0.8 is of type IV isotherms with a steep H2 hysteresis loop at the relative pressure of $P/P_0 = 0.45$ – 0.90 , characteristic of mesoporous materials with a cage-like pore structure [46]. The N_2 adsorption isotherm of NO_3 -NS-1.5 is similar to that of NO_3 -NS-0.8, but the two-step desorption isotherm were observed in the former sample. The desorption step at P/P_0 higher than 0.70 may be from the closely connected hollow nanospheres. The isotherms of NO_3 -NS-2.3 show very clear two-step capillary condensation, which is very similar to those of hollow nanospheres as shown in Fig. 3. The N_2 sorption isotherms of NO_3 -NS-1.5 are different from that of the highly

Fig. 2. SEM images of Fe-substituted hollow nanospheres: (a) NS-0.8 and (b) NS-1.5.

Fig. 3. Nitrogen sorption isotherms (A), BJH mesopore size distributions (B) and HK micropore size distribution (C) of Fe-substituted hollow nanospheres: (a) NS-0.8 and (b) NS-1.5 (+600 in the left panel means that the nitrogen isotherms of (b) are shifted manually upwards along y-axis by 600 cm³ g⁻¹ STP).

Table 1

Structural parameters of Fe-containing mesoporous silicas.

Material	pH		Fe content (wt. %)	S_{BET}^a (m² g⁻¹)	V_t^b (cm³ g⁻¹)	D_{BJH}^c (nm)
	Initial	Final				
NS-0.8	5.34	5.00	0.51	620	1.78	11.3
NS-1.5	5.41	4.90	0.85	655	2.39	8.8
NO3-NS-0.8	3.42	3.39	0.28	715	0.76	15.6
NO3-NS-1.5	3.28	3.28	0.56	745	0.97	18.8
NO3-NS-2.3	3.16	3.01	1.81	948	1.36	15.3

^a S_{BET} is the BET specific surface area.

^b V_t is the total pore volume determined at the relative pressure of 0.98.

^c D_{BJH} is BJH pore diameter calculated by the adsorption branches of the nitrogen sorption isotherms.

dispersed hollow nanospheres, which suggests that the hollow nanospheres in the sample are combined with each other more tightly. The nitrogen sorption isotherms clearly show the evolution from FDU-12 mesostructure to hollow nanospheres as the iron content in the initial mixture increases, consistent with TEM and SEM characterization.

Generally, the pH value of synthesis gel plays important role in the synthesis of porous silicas. We have measured the pH value of the synthesis gels before transferring into the autoclave (initial pH)

and the final pH value of reaction system (final pH), as shown in Table 1. For the hollow nanospheres NS-0.8 and NS-1.5, the initial pH and final pH are quite close and weak acidic (around 5), because the synthesis system does not introduce external acid sources and the acidity does not change dramatically during the hydrothermal process. We also reported previously the synthesis of pure siliceous hollow nanosphere in the F127-TMOS-TMB-K₂SO₄ system, and found that the pH value does not apparently affect the formation of hollow nanospheres when changing the pH from 6.33 to

Fig. 4. XRD patterns of $\text{NO}_3\text{-NS-}n$ samples: (a) $\text{NO}_3\text{-NS-0.8}$, (b) $\text{NO}_3\text{-NS-1.5}$, and (c) $\text{NO}_3\text{-NS-2.3}$.

3.80 with H_2SO_4 [43]. Different from $\text{Fe}(\text{acac})_3$ insoluble in water, $\text{Fe}(\text{NO}_3)_3$ can generate higher acidity when hydrolyzed in water medium, so the initial pH and final pH are both acidic in the range

of 3–4. This is also similar to the case of introducing divalent salts, i.e., CuSO_4 or MgSO_4 [43]. This acidity may strengthen the interaction between silica species and micelles [46,49], and thereby facilitate the formation of FDU-12 type mesostructure of $\text{NO}_3\text{-NS-0.8}$. Under neutral conditions, the monodisperse mesoporous silica nanospheres were recently synthesized successfully in a large scale [50]. Despite the silica nanospheres are not hollow, a three-step formation mechanism is well proposed and interpreted, in which the self-assembly may take place between polymerizing silicate oligomers and individual surfactant micelles [50].

On the other hand, the salt effect was also highlighted [43], that is, in the F127–TMOS–TMB system, univalent salts (such as K_2SO_4 and Na_2SO_4) facilitate the formation of hollow nanospheres, divalent salts (such as CuSO_4 and MgSO_4) help to produce FDU-12 structures. We here further extend the salt effect to trivalent salt (such as $\text{Fe}(\text{NO}_3)_3$). A certain amount of trivalent salt produces ordered FDU-12 structure in addition to the decrease of pH value, and higher concentration of trivalent Fe salt will lead to less ordered FDU-12 ($\text{NO}_3\text{-NS-1.5}$), in accordance with the case of divalent salt CuSO_4 [43]. Even higher concentration of $\text{Fe}(\text{NO}_3)_3$ forms less ordered hollow nanospheres ($\text{NO}_3\text{-NS-2.3}$), which is seemingly evolved from the disassociated cages of FDU-12. When the concentration of $\text{Fe}(\text{NO}_3)_3$ increases, however, the fast hydrolysis and condensation rate of siliceous species at lower pH value may disturb the assembly process of ordered mesoporous structure and the hydrolyzed silicon species tend to assembly around the surfactant micelles to form the hollow nanospheres. The structural evolution again indicates the facile conversion between cage-like and nanospherical structures [19,43]. This would be helpful to further understand the formation mechanism of the two kinds of mesoporous silicas.

Fig. 5. TEM images of $\text{NO}_3\text{-NS-}n$ samples: (a) $\text{NO}_3\text{-NS-0.8}$, (b) $\text{NO}_3\text{-NS-1.5}$, and (c) $\text{NO}_3\text{-NS-2.3}$.

Fig. 6. SEM images of $\text{NO}_3\text{-NS-}n$ samples: (a) $\text{NO}_3\text{-NS-0.8}$, (b) $\text{NO}_3\text{-NS-1.5}$, and (c) $\text{NO}_3\text{-NS-2.3}$.

Fig. 7. Nitrogen sorption isotherms (left) and BJH mesopore size distributions (right) of NO₃-NS-*n* samples: (a) NO₃-NS-0.8, (b) NO₃-NS-1.5, and (c) NO₃-NS-2.3 (+300 and +600 in the left panel mean that the nitrogen isotherms of the corresponding samples are shifted manually upwards along y-axis by 300 and 600 cm³g⁻¹ STP, respectively).

To study the role of TMB in the formation of hollow nanospheres and cage-like mesostructures, NS*-0.8 and NO₃-NS*-0.8 were synthesized without TMB, compared with their counterparts, NS-0.8 and NO₃-NS-0.8, respectively. The TEM images of the two samples are shown in Fig. 8. Clearly, NS*-0.8 show hollow structure but the nanospheres are not separated well. This is in accordance with our previous study in the F127-TMB system for the synthesis of hollow nanospheres [42], where the aggregated hollow organosilica nanospheres are formed in the absence of TMB. This may imply that TMB may act as a swelling agent to penetrate into the core of micelles formed by EO₁₀₆PO₇₀EO₁₀₆ (F127) copolymers. Compared with NO₃-NS-0.8, ordered cage-like mesostructure cannot be seen in the sample NO₃-NS*-0.8, but worm-like structures are formed instead. These two samples strongly demonstrate that TMB plays an important role in the synthesis of hollow nanospheres and cage-like FDU-12 in the present synthesis system.

Efforts to induce the phase transformation for ordered mesostructure to hollow nanospheres were made previously by varying synthetic parameters, for example, by variation of valence state

inorganic salt additive [43] and synthesis temperature [19]. Herein, for the first time, we realized the transformation between FDU-12 structure and hollow nanospheres by simply using different iron salts.

3.2. Characterization of iron species by UV-vis spectroscopy

The elemental analysis results of NS-*n* and NO₃-NS-*n* samples are compiled in Table 1. As expected, more iron ions are incorporated in the samples with increased Fe/Si ratio of the synthesis gel. Compared with NO₃-NS-*n* samples, NS-*n* samples have more incorporated iron. This is probably due to the neutral conditions in the synthesis of NS-*n* samples using Fe(acac)₃ as iron source.

UV-vis spectroscopy may be used to identify different iron species in porous materials [51–53]. UV-vis spectra of NS-*n* and NO₃-NS-*n* are displayed in Fig. 9. NS-0.8 displays peaks centered at ca. 220 and 250 nm, which can be assigned to isolated tetrahedrally-coordinated framework sites [54]. NS-1.5 only shows a weak shoulder at 350 nm, but tailing above 400 nm suggests the

Fig. 8. TEM images of samples synthesized without TMB: (a) NS*-0.8 and (b) NO₃-NS*-0.8.

Fig. 9. UV-vis spectra of Fe-containing mesoporous silicas: (a) NS-0.8, (b) NS-1.5, (c) NO₃-NS-0.8, and (d) NO₃-NS-1.5.

existence of a small quantity of aggregates [55,56]. This implies that not all the iron species in the initial mixture could be tetrahedrally-coordinated in the mesoporous framework when the iron content in the initial mixture is too high.

NO₃-NS-*n* samples show quite similar UV-vis spectra (Fig. 9), where the two distinct peaks centered at ca. 220 and 250 nm can be assigned to isolated tetrahedrally coordinated iron ions. The peaks in the UV-vis spectra of NO₃-NS-*n* samples are wider than that of NS-*n* samples. This shows that Fe(acac)₃ as iron source is more favorable for the formation of tetrahedral coordination of iron in the framework.

3.3. Characterization of iron species by UV-Raman spectroscopy

UV resonance Raman spectroscopy is a powerful technique to characterize transition metals in the framework of zeolites or mesoporous silicas [44,57]. Using UV excitation, low fluorescence interference and strong resonance Raman enhancement make it possible for the sensitive detection of highly-isolated Ti or Fe species in mesoporous silicas or microporous zeolites [58,59]. A 290 nm laser line was employed as the excitation line, which is close in energy to the charge transfer band as indicated in the UV-vis spectra of NS-*n* and NO₃-NS-*n* samples. The UV Raman spectra of NS-*n* and NO₃-NS-*n* samples (Fig. 10) primarily exhibit bands at 510, 978, 1090, and 1150 cm⁻¹. The bands at 510 and 1090 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibrations of the framework Fe-O-Si species, respectively, due to the resonance Raman effect [60,61]. Weak bands at 1150 cm⁻¹ are attributed to the Fe-O stretching vibration couple to stretching of four neighboring framework Si-O-Si bonds. The band at 978 cm⁻¹ is associated with the Si-O-Si bond near the isolated iron species or the surface silanol group [14,49]. The UV-Raman spectra of NO₃-NS-*n* samples are quite similar, also exhibiting some main bands at 510, 978, 1090, and 1150 cm⁻¹, indicative of isolated iron species are present in these samples. The spectroscopic results (UV-vis and UV-Raman spectra) strongly suggest that highly isolated Fe species are present in all these hollow nanospheres and FDU-12 materials.

Fig. 10. UV-Raman spectra of Fe-containing mesoporous silicas: (a) NS-0.8, (b) NS-1.5, (c) NO₃-NS-0.8, and (d) NO₃-NS-1.5.

3.4. Characterization of acidity by NH₃-TPD

The NH₃-TPD is generally used to characterize the acidity of zeolites and mesoporous silicas [62,63]. As shown in Fig. 11, for NS-0.8, there is only one ammonia desorption peak at ca. 170 °C, which can be attributed to ammonia adsorbed on weak acid sites. Compared with the strong acid sites on zeolites [62], the Fe-containing hollow nanospheres have relatively weak acidity, which may be favorable to the catalytic reactions requiring weak acidity.

Fig. 11. NH_3 -TPD spectrum of NS-0.8.

Scheme 1. Schematic illustration of the acid-free procedures for the synthesis of Fe-substituted mesoporous silicas.

From all the results and discussion above, the transformation has been realized between hollow nanospheres and cubic cage-like pore structure, by varying iron salts (Scheme 1). When the iron loading is relatively low, highly isolated iron centers are predominant in these materials. These isolated iron species are supposed to be responsible for the catalytic activity in certain reactions, especially oxidative reactions [52,61].

4. Conclusions

In summary, a facile synthesis procedure has been developed to prepare Fe-substituted hollow nanospheres and Fe-FDU-12 with well-isolated iron sites in the absence of mineral acid. The evolution between hollow nanospheres and cage-like structures was achieved by the variation of iron precursors. This is an environmentally friendly methodology of nanostructure synthesis. This acid-free route may potentially be viable with other acid- and base-sensitive synthesis and encapsulation procedures.

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