Metallic Ag arrays assembled in nanoporous VSB-5 nanocrystals by a simple method: A novel catalyst for the synthesis of olefin aldehyde from styrene

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Abstract

Needle-like nanoporous VSB-5 crystals with the crystal diameters of about 50–100 nm were prepared. Ordered uniform-sized 1.10 nm Ag(0) arrays were successfully assembled in the channels or pores of these VSB-5 nanocrystals, which exhibited a UV–vis surface plasmon resonance absorption peak at 355 nm with a narrow full width of half maximum (FWHM) of about 35 nm. The catalytic activity of these Ag(0)–VSB-5 composites was investigated and it was found to be highly efficient catalysts for the syntheses of olefin aldehyde from styrene.

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Keywords: Nano-silver; Nanoporous nickel phosphate VSB-5 nanocrystal; Olefin aldehyde; Styrene

1. Introduction

The miniaturization of materials is being driven by the development of microelectronics and chemical industry, which spurred worldwide interests in nano-research [1]. A variety of chemical reactions of industrial interest are catalyzed by zeolites or zeolite-analogue materials [2]. One of the reasons that limit a wider range of industrial applications is the sole existence of micropores which impose diffusion limitations on the reaction rate. To overcome this limitation, there exists a long-standing interest in either minimizing the size of zeolite crystals or increasing the pore size of zeolites. The later possibility has led to the discovery of larger-pore zeolites and zeolite analogues [3,4], and also the discovery of the mesoporous molecular sieves [5]. Another strategy results in the preparation of very small (< 50 nm) zeolite crystals [6]. However, the controlling of the crystal sizes and the separation of the small zeolite crystals are difficult owing to the colloidal properties of the materials [7].

Cluster science plays important roles in understanding the changes in fundamental properties of materials as a function of size from isolated atoms or small molecules to the bulk phases [8]. Structures of small sizes, high aspect ratios and ordered metallic morphologies may exhibit unusual quantum effects and enhanced physical and chemical properties, which will be good candidate materials for nano-devices and/or catalysts [9–12]. Silver nanostructures with well-defined dimensions are particularly interesting to study and synthesize owing to the potential applications in interconnectors and active components of the future nano-devices and in high-powered catalyses. Additionally, the Fermi wavelength for most metals is about 1 nm, the quantum confinement effects can be maximized at such a size and can be used to test the fundamental limitations of such effects imposing on the electronic properties [13]. Silver with nanostructures has been prepared using mesoporous silica [14,15], film [16–18], mordenite [19,20], and in solution [21]. These nanostructures have particle sizes of about 5 nm and a wide size distribution due to the requirements of large pore size and/or complicated experimental procedure. Self-assembly of nanoclusters on periodic nanoporous hosts may be a promising approach to the limitation. Recently, the Ag(0) arrays with uniform sizes of 0.9 nm were successfully prepared in the channels of nanoporous VSB-1 and showed unusually optical
properties [22]. The preparation of the high-quality structures with a size within sub-nanoscale may lead to a molecular-level understanding of the relationships between electronic properties and performances. As for catalyses, the electronic properties have crucial influences on the performances of catalyses for given materials. The dispersants of uniform-size properties have crucial influences on the performances of catalyses and performances. As for catalyses, the electronic properties [22]. The preparation of the high-quality structures such as multifunctional catalyses. Nanoporous VSB-5 [4], having a larger pore diameter of about 1.10 nm and one-dimensional channel structure and showing highly efficient alkalescence and selective catalyses, which may be applicable for making ordered, small size and highly dispersed nanostructures with enhanced quantum confinement effects. Recently, quick synthesis of nanoporous VSB-5 has been achieved by microwave irradiation method in only 4 h [24]. In this paper, we report the rapid preparation of needle-like VSB-5 nanocrystals with the diameters of about 50–100 nm with large quantities in 2 d under hydrothermal conditions. Further metallic silver nanoarrays were assembled in the channels or pores of these nanocrystals. And their quantum confinement effects and catalytic properties were studied.

2. Experimental

Nanoporous VSB-5 samples of were synthesized according to the literature [4] and under the modified conditions in the mixtures of nickel (II) chloride hexahydrate (1.19 g), phosphoric acid (0.34 mL, 85 wt.%), triethylamine (2.10 mL) and H2O (13.0–15.0 mL), which were stirred for 0.5 h and then heated at 170 °C for 2 d in Teflon-lined autoclaves.

To prepare the metallic silver arrays inside the channels of VSB-5, the ion-exchange reaction of Ag+ was carried out firstly. 0.50 g as-synthesized VSB-5 nanocrystals were put into the solution with different AgNO3 concentrations of 5.0, 8.0 and 10.0 mM, respectively. The mixture has been stirred for 2 d sheltered from light to avoid the reduction of Ag+ ions. Ion-exchange occurred between Ag+ ion and H+ ions on the channel surfaces of VSB-5, which can be determined from the changes of pH values (increase of a value of 1.05) along with the increases of ion-exchange times.

The green Ag+ containing solids (called Ag+–VSB-5) have been acquired with the Ag+ ions on the outsides of surfaces removed after centrifugal processes for several times. After heating under the gas-flow of mixture of hydrogen and nitrogen (3% H2, volume ratio) at 200 °C for 2 h, the gray sample with Ag(0) arrays assembled in the channels of VSB-5 has been obtained (called Ag(0)–VSB-5). The reduction of Ag+–VSB-5 can also be achieved using formaldehyde as the reducing agent.

Styrene oxidation and further condensation were carried under heterogeneous conditions. The as-synthesized Ag(0)–VSB-5 powders (0.15 g) were added into the mixture solution of styrene (4.6 mL), acetone (6.6 mL, used as solvent), and H2O2 (4.4 mL, used as the oxidant). The mixture was stirred constantly for 12 h under a constant temperature of 70 °C in a flask with water refluxed. The products were acquired every 2 h. The conversions of styrene along with the reaction times via the determination of benzaldehyde were acquired from gas chromatography (GC, SP6890 made in China) using internal standard analytic method. The products were confirmed by LC/MS recorded on Shimadzu LCMS-2010A. The alkalescence of VSB-5 powders was approximated 9.31 ± 0.02 by a pH recorder standing for 3 min in the solution with 0.15 g of the as-synthesized VSB-5 powders and 20 mL H2O.

X-ray diffraction (XRD) patterns of the as-synthesized samples were measured on a Rigaku D/max 2200 PC with Cu Kα radiation over the range of 3° ≤ 2θ ≤ 60°. Ultraviolet–visible (UV–vis) reflectance spectra of the samples were measured on a Shimadzu UV-3101 instrument equipped with an integrating sphere using BaSO4 as the reference. High resolution electron microscopy (HRTEM) images were operated on a JEM 2010 electron microscope at 200 kV, which equipped with the selected area electron diffraction (SAED). EDX analyses were conducted on an OXFORD Links ISIS EDX attached to the HRTEM. Inductively coupled plasma (ICP) analyses were measured on a Vista Axial CCD Simultaneous ICP-AES spectrometer.

3. Results and discussion

Powder XRD analyses (Fig. 1A) of VSB-5 crystals indicate that the products are pure VSB-5 samples for both large crystals (Fig. 1A (a)) and small crystals (Fig. 1A(b)) compared with that of the literature [4]. The FWHM of VSB-5 nanocrystals was a little larger than that of the micrometer ones from the enlarged patterns (the insert of Fig. 1A). The size decreases of VSB-5 crystals were achieved by simply reducing the amount of H2O added during the synthetic process, which could be clearly observed by TEM analyses (Fig. 2). The diameters of most needle-like large VSB-5 crystals were about 1–2 μm when 15.0 mL H2O was added (Fig. 2a); while their diameters were decreased to about 50–100 nm when a less amount of water (14.0 or 13.0 mL H2O) was added in the reaction system (Fig. 2b and c). The less amount of water may increase the nucleation concentrations and change the crystal kinetics which may be in favor of the growth of small crystals with a large quantity. More homogeneous size of VSB-5 nanocrystals can be acquired by ultrasonic separating the as-synthesized VSB-5 samples.

HRTEM and SEAD analyses (Fig. 2d and the inset of 2c) of the VSB-5 nanocrystal indicate that it was needle- or rod-like crystal with one-dimensional channels parallel along the long axis and the channel diameters were about 1.10 nm, which are in accordance with the result of crystal XRD analyses [4].

XRD patterns of the as-synthesized Ag(0)–VSB-5 are shown in Fig. 1B. The Ag(0)–VSB-5 samples had almost the same patterns as that of pure VSB-5, which indicates that the structures of the hosts are well preserved. However, the intensities of peaks of the hosts decreased with the increases of concentrations of the Ag+ ions after assembly of Ag(0) in the channels, which may be due to the decreases of the scattering ratios between the walls of the host channels and the Ag(0) guests (see the inset of enlarged patterns of Fig. 1B). This was also observed in the cases of mesoporous silica and Ag(0)–VSB-1 and suggests that Ag(0) may be confined in the channels of VSB-5 [25a]. The low intensities of the XRD peaks for the Ag(0)–VSB-5 samples
may also come from the formation of the structural defects of host VSB-5 during the treatment processes of assembly. Two new diffraction peaks in the inset of Fig. 1B assigned to the cubic Ag (111) and (200) peaks (JCPDF# 04-0783), respectively, appeared when the Ag⁺ concentration was increased to 8.0 mM for the assembly. The diffraction peak of Ag(0) in the channels of VSB-5 prepared by 5.0 mM was not observed, which is due to the lower contents of Ag(0) in this sample (see the Ag contents of Ag(0)–VSB-5 in Table 1, based on the ICP analyses). The Ag(0) diffraction peaks prepared in 10.0 mM solution may come from part contribution of Ag(0) outside the channels in correspondence with the UV–vis analyses.

UV–vis spectra based on the Kubelka–Munk transformation from the solid state diffuse reflection spectra are given in Fig. 3. One unusually prominent UV–vis absorption peak at 360 nm was clearly present, which may be attributed to the characteristic dipole-like oscillation surface plasmon resonance of Ag(0) nanoparticles [22]. The significant blue shift of the plasmon peak was up to 150 nm, compared with that of 510 nm for the 100 nm Ag(0) particles [25]. This Ag(0) plasmon resonance peak with the large blue shift is due to the quantum size effects of smaller size Ag(0) inside of the channels of VSB-5, which is consistent with the size dependence of plasmon resonance energy of 1–6 nm Ag(0) particles [26]. The plasmon resonance peak shift to higher energy along with the size decreases when the particle size was below 6 nm. The plasmon peak was distinguished from the d–d electron transition of Ni²⁺ in the framework of VSB-5 using Gaussian distribution analyses (see the inset of Fig. 3). The narrow separated peaks with the FWHM of about 35 nm and the unchangeable plasmon peak positions of the Ag
VSB-5 samples prepared with different concentrations of AgNO$_3$ in the solutions indicate that the Ag(0) particles have focusing size distribution and are limited by the channels of VSB-5, which mean that the diameters of most Ag(0) particles are equal or very close to that of the VSB-5 channels, e.g., 1.10 nm. It is known that the absorption strength is proportional to the density of states in K space and increases rapidly along with the decreases of particle sizes [11]. The maximum of the quantum confinement effects was indicated by the UV-vis spectra. The Ag atoms vs. the ring-like unit cell of the as-synthesized Ag(0)–VSB-5 prepared in the 5.0 mM AgNO$_3$ solution is 0.50, based on the EDX analyses. While the integral area ratio of the plasmon resonance peak compared with that of the absorption of d–d transition Ni$^{2+}$ was 31.4% despite the amount of Ag(0) was only 0.50 Ag atoms per unit cell. The integral absorption area ratio of every molar Ag(0) of Ag(0)–VSB-5 compared with that of Ag(0)–VSB-1 was 22%. This may result from the smaller size of Ag(0) assembled in VSB-1 demonstrating a more prominent quantum confinement effects. The intensity of the plasmon peak at 360 nm increased along with the increases of Ag$^+$ ions concentrations in the solution, using the electron transition peak at 410 nm of Ni$^{2+}$ in the framework of VSB-5 as the standard. This may be due to the increased length (volume) along the channels of VSB-5 for the precipitated Ag(0) particles [22]. When the Ag$^+$ concentration was higher than 10.0 mM, the growth of Ag(0) particles outside the channels occurred even if the Ag$^+$–VSB-5 samples had been washed by centrifugal processes for many times in our experiment. The position of the plasmon resonance peak (360 nm) is a little red shift of 5 nm compared to that of Ag(0) (355 nm)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ag (wt.%)</th>
<th>Ni (wt.%)</th>
<th>Ag/Ni (mol%)</th>
<th>P (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(0)–VSB-5 in 10.0 mM</td>
<td>4.47</td>
<td>39.74</td>
<td>6.2</td>
<td>11.70</td>
</tr>
<tr>
<td>Ag(0)–VSB-5 in 8.0 mM</td>
<td>4.20</td>
<td>41.56</td>
<td>5.5</td>
<td>12.24</td>
</tr>
<tr>
<td>Ag(0)–VSB-5 in 5.0 mM</td>
<td>1.79</td>
<td>20.15</td>
<td>2.4</td>
<td>11.56</td>
</tr>
</tbody>
</table>

The composition of VSB-5 is Ni$_{20}$[(OH)$_{12}$(H$_2$O)$_6$][(HPO$_4$)$_8$(PO$_4$)$_4$]12H$_2$O (see Ref. [4]).

Fig. 2. TEM image of the as-synthesized pure VSB-5 prepared from the reaction systems with the water values of 15 mL (a) and 13 mL (b, c), respectively. HRTEM images of VSB-5 nanocrystal (d) and that of Ag(0)–VSB-5 (e, f) prepared in the 5.0 mM AgNO$_3$ solution. SAED are shown as insets.

Fig. 3. UV–vis absorption spectra analyzed by Kubelka–Munk function of the pure VSB-5 and Ag(0)–VSB-5 samples prepared from the AgNO$_3$ solutions with different concentrations. The inset shows the peak fitting spectrum of Ag(0)–VSB-5 prepared in 5.0 mM AgNO$_3$ solution by Gaussian analyses.
assembled in VSB-1. This may be due to the fact that the pore diameter of VSB-5 (ca. 1.10 nm) is larger than the 0.9 nm diameter of VSB-1, which is well in correspondence with the fact that the blue shift of the plasmon resonance absorption peak along with the size decreases of nanocrystals. The stable ability of Ag(0) was studied by the UV–vis spectra. The 360 nm plasmon peak has been unchanged for more than 12 months at room temperature, which shows that the nanosized Ag(0) is quite stable in the channels of VSB-5 from the UV–vis spectra analyses. The unchangeable position of the d–d electron transition of Ni2+ after the assembly Ag(0) in the channels of the VSB-5 and the large amount existence of Ni2+ in the stable framework of VSB-5 suggest that the Ni2+ was not reduced by the H2 in the heating process.

More evidence that Ag(0) particles have been assembled inside the channels of VSB-5 is provided by the direct observation using HRTEM. A little obscure morphology of Ag(0) particles were observed (Fig. 2e and f), which may be due to the fact that the contrast between the nickel phosphate framework of VSB-5 and Ag (0) is low. However, one can obviously see the gray-dark arrays of Ag(0) containing samples and the channel diameters became narrower compared with that of pure VSB-5 (Fig. 2d). This suggests that the defects may be created corresponding to the results of XRD and apparent irregular channels are found at the end channels of Ag (0)–VSB-5 (Fig. 2f). No Ag(0) particle was observed outside the channels of VSB-5 based on the HRTEM analyses; while the EDX and XRD analyses demonstrate that there was Ag(0) in the samples indicating that Ag(0) existed in the channels of VSB-5. The Ag(0)–VSB-5 are also studied by SAED. As shown in the inset of Fig. 2f, the Ag(0)–VSB-5 samples are crystalline, which confirms that the Ag(0) containing samples have well preserved structure of VSB-5 in good agreement with the results of HRTEM and XRD analyses. The d-spacing of VSB-5 acquired from the SAED analyses was 1.14 nm.

While the d-spacing of Ag(0)–VSB-5 acquired from the results of SAED analysis was 1.26 nm. The enlarged d value of Ag(0)–VSB-5 than that of pure VSB-5 indicates that Ag(0) may be plated onto the channels of VSB-5 and increase the thickness of the pore walls. This could be directly observed from the HRTEM images showing the broadened wall thickness (Fig. 2e and f). The channels or pore sizes, which are believed to be related to the diameters of Ag(0) particles of the arrays, are about 1.10 nm observed from the HRTEM images (Fig. 2e and f) corresponding to that of reported crystal XRD analyses [4].

The effect of AgNO3 concentration in the aqueous solution can be observed clearly on the UV–vis spectra with different AgNO3 concentrations resulted in different absorption intensities of Ag(0) particles (Fig. 3). These results further prove the fact that the increase of quantity (volume) and high aspect ratio of Ag(0) nanoparticles with the particle diameter of 1.10 nm formed in the channels of VSB-5 for the Ag(0) array prepared in AgNO3 solution, which is consistent with the EDX and UV–vis analytic results. Ag(0) may also exist outside the channel when the concentration was as high as 10.0 mM, since another absorption band with the peak position centered at 450 nm was observed which may be due to the absorption of the larger size of Ag(0).

The structures and functions of very small metal particles often show catalytic properties different from conventional ones, and this was, at least partly, attributed to the small sizes of the catalyst particles [27]. The particle sizes as well as the distribution of the particles on the high-surface area support can affect the performance of catalysts. The specific characters of the hosts can also affect the catalyses. Selective oxidation is an active field of research due to the complex chemical processes. The styrene oxidation at side chain is of academic and commercial interests for the synthesis of two important products of styrene oxide and of

![Fig. 4. (a) The conversion of styrene with the reaction time. (b) The scheme of the reaction route.](image-url)
phenylacetaldehyde \[28\]. While phenylacetaldehyde could be further polymerized to produce oligomeric aldehyde using costly Wilkinson’s catalyst (RhCl(PPh₃)₃) or other diphosphine complexes catalysts \[29\], which is interesting in the organic chemical industry. The reaction was generally carried under a high pressure of 11 MPa with a complex process and the selectivity of the new oligomeric aldehyde was lower than 20%. The preparation of cheap and highly efficient catalyst together with the control of polymerization degree is interesting and important for the aldol reaction. In our experiment, a 4.20 mol.% Ag(0) (0.50 Ag atoms per unit cell) containing nanocomposite was quite active for the oxidation and further condensation of styrene under a relatively mild condition at normal pressure. The products were confirmed by LC/MS instrument and gas chromatography (GC). The product was 3,5-dioxo-2,6-triphenyl-hexanal (A) for a reaction time of 2 h and the yield selectivity was 95.2%. However, when the reaction time increased to more than 4 h, a different product of 2,4,6,8-tetraphenyl-octa-2,4,6-trienal (B) was produced without any product A detected. The selectivity of B was 94.5% at 4 h and remained as the main product until 12 h, with a selectivity of 89.4% at 12 h (Fig. 4). The exact reason for the transformation is not clear. We presume the reaction route was as the following process shown in Fig. 4b. Styrene was oxidized to phenylacetaldehyde and polymerized to the trimerization of product A immediately at the initial process. No phenylacetaldehyde was detected and a small amount benzaldehyde was produced in the experiment. This may be due to that polymerization of phenylacetaldehyde was rather fast in the experiment and partly phenylacetaldehyde was converted to benzaldehyde from the cleavage of the C-C bond. However, sample A was transformed into sample B as the reaction was processed, and this may be due to adequate phenylacetaldehyde produced. It is known that alkalescence favors the aldol-type reaction to the yield selectivity of a new aldehyde \[29\]. The alkalescence of VSB-5 together with Ag(0) nanoclusters assembled in the channel of VSB-5 facilitated the aldol reaction and the formation of the oligomeric products. To verify this assumption, pure VSB-5 and Ag(0)–VSB-1 samples were carried out under the same experiment conditions. The activity of both of them was quite low and unidentified heavier products were produced using pure VSB-5 as catalyst, but no product A or B was detected. The reason for the low activity for Ag(0)–VSB-1 and pure VSB-5 may be due to the acidity of VSB-1 and the lack of Ag(0). The conversion of styrene vs. the reaction time is shown in Fig. 4. As shown, the conversion increased along with the reaction times. The yield selectivity of product B was 94.5% at 2 h and decreased slightly to 89.4% at 12 h along the reaction process. The decrease of yield selectivity along the reaction processed may be due to the production of benzaldehyde and other byproducts. Further experiments should be carried out to understand the reaction mechanism. However, the reaction conditions required in the experiment was rather mild (70 °C) and simple in comparison with traditional aldol reactions which required high pressure or complex experiment conditions. Additionally, the novel olefin aldehyde was directly synthesized from styrene compared to those reacting with phenylacetaldehyde using metalloocene as catalyst \[29\].

4. Conclusions

To summarize, large amounts of nanoporous VSB-5 needle-like nanocrystals with diameters of 50–100 nm have been prepared by simply reducing the values of water from 15 mL to 14 or 13 mL in the reaction systems. Using VSB-5 nanocrystals as the hosts, 1.10 nm Ag(0) arrays were successfully assembled in their channels, which possess obvious quantum confinements. These Ag(0)–VSB-5 materials demonstrate highly catalytic activity and yield selectivity for the oxidation and further aldol reaction of styrene. Novel oligomeric olefin aldehyde with tunable polymerization degree could be directly synthesized from styrene over the low-cost Ag(0)–VSB-5 catalysts under mild conditions. This work also indicates the nanoporous VSB-5 nanocrystals containing functional components may pose potential applications in the theoretical research and in fabrication of future novel multifunctional catalysts.

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Appendix A. Supplementary data


References