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In situ synthesis of copper nanoparticles on SBA-16 silica spheres

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Abstract   A chemical method for in situ synthesis of copper nanoparticles on SBA-16 silica spheres under ambient conditions has been reported. The silica support has been introduced into copper precursor solution before chemical reduction. Metal ions diffuse into mesopores (pore diameter 5–7 nm) of silica where in situ reduction by hydrazine leads to formation of nanoparticles. These mesopores act as nanoreactor and their walls prevent metal particle's agglomeration by providing a physical barrier. The obtained copper nanoparticles have been investigated by electron microscopy, X-ray diffraction, UV–Visible spectroscopy, Fourier transform Infra-red spectroscopy and thermogravimetric analyzer. SEM, TEM and UV–Visible spectroscopic images revealed that nano-sized particles have been successfully synthesized by this method. Thermogravimetric investigations revealed that copper nanoparticles impregnated on silica were thermally more stable compared to unsupported nanoparticles. Silica not only helps in maintaining the particle size but also makes nanoparticles stable at high temperatures due to its thick pore walls. Macro sized silica support also makes separation/handling of nanoparticles easy and simple.

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1. Introduction

Nanoparticles have gained a lot of importance in the last two decades due to their size dependent properties and high activity owing to the large surface area (Wu and Chen, 2004). They present many potential applications in the fields of optics, catalysis, mechanics, magnetic materials, biomaterials etc. (Schmid, 1992; Devaux et al., 1993; He et al., 2003) However,

handling, separation and flocculation of nanoparticles are some existing issues due to their small size. Recently, nanoparticles dispersed in support are receiving attention due to easy handling and isolation (He et al., 2003; Jiang et al., 2005). But in an aqueous synthesis of metal nanoparticles the particle size and geometry are difficult to control due to rapid aggregation and ionic interaction problems. Mesoporous materials such as MCM-41 and SBA-15 with cage like structure and pore size in the range of 2–50 nm have been used as support for preparation of nanoparticles (Yang et al., 2002; Carta et al., 2011). SBA-16 is a novel pure siliceous mesoporous material, which possesses cubic mesoporous structure with three-dimensional ordered network of interconnected pores and large surface area (Shah et al., 2009; Rivera-Muñoz and Huirache-Acuña, 2010; Shah et al., 2010, 2011). These characteristics make SBA-16 a promising support for catalytic applications (Grudzien et al., 2007). There are very few reports on the use of SBA-16 support for metal nanoparticle synthesis (Chen et al., 2010). SBA-16 possesses mesopores of the size range 3–12 nm which can be used as nanoreactors for production of metal nanoparticles of homogeneous size and specific geometry. According to Veith et al. (2009) inside these pores once the metal particles reach a size equal to the pore diameter, particle migration and coalescence cease and Ostwald ripening becomes the only mechanism of sintering. Thus using these nanoreactors the particle size of metals can be controlled by tuning their pore size.

Here we present an easy method for the in situ synthesis of copper nanoparticles supported on SBA-16. The metal ions diffuse into mesopores of silica and their in situ reduction results in the formation of nanoparticles of size similar to the pore size. The use of SBA-16 support also facilitates particle extraction/separation from the reaction media and prevents particle aggregation in high temperature applications. The resulting supported metal nanoparticles offer added advantages like high activity, selectivity and reusability of the materials.

2. Experimental

2.1. Characterization techniques

X-ray powder diffraction (XRD) measurements were carried out by using a Rigaku D/Max 2500 VBZ+/PC diffractometer. Scanning electron microscopy (SEM) photographs were obtained using a Hitachi S-4800 microscope. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) was used to investigate the composition of copper. FTIR results were recorded on spectrometer RX-1 FTIR from Perkin Elmerol. High-resolution transmission electron microscope (HRTEM) images of samples were obtained on JEM-3010 transmission electron microscope. The thermogravimetric analysis (TGA) was performed on SDT Q 600 TA Instrument. The UV–Visible analysis was carried out using Labomed Model D 3500 spectrophotometer.

2.2. Materials and method

All chemicals were purchased from Sigma Aldrich and Fischer and were used without further purification. SBA-16 was synthesized by the procedure reported in our previous paper without adding any metal salt (Shah et al., 2010). Certain

amount of non-ionic block co-polymer Pluronic F127 was dissolved in 2 M HCl soln. and stirred for 30 min, and then 8.5 g of TEOS (tetraethyl orthosilicate) was added drop-wise into this solution and stirred for 16 h. The material was placed in Teflon lined stainless steel vessel at 100 °C for 24 h. Then it was filtered, washed, dried and calcined at 550 °C at ram 1 °C/min. The synthesized material with surface area 1081 m^2/g and pore size 5–7 nm was used as support. 1 g of SBA-16 silica support was added into the mixture containing 0.01 M Cetyltrimethyl Ammonium Bromide (CTAB) solution and 0.03 mM anhydrous copper sulfate solution with pre-set pH value 10 (adjusted with liquid ammonia) and stirred vigorously. The copper ions from the solution diffuse into the pores of SBA-16 and also accumulate on silica surface during stirring. Then 0.12 M hydrazine diluted with 0.01 M CTAB solution was added to the above mixture. The pH of mixture was adjusted to 10 using ammonia solution and allowed to stir for 2 h in a capped bottle. Hydrazine is a strong reducing agent and it reduces the copper ions on surface and inside the pores into copper metal. The solution turned light wine red, the mixture was refluxed for 2 h. The resulting material was filtered, washed with deionized water and dried. The sample was labeled as Cu-NPs/SBA-16. The same experiment was repeated in the absence of silica to prepare unsupported copper nanoparticles.

3. Results and discussion

UV–Visible is a simple technique to evaluate the formation of nanoparticles. The UV–Visible spectrum of synthesized copper nanoparticles is given in Fig. 1. The spectrum shows a surface plasmon resonance (λ_{spr}) absorption band in the range of 550–580 nm which is a characteristic band of copper nanoparticles and confirms the formation of metal NPs (Dhas et al., 1998). The absorption spectrum also provides information about the shape of nanoparticles. A single surface plasmon resonance absorption band shows that the shape of particles is spherical because the reflection of light is same from all the sides of spherical nanoparticles.

Fig. 2 shows the spectroscopic images of the synthesized supported nanoparticles. There are two types of nanoparticles; one inside the nanopores and the other on the surface of spheres. Nanoparticles inside the pores have smaller diameter in the range of 3–4 nm and can be seen in TEM image, while bigger nanoparticles on the surface of the spheres are visible
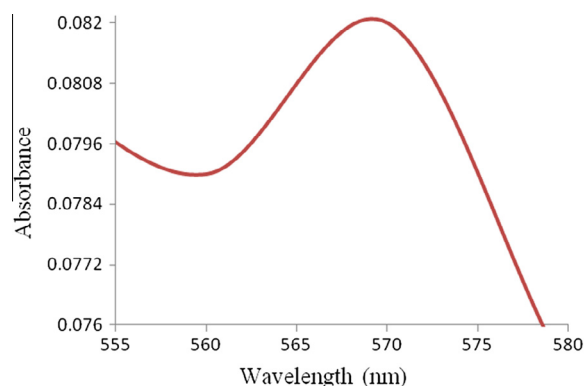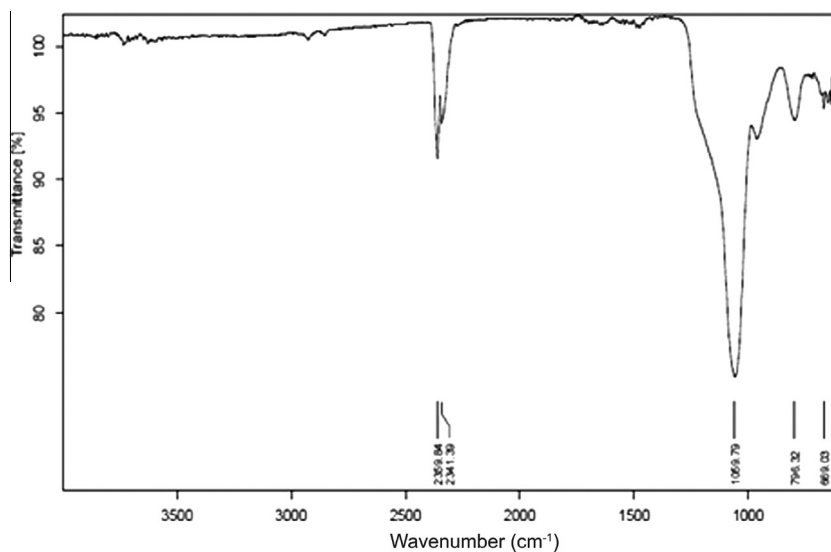

Figure 1 UV–Visible absorption spectrum of synthesized copper nanoparticles.
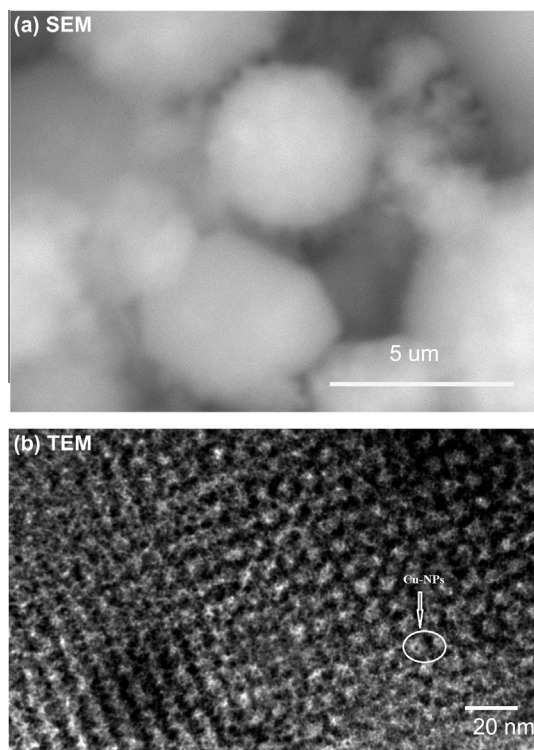
**Figure 2** Images of the synthesized supported nanoparticles (a) SEM, (b) TEM.

in SEM image. SEM image (Fig. 2a) shows that the size of the SBA-16 spheres is about 5–6 μm and copper nanoparticles are dispersed on their surface. SEM–EDX results reveal that the percentage of copper in silica is about 0.23 wt.%. The TEM image (Fig. 2b) shows dark spots on silica surface, these spots are metal nanoparticles present inside the mesopores. The diameter of these nanoparticles is about 3–4 nm, which is smaller than the diameter of the mesopores (5–7 nm). The size of nanoparticles on surface is larger than the particles present inside the nanopores.

The FTIR spectrum of SBA-16 supported copper NPs is shown in Fig. 3. In this spectrum, a band at 964 cm^{-1} is observed which is due to stretching vibration of copper–oxygen (M–O) and indicates the presence of Si–O–Cu linkage. The absorption band at 796 cm^{-1} is due to the symmetric stretching vibrations of Si–O bond (Shah et al., 2010), while the characteristic peak at 610 cm^{-1} is due to the Cu–O bending vibrations in low energy region of the spectrum (Suraja et al., 2011). These results show that copper metal is successfully loaded on SBA-16.

The thermo gravimetric analysis of both SBA-16 and Cu-NPs/SBA-16 is carried out and the corresponding curves are given in Fig. 4. As expected, the TGA of SBA-16 exhibits no remarkable weight loss with the increase in temperature indicating its high thermal stability. While Cu-NPs/SBA-16 shows a sharp weight loss between 30 and 100 °C owing to the removal of entrapped solvent molecules. The weight loss at 200–350 °C and 350–450 °C can be related to the decomposition of bilayer CTAB molecules (Wu and Chen, 2004). The rate of thermal degradation (weight loss) for SBA-16 supported CTAB capped nanoparticles is slow compared to reported unsupported CTAB capped metal particles (Wu and Chen, 2004), which might be attributed to the presence of silica
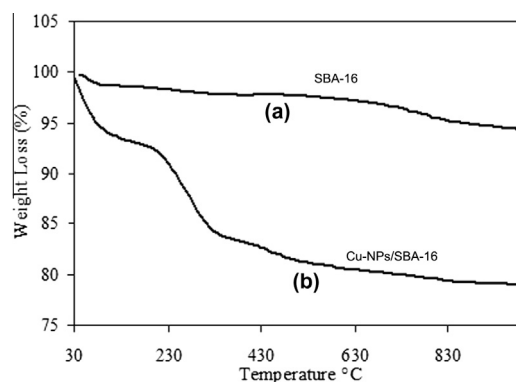
Figure 4 TGA curves of (a) SBA-16 (b) SBA-16 supported Cu nanoparticles.

Figure 3 FTIR spectrum of SBA-16 supported copper nanoparticles.

support that stabilizes the catalyst. The total weight loss at 550 °C for Cu-NPs/SBA-16 and SBA-16 has been found to be 20 and 5 wt.%, respectively. A previous report (Wu and Chen, 2004) has shown that Cu-NPs show almost 80% weight loss which is much more than synthesized silica supported metal nanoparticles. This is because silica is a refractory material and it prevents the sintering and decomposition of NPs present inside the mesopores at high temperatures (Song et al., 2013). Thus Cu-NPs/SBA-16 is thermally more stable than simple Cu-NPs because they are entrapped inside highly stable SBA-16.

Additionally, the handling and separation of loaded NPs becomes easy due to macro-size (5–6 μm) of silica spheres. Nanoparticles are present inside the mesopores of silica or on its surface, thus they can be easily filtered or separated from the aqueous solution.

Small angle XRD patterns of SBA-16 and Cu-NPs/SBA-16 are shown in Fig. 5. The SBA-16 support exhibits diffraction peaks at 2θ value of about 0.7° corresponding to (110) reflection and unresolved peaks between 1.0° and 2.0°, these are characteristic peaks of three-dimensional cubic (1m3m) structure of SBA-16 (Yang et al., 2002; Shah et al., 2010). Cu-NPs/SBA-16 also possesses these characteristics peaks which indicate that silica cubic structure is not affected during loading.

3.1. Mechanism of formation of Cu NPs supported on silica spheres

SBA-16 possesses 1m3m cubic cage like three dimensional (3-D) mesoporous structure with interconnected channels (Shah et al., 2011). Copper ions from their aqueous solution get diffused into the mesopores of the SBA-16 cage. When reducing agent hydrazine is added into the silica suspension, it also diffuses into the silica mesopores due to its small size and reduces copper ions into copper metal as discussed by Wu and Chen (2004). Thus nanoparticles are deposited on the surface and inside the mesopores of the silica as also discussed in SEM and TEM results.

The presence of silica prevents aggregation of nanoparticles at elevated temperatures. The tammann temperature (the temperature at which point atoms from the bulk exhibit mobility)
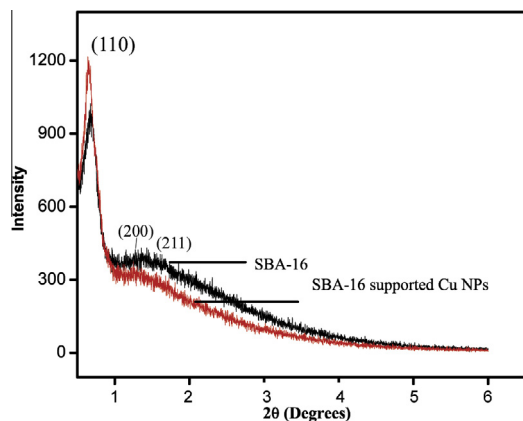
for copper metal is 405 °C, above this temperature coarsening is started. Silica is a refractory material and its use as support limits the sintering of copper nanoparticles above tammann temperature (Song et al., 2013). Further Budroni and Corma (2006) have reported that pores act as physical barriers to control the rate of particle growth, such that the metal particles inside the pores remain much smaller than those on the surface. Thus these barriers cease particle migration and coalescence inside the pores even when the material is being sintered at high temperatures (Gabaldon et al., 2007). Also SBA-16 possesses three-dimensional ordered network of interconnected ink bottle shaped pores with narrow openings (Kapil et al., 2013), which reduces the migration of metal nanoparticles during sintering and avoids Ostwald ripening.

Therefore silica loaded Cu-NPs are thermally more stable than unloaded NPs and pore walls of silica prevent the aggregation of these nanoparticles at elevated temperatures. These supported nanoparticles possess uniform morphology and are suitable for high temperature applications.

4. Conclusion

"SBA-16 supported Cu nanoparticles" were prepared by the modified reduction method using SBA-16 as support. The mesoporous cage like silica support helps in controlling the particle size of the nanoparticles. Any desired particle size range can be achieved by using the support of particular pore size. The silica support also prevents particle agglomeration and induced stability at high temperatures where other organic capping agents may degrade. The use of support makes the separation of nanoparticles very easy from aqueous solution.

Figure 5 Small angle XRD of SBA-16 support and Cu-NPs/SBA-16.

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