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1. Introduction

Nanosized coinage metal particles have been the centre of attention in recent years owing to their exceptional physiochemical properties like quantum confinement and surface effects1 which makes them ideal for use in catalysis2 and optical devices.³ Progressive developments in tuning the shape and size of nanoparticles (NPs) have increased the chances of optimizing their geometry which ultimately affects their catalytic efficiency. Due to presence of highly active centers,⁴ NPs are thermodynamically unstable so they are immobilized/supported over inorganic⁵ and organic frameworks. Recently, Li et al.⁶ reported the formation of Pd NPs over urea based porous organic frameworks exhibiting high catalytic activity for selective reduction of nitroarenes and Suzuki-Miyaura cross coupling reactions. Among the inorganic frameworks, silica based mesoporous materials (MMs) display many attractive physicochemical properties such as high porosity, large specific surface area, high mechanical stability and easy surface functionalization, etc. which enable them to be used as ideal scaffolds for

Highly dispersed Au, Ag and Cu nanoparticles in mesoporous SBA-15 for highly selective catalytic reduction of nitroaromatics[†]

Shweta Sareen,^a Vishal Mutreja,^b Satnam Singh^a and Bonamali Pal*^a

This paper demonstrates a homogeneous dispersion of 4 wt% coinage metal nanoparticles (Au, Ag and Cu) of different morphologies in the pores (~8 nm) of 3-aminopropyltriethoxysilane (APTES) modified mesoporous SBA-15 for selective catalytic reduction of *m*-dinitrobenzene to phenylenediamine. EDX, elemental mapping and HR-TEM analysis confirmed the uniform dispersal of metal nanoparticles within the mesoporous matrix having lattice fringes with a *d*-spacing of 0.232 nm for Au (111), 0.23 nm and 0.20 nm for Ag (111) and (200) and 0.25 nm for CuO (111) planes. XPS results illustrated the presence of Au and Ag in their metallic states whereas Cu was oxidized to CuO. XRD, TEM and surface area analysis revealed that formation of metal nanoparticles within the sieves led to a significant change in the surface structural and physicochemical properties. Metal nanospheres with increasing size *i.e.*, ~5 nm (Au) < ~11 nm (Ag) < ~13 nm (Cu) were formed within the channels of SBA-15, while small nanorods (aspect ratio ~2–4 nm) were also formed in the case of Ag and Cu impregnation. The catalytic activity was found to depend on the nature, size and dispersion of metal nanoparticles relative to negligible reactivity of bare SBA-15. Au nanosphere (~5 nm) impregnated SBA-15, having the lowest surface area (292 m² g⁻¹), exhibited the best catalytic activity for *m*-dinitrobenzene reduction (*k* = 1.765 × 10⁻¹ min⁻¹) with 89% selectivity to *m*-phenylenediamine.

catalytic applications.⁷ A review by Lofgreen *et al.*⁸ also summarized the synthetic procedure for formation of imprinted silica materials based on the concept of molecular imprinting involving the assembly of cross linked polymer matrix around an imprint molecule bonded through covalent/noncovalent interactions by judiciously chosen functional monomers. Later on, removal of imprint molecule generate cavity of specific shape and size. This ease with which the morphology of silica based materials can be controlled earns them a significant advantage over other organic polymer systems that uses toxic organic solvents. So, silica is most frequently used inorganic materials. A major amount of research has been dedicated to the synthesis of advanced nanostructured silica materials like mesoporous silica nanotubes based on sol–gel process and silane chemistry.^{9,10}

Among different mesoporous silica materials, SBA-15 exhibited excellent properties to be used for catalytic support *viz.*, large surface areas, tunable pore diameter, thick framework walls and high hydrothermal stability.¹¹ Despite the presence of all these promising properties, bare SBA-15 does not exhibit any catalytic activity. Thus, incorporation of metal NPs in SBA-15 is desirable to improve its catalytic efficiency. However, functionalization of mesoporous surface by organic functional groups like –SH,¹² –COOH¹³ is required for loading of metal to improve interaction between metal complexes and silica surface leading to high dispersion of metal NPs within pores. Coinage

 ^aSchool of Chemistry and Biochemistry, Thapar University, Patiala 147004, Punjab, India. E-mail: bpal@thapar.edu; Fax: +91-175-2364498; Tel: +91-175-2393491
^bMaharishi Markandeshwar University, Mullana, Ambala 133207, Haryana, India
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metals like Au,^{14,15} Ag^{16,17} and Cu¹⁸ have been impregnated on SBA-15 surface by different methods but comparison of their morphological features, physicochemical properties and catalytic activity has seldom been reported. Therefore, current research deals with the preparation of highly dispersed coinage metal NPs within channels of SBA-15 for studying their comparative surface structural morphology and catalytic activity for dinitrobenzene reduction.

2. Materials and methods

Hydrogen tetrachloroaurate (HAuCl₄·3H₂O, 99.99%), silver nitrate (AgNO₃, 99.0%), copper(II) chloride, Pluronic (triblock copolymer EO₂₀.PO₇₀.EO₂₀), tetraethoxysilane (TEOS), m-dinitrobenzene (DNB), m-phenylenediamine (PDA), m-nitroaniline borohydride $(NaBH_4)$ (NA), sodium and 3-aminopropyltriethoxysilane (APTES) were obtained from Sigma Aldrich. All other reagents were obtained from Loba Chemie, India and used as received without further purification. Deionized water was used throughout the experiments which was obtained using an ultra filtration system (Milli-Q, Millipore) with measured conductivity above 35 mho cm⁻¹ at 25 °C.

2.1. Preparation of coinage metal incorporated ap-SBA-15

Mesoporous SBA-15 was prepared by method reported by Zhao *et al.*¹⁹ For the synthesis of SBA-15, 4 g of Pluronic 123 was suspended in 120 ml of 2 M HCl at 40 °C under stirring. Upon dissolution of the polymer a clear solution was obtained, 0.041 mol of TEOS was added and the contents were stirred at 40 °C for 24 h. The solution thus obtained was transferred into Teflon autoclave and kept at 95 °C for 3 days. It was filtered, dried and calcined at 550 °C for 8 h resulting in SBA-15. For surface functionalistaion of SBA-15, 2 g of prepared SBA-15 was suspended in 100 ml of 2 wt% of ethanolic solution of APTES under stirring for 3 h. It was then, filtered, washed with ethanol, dried at 60 °C and was designated as ap-SBA-15.

Metal deposition was carried out by stirring 0.5 g of ap-SBA-15 with 101.5 ml, 185.2 ml and 314.9 ml of 1 mM HAuCl₄·3H₂O, AgNO₃ and CuCl₂·2H₂O solutions respectively for 2 h. The contents were filtered, rinsed three times with deionized water and dried at 60 °C. The resulting solid was calcined at 350 °C for 3 h. The corresponding catalysts were named as M/ap-SBA-15 (where M is Au, Ag or Cu). The outline for the preparation of noble metal (Au, Ag and Cu) incorporated SBA-15 catalysts is shown in ESI-Scheme 1.†

2.2. Catalytic activity

Catalytic activity of the prepared catalysts was investigated using reduction of *m*-dinitrobenzene (DNB) by mixing catalyst (5 mg), substrate (5 mM) in ethanol and NaBH₄ (0.5 M) in a 10 ml round bottom flask with constant stirring at 298 K. The progress of the reaction was monitored by HPLC (Agilent, 1120 compact LC using C-18 column) at 254 nm using MeOH : H₂O (70 : 30) as mobile phase with flow rate of 1 ml min⁻¹. GC-MS using Shimadzu, GC-2010 and GC-MS-QP 2010 plus with RTX-5Sil-MS column (30 mm × 0.25 mm × 0.25) was used to analyze the products. Helium was used as a carrier gas with a flow rate of 1 ml min⁻¹. Injector was maintained at 240 °C. Oven was programmed at 60 °C to 290 °C (a) 6 °C min⁻¹ rise of temperature.

2.3. Catalyst characterization

The prepared catalysts were characterized by powder XRD, XPS, EDX, elemental mapping, transmission electron microscope (TEM), BET and Solid state UV-vis absorbance spectra. Powder X-ray diffraction (XRD) were carried on PANalytical X'pert Pro diffractometer using Cu K α radiation ($\lambda = 1.54060$ Å) over the 2θ range of 0.5-5° and 10-80°. Transmission electron micrographs were recorded on Hitachi (H-7500) operating at 120 kW. HR-TEM, EDX and elemental mapping were performed using FEI Tecnai F20 transmission electron microscope operating at an accelerating potential of 200 kV. X-ray photoelectron spectroscopy (XPS) signals were collected on KRATOS-AXIS DLD spectrometer (Kratos Analytical, U.K.) using monochromatic Al Ka radiation at 1486.6 eV operated at 10 kV. Binding energies were calibrated with C1s binding energy of standard hydrocarbons (284.6 eV). Solid state UV-visible absorption spectra were recorded in the range of 400-800 nm using Analytikjena Specord 205 spectrophotometer. Surface area, pore volume and pore size distribution were determined using BET surface area analyzer (BEL Sorp-max) by pretreating 20 mg of all samples for 2 h at 200 °C under vacuum.

3. Results and discussion

3.1. Optical properties

Fig. 1 revealed an absorption band at 518 nm for Au/ap-SBA-15 confirming the presence of Au in the samples^{20,21} while no absorption band for bare SBA-15 was observed. Presence of a broad but weak band at 480 nm for Ag/ap-SBA-15 was found to be consistent with surface plasmon resonance band of large sized AgNPs.^{22,23} A broad band centered at 756 nm for Cu/ap-SBA-15 attributed to d–d transitions of Cu²⁺ ions in a pseudo-octahedral ligand oxygen environment indicating the presence of CuO particles.²⁴ A change in color of samples was observed



Fig. 1 Solid state absorption spectra of (a) bare SBA-15, (b) Au/ap-SBA-15, (c) Ag/ap-SBA-15 and (d) Cu/ap-SBA-15 catalysts.

with metal loading from white colored bare SBA-15 to deep red, dark gray and light green for gold, silver and copper respectively, indicating the inclusion of metallic species in the mesoporous support.

3.2. Surface structural morphology

Low angle powder XRD patterns of prepared materials (Fig. 2a) displayed characteristic diffraction peaks at 0.8, 1.5 and 1.8° indexed to 100, 110 and 200 planes corresponding to 2D hexagonal symmetry¹⁹ of SBA-15. This signified the retention of long range ordering of mesochannels even after functionalization with APTMS and metal loading. However, observed decrease in the intensity of peaks for 110 and 200 planes was due to grafting of metal precursor on the surface of functionalized SBA-15 partially filling the pores. Takai et al.¹⁶ and Zhang et al.25 also observed decrease in diffraction intensities due to incorporation of Pt and Ag ions within SBA-15. Structural parameters viz. unit cell parameter (a_0) , pore wall thickness and d-spacing (Table 1, ESI-Fig. 3[†]) were found to increase for M/ap-SBA-15 indicating that metal has been incorporated in the sieves. For Ag/ap-SBA-15 and Cu/ap-SBA-15, peak corresponding to 100 plane is shifted to lower angle from 0.8° to 0.7° due to the development of strain that resulted from inclusion of comparatively large sized Ag and Cu NPs within the mesoporous sieves indicating increase in structural parameters. Similar results have also been reported by Gu et al.5 for highly dispersed Cu species within SBA-15. Wide angle XRD patterns (Fig. 2b) exhibited a broad band at $2\theta = 22^{\circ 26}$ characteristic of the



Fig. 2 (a) Low angle and (b) wide angle XRD patterns of SBA-15, ap-SBA-15 and M/ap-SBA-15 catalysts.

amorphous walls of SBA-15. In addition to the broad band, four distinct diffractions at 38°, 44.3°, 64.3°, and 77.3° corresponding to (111), (200), (220) and (311) planes of nanocrystalline Au [JCPDS: 04-0784] were observed. In Ag/ap-SBA-15 four distinct diffractions at 38.3°, 44.3°, 64.6°, 77.5° for (111), (200), (220) and (311) lattice planes confirmed the presence of Ag NPs [JCPDS: 04-0783]. However, in case of Cu/ap-SBA-15 sharp diffraction peaks were observed at 35.6°, 38.8°, 48.5°, 61.5°, 66° that could be assigned to CuO indicating the presence of comparatively large metallic crystallite size in the catalyst [JCPDS-48-1548].

TEM images of M/ap-SBA-15 catalysts (Fig. 3b–d) displayed well defined hexagonal symmetry of mesoporous channels with pore diameter ~8 nm indicating the preservation of hexagonal structure of SBA-15 (Fig. 3a). Nanospheres (NS) were observed with Au loading where as loading of Ag and Cu resulted in the formation of small nanorod (NR) of aspect ratio of 2–4 nm along with NS depicted as dark structures homogeneously dispersed against light background of SBA-15 matrix. The average particle size of NS for Cu, Ag and Au was found to be 13, 11 and 5.5 nm respectively (ESI-Fig. 1†). Moreover, STEM images and corresponding elemental mapping of the M/ap-SBA-15 catalysts (Fig. 4a–f) demonstrated the homogeneous dispersion of metallic NPs over the mesoporous support. HR-TEM micrographs and the corresponding EDX spectra of various catalysts were depicted in Fig. 5a–c. The HR-TEM images revealed that



Fig. 3 TEM images of (a) SBA-15, (b) Au/ap-SBA-15, (c) Ag/ap-SBA-15 and (d) Cu/ap-SBA-15 catalysts.

Fable 1	Physiochemical	parameters for	pure SBA-15	and M/	ap-SBA-15	catalysts
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Sample	<i>d</i> -Spacing, d_{100} (nm)	Unit cell parameter, a_0^a (nm)	Wall thickness, $d_{w}^{\ b}$ (nm)	Surface area m ² g ⁻¹	Pore volume $(cm^3 g^{-1})$	Pore diameter (nm)
SBA-15	11	12.70	1.70	664	1.3317	8.02
Ap-SBA-15	11.66	13.46	1.8	373.15	0.7132	7.64
Au/ap-SBA-15	11.11	12.82	1.71	292.67	0.6031	8.24
Ag/ap-SBA-15	11.55	13.33	1.78	694.84	1.2846	7.39
Cu/ap-SBA-15	12.28	14.18	1.90	714.81	1.33	7.48

^{*a*} $a_0 = 2/3^{1/2} d_{100}$. ^{*b*} $d_w = a_0 - d_{100}$.



Fig. 4 STEM images and elemental mapping of (a and b) Au/ap-SBA-15, (c and d) Ag/ap-SBA-15 and (e and f) Cu/ap-SBA-15 catalysts.

particles exhibited single crystalline structures with lattice fringes giving d-spacing of 0.232 nm which is close to the spacing of 0.236 nm for Au (111) planes (Fig. 5a, marked section of ESI-Fig. 6a[†]), 0.23 nm and 0.20 nm for Ag (111) and (200) planes (Fig. 5b, marked section of ESI-Fig. 6b⁺). However, lattice fringes giving d-spacing of 0.25 nm were observed for Cu/ap-SBA-15 catalyst in agreement with that of crystalline CuO (111) plane (Fig. 5c, marked section of ESI-Fig. 6c[†]) revealing that metallic CuNPs may not be formed instead, highly dispersed and crystalline CuO may be formed on the surface of the SBA-15 support as a result of oxidation of Cu in consonance with wide angle powder XRD studies. The corresponding EDX analysis further confirmed the presence of Au, Ag and CuO on the mesoporous support with Au, Ag and Cu showing 3.9, 4.25 and 0.29 wt% loading. Moreover, change in the color of prepared samples in comparison to bare SBA-15 illustrated the deposition of metallic species on the mesoporous support.

The incorporation of metallic species within SBA-15 and the elemental state of the nanocomposite materials was analyzed using XPS (Fig. 6). Au/ap-SBA-15 catalyst (Fig. 6a) showed a doublet at 83.4 eV and 87.3 eV corresponding to Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks respectively, implying the presence of metallic Au⁰ within the catalyst.^{27,28} Moreover, Ag/ap-SBA-15 catalyst



Fig. 5 HR-TEM images and EDX spectra of (a) Au/ap-SBA-15, (b) Ag/ ap-SBA-15 and (c) Cu/ap-SBA-15 catalysts.

exhibited binding energy of 367.9 eV and 373.5 eV corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ indicating Ag⁰ state and is in consonance with the reported data^{29,30} of metallic Ag (Fig. 6b). However, in Cu/ap-SBA-15 (Fig. 6c), the Cu $2p_{3/2}$ peak appeared at binding energy of 932.5 eV implying the presence of either Cu⁰ or Cu⁺¹ species³¹ suggesting that Cu may have been oxidized to Cu⁺¹ by oxygen at high temperature. Moreover, being highly susceptible to oxidation, there is a possibility that it may further reoxidise back to Cu⁺² species (as revealed in XRD studies).

Nitrogen adsorption and desorption isotherms of prepared materials (Fig. 7a) exhibited typical type IV isotherms with H₁ hysteresis curve characteristic of MMs.32 The BET profile of SBA-15 represented three well distinguished regions with monolayer multilayer adsorption ($p/p_0 = 0-0.5$), capillary condensation (p/ $p_0 = 0.5-0.8$) and multilayer adsorption on the outer surface (p/ $p_0 = 0.8$ –1.0). Moreover, a sharp inflexion was observed at relative pressure in the range of 0.5-0.8 indicative of uniform pore size distribution of SBA-15.26,33 The nitrogen adsorptiondesorption isotherm of ap-SBA-15 showed a single step adsorption-desorption branch implying no obstruction or pore blockage of silica by organic functionalities. Further observed decrease of surface area is due to presence of thin layer of APTES over SBA-15 (Table 1, ESI-Fig. 2[†]). Similar findings have been reported by Fattori et al.34 for surface functionalisation of SBA-15 with viologen. The shifting of the inflexion point to the lower pressure $(p/p_0 \sim 0.5)$ further signified the decrease in pore



Fig. 6 XPS spectra of (a) Au/ap-SBA-15, (b) Ag/ap-SBA-15 and (c) Cu/ap-SBA-15 catalysts.



Fig. 7 (a) N_2 adsorption-desorption isotherm and (b) pore size distribution of M/ap-SBA-15 catalysts.

diameter²⁶ (Fig. 7b). However, gold doped ap-SBA-15 represented a single step capillary condensation indicating presence of uniform mesopores but a two step capillary evaporation with pronounced tailing at $p/p_0 \sim 0.4$ suggested the plugging of the pores with Au during loading, consistent with pore blocking effect^{35,36} resulting in decrease of surface area and pore volume. However, a slight increase in the pore diameter was observed due to the encapsulation of metal NPs within the sieves at high calcination temperature. This leads to the development of strain resulting in decrease in surface area but increase in pore diameter. On the other hand, Ag and Cu incorporated ap-SBA-15 exhibited isotherms similar to that of bare SBA-15 with an unexpected increase in surface area possibly due to deposition of some large Ag and Cu species onto the surface of pores as can be seen in TEM images.

3.3. Catalytic activity

The reduction of *m*-DNB (Scheme 1) showed linear plots (Fig. 8a) for change in concentration of *m*-DNB ($-\ln C/C_0$ versus



Scheme 1 Selective reduction of m-dinitrobenzene to m-phenylenediamine and m-nitroaniline by M/ap-SBA-15 catalysts where M is Au, Ag or Cu.



Fig. 8 (a) Time course graph of reduction of m-DNB ($-\ln C/C_0$) by SBA-15 and M/ap-SBA-15 catalysts and (b) product distribution of m-DNB reduction (5 mM) to m-PDA and m-NA by SBA-15 and M/ap-SBA-15 catalysts.

time) for all metal loaded catalysts indicating pseudo first order kinetics. However, no change in concentration of *m*-DNB was observed with bare SBA-15. With metal loading catalytic activity improved abruptly in comparison to SBA-15 indicating that metal NPs were real active sites. However, the order of catalytic activity was found to be dependent upon nature of metal, size and metallic dispersion which inturn rely on the synthetic conditions. During the synthesis, surface of SBA-15 was functionalized with APTES, followed by metal deposition. As a result, the amine groups present on the silica surface interacted with metal species (Au/Ag/Cu) leading to uniform dispersion of metal throughout the pore channels.37-42 APTES acted as stabilizing agent by improving the interaction between metal and silica surface thus preventing aggregation of metal NPs. After metal impregnation the prepared materials were calcined to reduce metal (Au/Ag/Cu) and remove organic moieties resulting in the formation of highly dispersed metal NPs within mesoporous silica⁴³ (ESI-Scheme 1[†]). Among all the prepared catalysts, Au and Ag were reduced to metallic state with Au exhibiting the smallest particle size whereas Cu being susceptible to oxidation formed large CuO NPs (as revealed by wide angle XRD and EDX analysis). Thus, Au with smallest particle size and better metallic dispersion produced greater number of active metal sites resulting in easy accessibility of reactants and enhanced reaction rate and selectivity. Au/ap-SBA-15 exhibited the highest selectivity (89%) for m-PDA (Fig. 8b) with m-NA as an intermediate as confirmed by HPLC (ESI-Fig. 4[†]) and GC-MS (ESI-Fig. 5[†]) analysis. Rojas et al.⁴⁴ also reported the influence of particle size and metal dispersion on catalytic activity of supported platinum catalyst for the reduction of *m*-DNB. However, lower catalytic activity for Ag/ap-SBA-15 in comparison to Au/ap-SBA-15 can be explained on the basis of comparatively large sized NPs embedded on the external surface resulting in lesser number of exposed active sites and hence decreased reaction rate. In case of Cu/ap-SBA-15, Cu being highly reactive got oxidized to large CuO NPs, which present on the external surface does not allow reactant molecules to access all the reaction sites resulting in lower catalytic activity.

4. Conclusion

In summary it is represented that mesoporous SBA-15 having negligible reactivity could be effectively utilized by metal nanoparticles dispersion into pores of SBA-15 and its catalytic activity could be well tuned to the desired reach as a function of nature of metal and its dispersion density. Among the coinage metals, Au nanoparticle incorporation led to notable decrease in the surface area of SBA-15 as compared to Ag and Cu impregnation with highest catalytic activity for nitroaromatic reduction and can also be used for other industrially important reactions.

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