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Synthesis of Supported Metal Nanoparticles: Future Scope

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ABSTRACT

Octahedral Molecular Sieves (OMS-2) material was prepared by redox method and was employed as catalyst support for the preparation of heterogeneous OMS-2 supported metal catalysts. All the materials were systematically characterized using various techniques such as X-ray diffraction (XRD), N_2 adsorption-desorption, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Transmission Electron Microscopy (TEM), etc. Highly dispersed supported metal nanoparticles were synthesized using ion-exchanged method. Characterization studies confirmed that metal particles are homogeneously distributed over OMS-2 support.

Keywords: Heterogeneous catalyst, metal nanoparticles, ion-exchange method, catalysis.

INTRODUCTION

Heterogeneous catalysts widely used in numerous catalytic transformations such as dehydrogenation, hydrogenation, hydrogenolysis, oxidation, dehydration, carbon-carbon bond formation, ammonia formation, Fischer–Tropsch Synthesis, etc (Suib *et al.*, 1997; Chen *et al.*, 2001; Amin *et al.*, 2000; Suib *et al.*, 2000). Manganese containing octahedral molecular sieves (OMS-2) materials was exploited as efficient heterogeneous catalysts support for synthesis of several supported metal catalysts. OMS-2 materials possess various important features such as highly porous nature, good adsorption-desorption property, ion-exchange capacity, moderate surface acidity-basicity, etc (Suib *et al.*, 1997). Moreover, doping of other metal predominantly divalent or trivalent cations in OMS-2 changes its electronic, structural as well as catalytic properties (O'Young *et al.,* 2002). The metal-doped OMS-2 material was found to be an excellent heterogeneous catalysts for oxidation of 2-propanol (O'Young *et al.,* 2002), oxidative dehydrogenation of ethanol (O'Young *et al.,* 2002), supercritical water oxidation of pyridine (Abraham *et al.*, 1999), phenol (Abraham *et al.*, 1995), ammonia (Gloyna *et al.*, 1998), etc. In recent time we have reported efficiency of OMS-2 supported Ru nanoparticles catalyst for selective hydrogenolysis of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran and selective oxidation of HMF to 2,5-furandicarboxylic acid (Nagpure *et al.*, 2014). In the current study we have revealed the usefulness of K-OMS-2 material for the preparation of highly dispersed Cu metal nanoparticles.

MATERIAL AND METHOD

Chemicals

All chemicals utilized were of reagent grade and used without any purification. $KMnO_4$ (99%), $MnSO_4.H_2O$ (99%), $CuCl_2{\cdot}2H_2O$ (99%), HNO_3 (70%) and $NaBH_4$ were obtained from Loba chemicals, Mumbai, India.

Preparation of materials

Preparation of catalyst support (K-OMS-2)

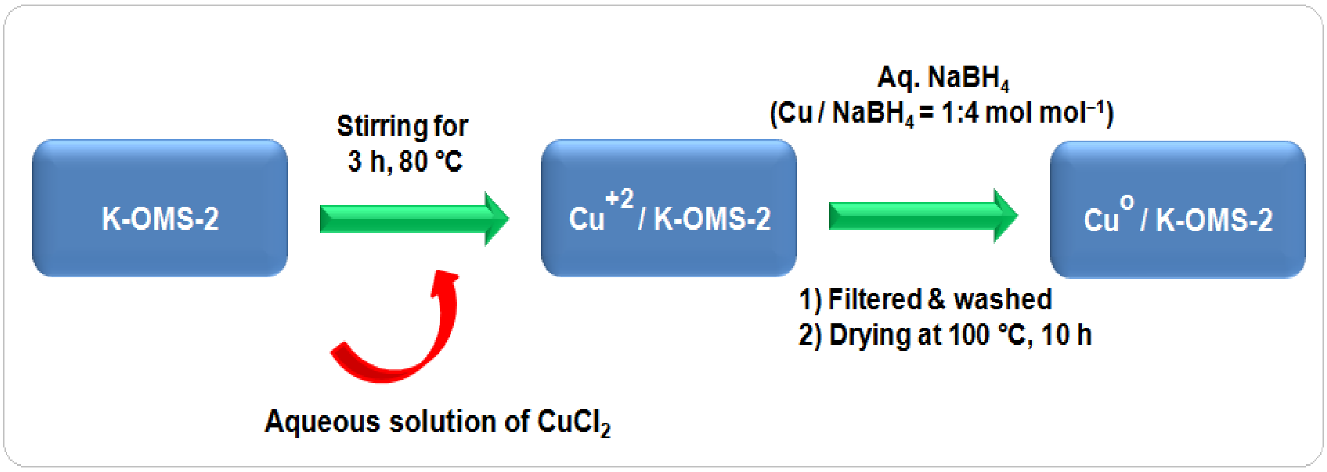
Support K-OMS-2 material was prepared according to the earlier reported literature (Newsam *et al.*, 1994). In a typical synthesis method, $KMnO_4$ (5.89 g) was added in distilled water (100 mL) and the obtained suspension was added drop by drop to a solution containing mixture of $MnSO_4$ (8.8 g in 30 mL water) and concentrated HNO_3 (3 mL) under continuous stirring at room temperature. The resulting black precipitated was reflux for 24 h (at 100 ºC). Afterward, the material was washed with distilled water until the pH become neutral. Finally, the sample was dried for 12 h (at 100 ºC) and was calcined for 3 h (at 350 ºC) to get K-OMS-2 material.

Preparation of Cu catalysts supported on K-OMS-2

Cu catalysts supported on K-OMS-2 were prepared by ion-exchange method (Scheme 1) according to previous literature (Nagpure *et al.*, 2015). In a typical synthesis procedure, K-OMS-2 material (1.96 g) was dispersed in 50 mL of deionized water in a 100 mL round-bottomed flask. To it, aqueous solution of $CuCl_2{\cdot}2H_2O$ (Cu amount was calculated for desired Cu loading) was added drop by drop under constant stirring and the obtained slurry was stirred for 3 h (at 80 °C). The solution was cooled to room temperature. Subsequently, $NaBH_4$ ($Cu/NaBH_4$ = 1:4 mol mol^{-1}) in water was added to the above solution with stirring at room temperature for 1 h to get Cu in metallic state. The mixture was filtered and washed until no chloride ions were detected (confirmed by $AgNO_3$ test). After all, the sample was dried in an oven at 100 °C for 10 h. The prepared catalysts were designated as 2wt% Cu / K-OMS-2 and 5wt% Cu / K-OMS-2.

Material Characterization

All the materials were systematically characterized by several physico-chemical characterization techniques such as X-ray diffraction (XRD), N_2 sorption, Transmission Electron Microscopy (TEM) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).



Scheme 1. Preparation of Cu / K-OMS-2 catalyst by ion-exchange method.

RESULTS AND DISCUSSION

Structural characteristics of the materials

X-ray diffraction (XRD)

The XRD patterns of K-OMS-2 and as synthesized K-OMS-2 supported Cu catalysts are depicted in Figure 1. The XRD peaks of Cu catalysts are in good agreement with the reported data (*JCPDS card 29-1020*) of cryptomelane K-OMS-2 material (Chen *et al.*, 2001; Amin *et al.*, 2000; Suib *et al., 2000*). This result signifies that cryptomelane structure of K-OMS-2 remained intact even after Cu exchanged. Importantly, the XRD peaks intensity of Cu catalysts enhances with the increased in the Cu content, demonstrating that the Cu metal assisting the crystallization. No additional peaks were detected pertaining to the metallic Cu or Cu oxides (CuO/Cu_2O), indicating that Cu nanoparticles are highly dispersed on K-OMS-2 support.

N_2 physisorption

N2 adsorption-desorption isotherm of as synthesized K-OMS-2 and Cu catalysts are given in Figure 2. All the samples showed a characteristic type II sorption, which can be attributed to the microporous nature of the samples (Nagpure *et al.*, 2016). The Brunauer–Emmett–Teller (BET) surface area values for samples are given in Table 1. The BET surface area for K-OMS-2, 2wt% Cu / K-OMS-2 and 5wt% Cu / K-OMS-2 was found to be 96, 78 and 65 m^2/g, respectively.

This result shows decreased in BET surface area of samples with increased in Cu content of the catalyst. This may be due to the blockage of pores by the Cu particles in the framework.

Table 1. Chemical composition and structural characteristics of materials

Catalyst	BET surface area (m^2/g)	Total pore volume [a] (cm^3/g)	Cu content [b] (wt%)	Average Cu particle size [c] (nm)
K-OMS-2	96	0.13	--	--
2 wt% Cu / K-OMS-2	78	0.11	1.9	2.2
5 wt% Cu / K-OMS-2	65	0.09	4.7	3.3
[a] Total pore volume at $P/P_0 = 0.899$. [b] Estimated by ICP-OES. [c] Measured by TEM.				

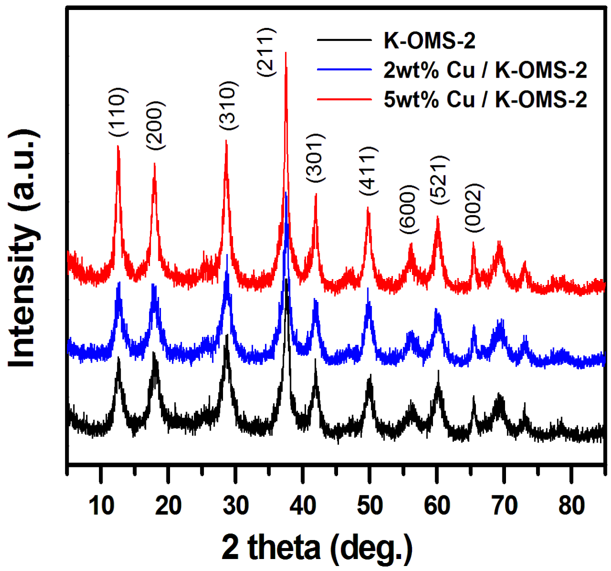


Figure 1

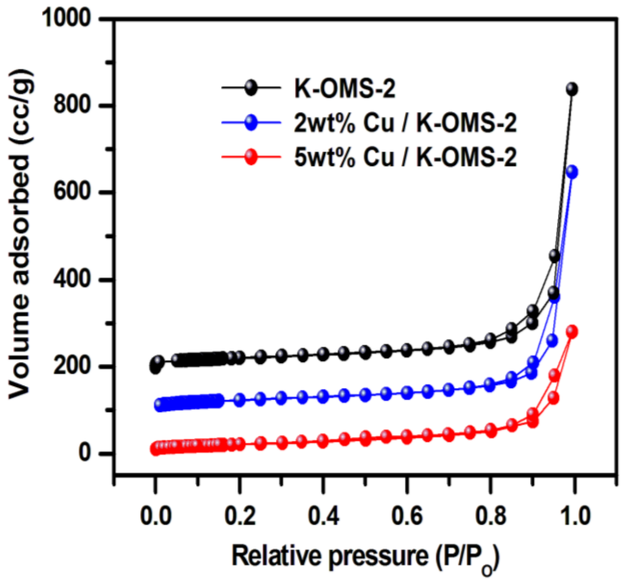


Figure 2

Figure 1. XRD patterns of K-OMS-2 and Cu catalysts.
Figure 2. N_2 adsorption-desorption isotherm of K-OMS-2 and Cu catalysts.

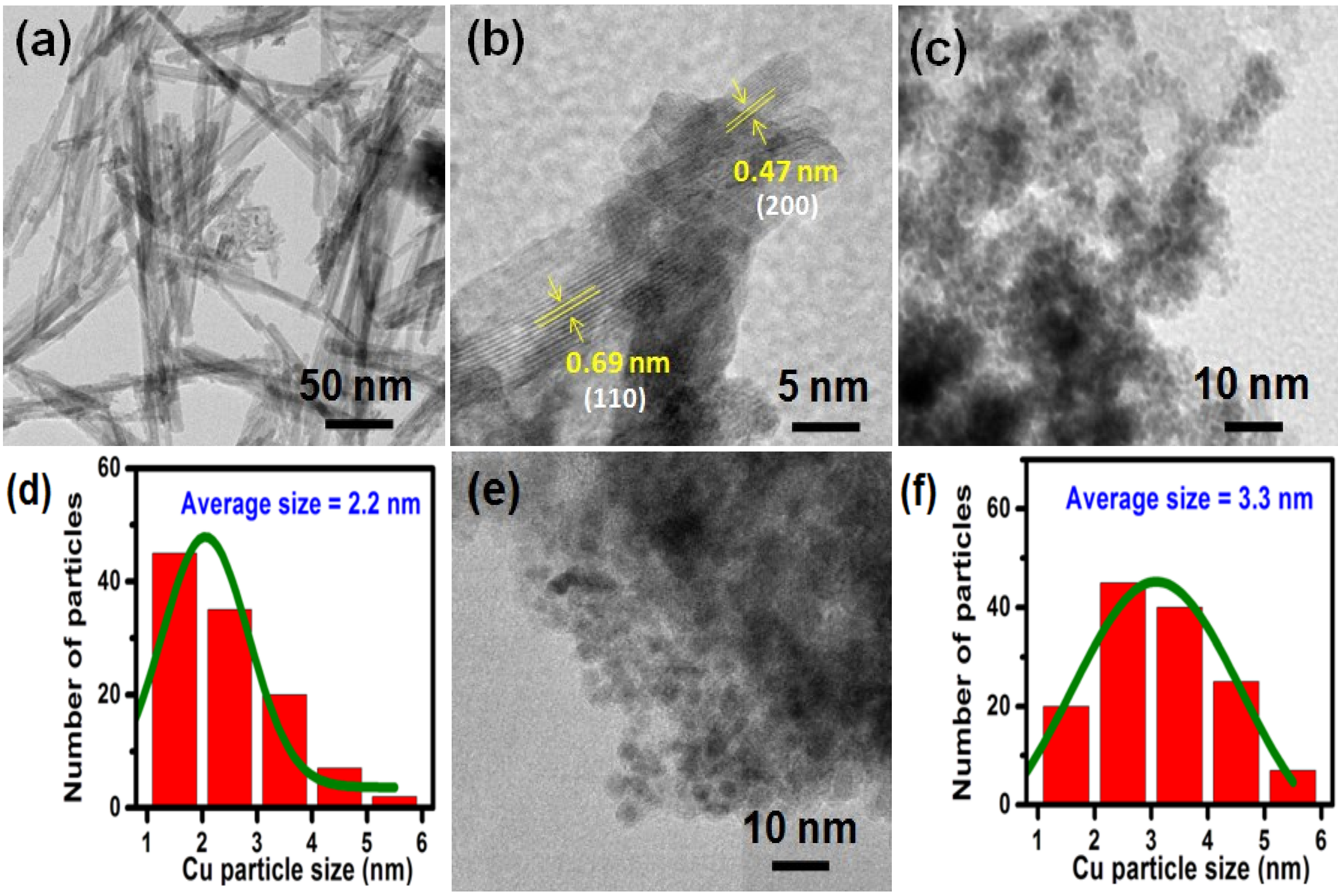


Figure 3. TEM images of K-OMS-2 (a and b), TEM images and the Cu nanoparticles size distribution for 2wt% Cu / K-OMS-2 (c and d) and for 5wt% Cu / K-OMS-2 (e and f).

Transmission electron microscopy (TEM)

TEM images of K-OMS-2 material and K-OMS-2 supported Cu catalysts are given in Figure 3. The TEM micrograph of K-OMS-2 is consist of well-defined lattice planes, confirming the good crystallinity of K-OMS-2 material (Figure 3a, b). The lattice fringes spacing of 0.47 and 0.69 nm in K-OMS-2 material are the characteristic of (200) and (110) crystal planes, respectively, which are related to the planes of the cryptomelane structure (Suib *et al.*, 1997; Chen *et al.*, 2001; Amin *et al.*, 2000; Suib *et al.,* 2000). It can be seen that the Cu nanoparticles are homogeneously distributed throughout the K-OMS-2 support. The average particle size of Cu nanoparticles in 2wt% Cu / K-OMS-2 and 5wt% Cu / K-OMS-2 catalyst was found to be 2.2 and 3.3 nm, respectively (Figure 3c, d, e, f). Therefore, it can be concluded that the K-OMS-2 support play a vital role for the stabilization of Cu nanoparticles, hence leading to smaller Cu particles.

CONCLUSIONS

Octahedral Molecular Sieve (**K-OMS-2**) material was synthesized by redox method and was used for preparation of well dispersed Cu metal nanoparticles catalysts by ion-exchange method. All the materials were studied by various physico-chemical characterizations techniques such as XRD, N_2 sorption, ICP-OES and TEM. Highly efficient Cu nanoparticles catalysts would be promising heterogeneous catalyst.

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Conflicts of interest:
The authors stated that no conflicts of interest.

REFERENCES

Aki S and Abraham MA (1999) Catalytic Supercritical Water Oxidation of Pyridine: Comparison of Catalysts, Ind. Chem. Eng. Res. 38 (2):358-367.

Chen X, Shen YF, Suib SL and O'Young CL (2001) Catalytic Decomposition of 2-Propanol over Different Metal-Cation-Doped OMS-2 Materials, J. Cat. 197 (2): 292-302.

Chen X, Shen YF, Suib SL and O'Young CL (2002) Characterization of Manganese Oxide Octahedral Molecular Sieve (M–OMS-2) Materials with Different Metal Cation Dopants, Chem. Mater. 14 (2): 940-948.

Deguzman RN, Shen Y, Neth EJ, Suib SL, Young CO, Levine S and Newsam JM (1994) Synthesis and Characterization of Octahedral Molecular Sieves (OMS-2) Having the Hollandite Structure, Chem. Mater. 6 (6):815-821.

Ding ZY, Aki S and Abraham MA (1995) Catalytic Supercritical Water Oxidation: Phenol Conversion and Product Selectivity, Environ. Sci. Tech. 29 (11): 2748-2753.

Ding ZY, Li L, Wade D and Gloyna EF (1998) Supercritical Water Oxidation of NH3 over a MnO2/CeO2 Catalyst, Ind. Chem. Eng. Res. 37 (5): 1707-1716.

Dyer A, Pillinger M, Newton J, Harjula R, Moller T and Amin S (2000) Sorption Behavior of Radionuclides on Crystalline Synthetic Tunnel Manganese Oxides, Chem. Mater. 12 (12): 3798- 3804.

Lucas N, Kanna NR, Nagpure AS, Kokate G and Chilukuri S (2014) Novel catalysts for valorization of biomass to value-added chemicals and fuels, Journal of Chemical Sciences, 126 (2): 403-413.

Luo J, Zhang Q, Huang A and Suib SL (2000) Total oxidation of volatile organic compounds with hydrophobic cryptomelane-type octahedral molecular sieves, Micro. Meso. Mater. 35–36: 209-217.

Nagpure AS, Gurrala L, Gogoi P and Chilukuri S (2016) Hydrogenation of cinnamaldehyde to hydrocinnamaldehyde over Pd nanoparticles deposited on nitrogen-doped mesoporous carbon, RSC Adv., 6 (50): 44333-44340.

Nagpure AS, Lucas N and Chilukuri S (2015) Efficient Preparation of Liquid Fuel 2,5-Dimethylfuran from Biomass-Derived 5-Hydroxymethylfurfural over Ru–NaY Catalyst, ACS Sustainable Chemistry & Engineering, 3 (11): 2909-2916.

O'Young CL, Sawicki RA and Suib SL (1997) Micropore size distribution of octahedral molecular sieves (OMS), Micro. Mater. 11 (1-2): 1-8.