

Original Research Article

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## EFFICIENT METHOD FOR PREPARATION OF HIGHLY DISPERSED METAL NANOPARTICLES SUPPORTED ON OCTAHEDRAL MOLECULAR SIEVES

Atul S. Nagpure<sup>1\*</sup>, Pranjal Gogoi<sup>2</sup>, Nilesh G. Gode<sup>1</sup>, Anil N. Korpenwar<sup>3</sup>

1. Department of Chemistry, Rashtrapita Mahatma Gandhi Arts & Science College, Nagbhid, Dist-Chandrapur, Maharashtra-441205, INDIA.
2. Catalysis & Inorganic Chemistry Division, CSIR-National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune-411008, INDIA.
3. Department of Botany, Rashtrapita Mahatma Gandhi Arts & Science College, Nagbhid, Dist-Chandrapur, Maharashtra-441205, INDIA.

**ABSTRACT:** Cryptomelane type microporous manganese oxide Octahedral Molecular Sieve (K-OMS-2) material was synthesized through redox method. This novel K-OMS-2 material was employed as a catalyst support for the preparation of highly dispersed Cu nano catalysts via ion-exchange process. The chemical composition, structure, texture and morphology of all the materials were investigated by various physico-chemical characterization techniques such as X-ray diffraction (XRD), N<sub>2</sub> sorption, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), etc. Highly dispersed Cu nanoparticles supported on K-OMS-2 catalysts hold significant potential as a good heterogeneous catalyst in numerous chemical processes like hydrogenation, oxidation, dehydrogenation, coupling reaction, etc.

**KEYWORDS:** Octahedral Molecular Sieve; Cu nano catalyst; high metal dispersion; catalysis.

**\*Corresponding Author: Dr. Atul S. Nagpure, Ph.D.,**

Department of Chemistry, Rashtrapita Mahatma Gandhi Arts & Science College, Nagbhid, Dist-Chandrapur, Maharashtra-441205, INDIA. \* **Email Address:** atulnagpure43@gmail.com

### 1. INTRODUCTION

Manganese oxide octahedral molecular sieve (OMS) type materials were extensively employed as efficient catalysts in many chemical transformations because of their highly porous structure,

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adsorption-desorption property, ion-exchange ability and moderate surface acidity–basicity [1]. Microporous manganese oxide OMS materials have pore dimensions close to zeolites [1]. Importantly, transition metal ion incorporated (especially divalent and trivalent ion) cryptomelane type manganese oxide (**OMS-2** type material with 2 x 2 matrix) having one dimensional tunnel structure, has been emerged as highly efficient catalyst for oxidation of alcohols and side chains in organic molecules [2]. Incorporation or doping of foreign metal mostly divalent or trivalent cations in **OMS-2** changes its structural, electronic and catalytic properties as well [3]. The choice of metal cations ( $M^{+2}/M^{+3}$ ) was mainly determined by their charge, polarizability and size. The metal doped **OMS-2** catalyst has been verified as a potential catalyst for oxidation of 2-propanol [3], oxidative dehydrogenation of ethanol [3], supercritical water oxidation of pyridine [4], phenol [5], ammonia [6], etc. Recently, we have reported the effectiveness of Ru doped K-OMS-2 catalyst for hydrogenolysis and oxidation of biomass-derived 5-hydroxymethylfurfural [7]. In the present study we have demonstrated the utility of K-OMS-2 material for the preparation of highly dispersed Cu nanoparticles via ion-exchange method. This K-OMS-2 supported Cu nanoparticles catalysts hold considerable potential as an excellent heterogeneous catalyst in several chemical processes.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

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

### 2.2. Synthesis of materials

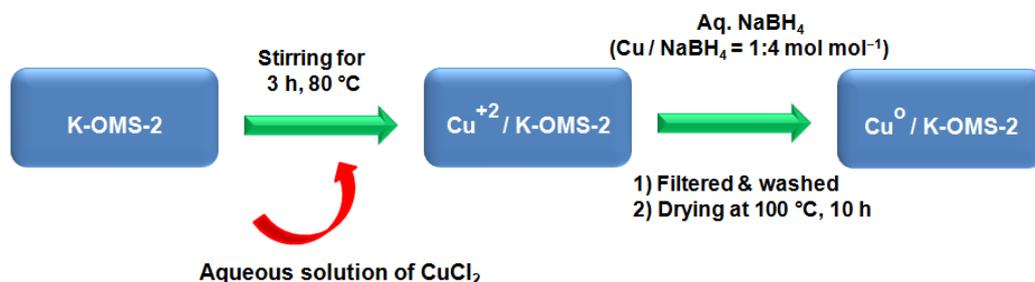
#### 2.2.1. Synthesis of K-OMS-2

Support K-OMS-2 material was synthesized according to the reported literature [8]. In a typical synthesis method,  $KMnO_4$  (5.89 g) was dispersed in distilled water (100 mL) and the resulting 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 constant stirring at room temperature. The obtained black precipitated was reflux for 24 h at 100 °C. The resulting material was washed with distilled water until the pH become neutral. Lastly, the sample was dried for 12 h at 100 °C and was calcined at 350 °C for 3 h to get K-OMS-2 material.

#### 2.2.2. Synthesis of K-OMS-2 supported Cu catalysts

K-OMS-2 supported Cu catalysts were synthesized by ion-exchange method according to previous literature [9] and the synthesis method is shown in Scheme 1. 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 continuous stirring and the obtained slurry was stirred for 3 h at 80 °C. The solution was cooled to room temperature. Afterwards,  $NaBH_4$  ( $Cu/NaBH_4 = 1:4 \text{ mol mol}^{-1}$ )

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 in water was added to the above solution with stirring at room temperature for 1 h to get Cu in its metallic state. The mixture was filtered and washed until no chloride ions were detected (confirmed by AgNO<sub>3</sub> test). Finally, the sample was dried in an oven at 100 °C for 10 h. Above procedure was used to prepare 2wt% Cu / K-OMS-2 and 5wt% Cu / K-OMS-2 catalysts.



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

### 2.3. Material Characterization

All the materials were characterized by various physico-chemical characterization techniques like X-ray diffraction (XRD), N<sub>2</sub> sorption, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). XRD patterns of all the samples were collected using a PANalytical X'pert Pro dual goniometer. Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 40 kV, 30 mA) with Nickel filtered was employed. The analysis was recorded using a flat holder in Bragg–Brentano geometry. The data were collected in the range of  $2\theta = 5\text{--}90^\circ$  (with  $0.02^\circ$  step size). The BET surface area of the samples was calculated by using N<sub>2</sub> sorption isotherm at  $-196^\circ\text{C}$  (Quantachrome Autosorb IQ). The material was evacuated at  $250^\circ\text{C}$  for 3 h at a residual pressure of  $2 \times 10^{-3}$  Torr before analysis. SEM images of the samples were recorded using JEOL-JSM-5200 to study the morphology. The samples were prepared by dispersing them ultrasonically in 2-propanol, transferring them on to a sample holder and subsequently dried and gold coated before analysis. TEM images of samples were obtained using a FEI Technai TF-30 instrument operating at 300 kV. The samples for TEM analysis were prepared by placing a droplet of the sample suspension prepared in 2-propanol using ultrasonication on a carbon coated copper grid and by leaving them for drying at room temperature. The amount of Cu present in the catalysts was estimated by ICP-OES (Spectro Arcos, FHS-12) instrument equipped with the Winlab software. Standard solutions containing different concentration of Cu were used for the calibration purpose. The solid samples were digested with aqua-regia before analysis.

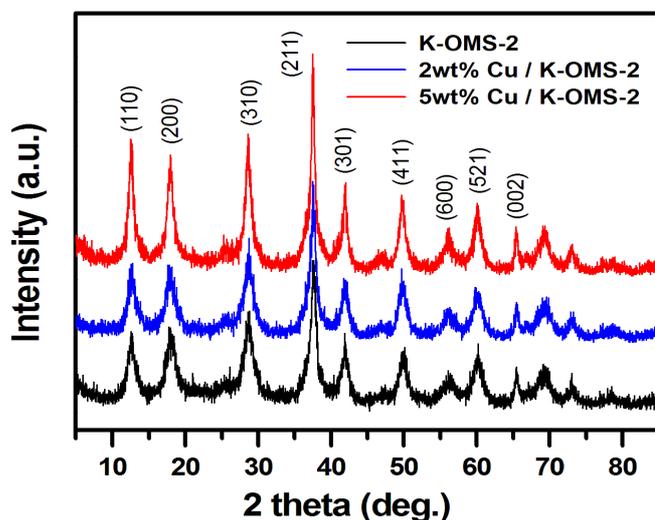
## 3. RESULT AND DISCUSSION

### 3.1. Structural characteristics of the catalysts

#### 3.1.1. 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 [2] of

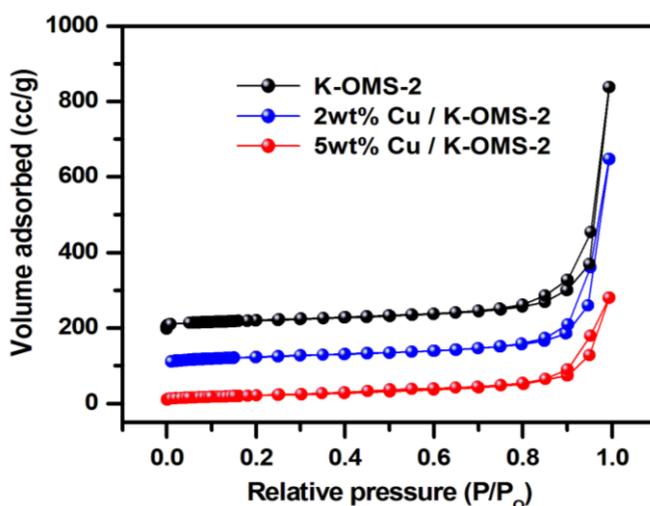
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 cryptomelane K-OMS-2 material (JCPDS card 29-1020). This result signifies that cryptomelane structure of K-OMS-2 remained intact even after Cu exchanged. Importantly, the XRD peaks intensity of Cu catalysts enhances with the increased in the Cu content, demonstrating that the Cu metal assisting the crystallization. No additional peaks were detected pertaining to the metallic Cu or Cu oxides (CuO/Cu<sub>2</sub>O), indicating that Cu nanoparticles are highly dispersed on K-OMS-2 support.



**Figure 1.** XRD patterns of K-OMS-2 and Cu catalysts.

### 3.1.2. N<sub>2</sub> physisorption

N<sub>2</sub> 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 [10]. 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<sup>2</sup>/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.



**Figure 2.** N<sub>2</sub> adsorption-desorption isotherm of K-OMS-2 and Cu catalysts.

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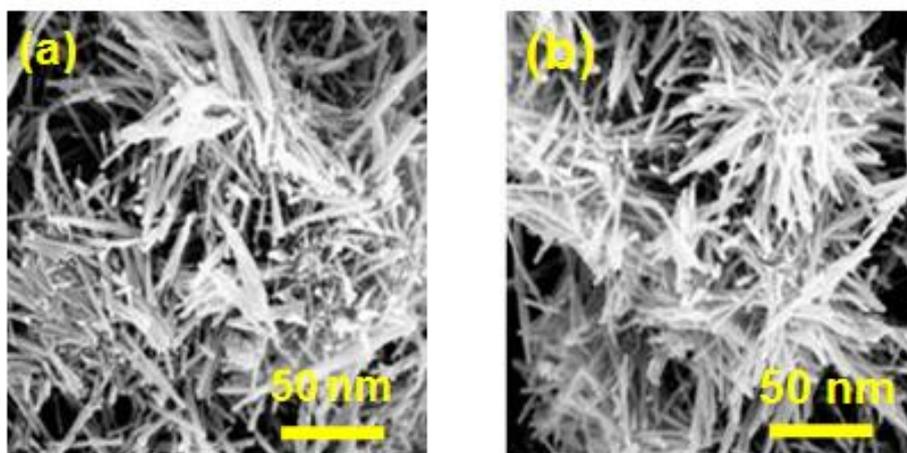
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<b>Table 1.</b> Chemical composition and structural characteristics of materials.				
Catalyst	BET surface area (m <sup>2</sup> /g)	Total pore volume <sup>[a]</sup> (cm <sup>3</sup> /g)	Cu content <sup>[b]</sup> (wt%)	Average Cu particle size <sup>[c]</sup> (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

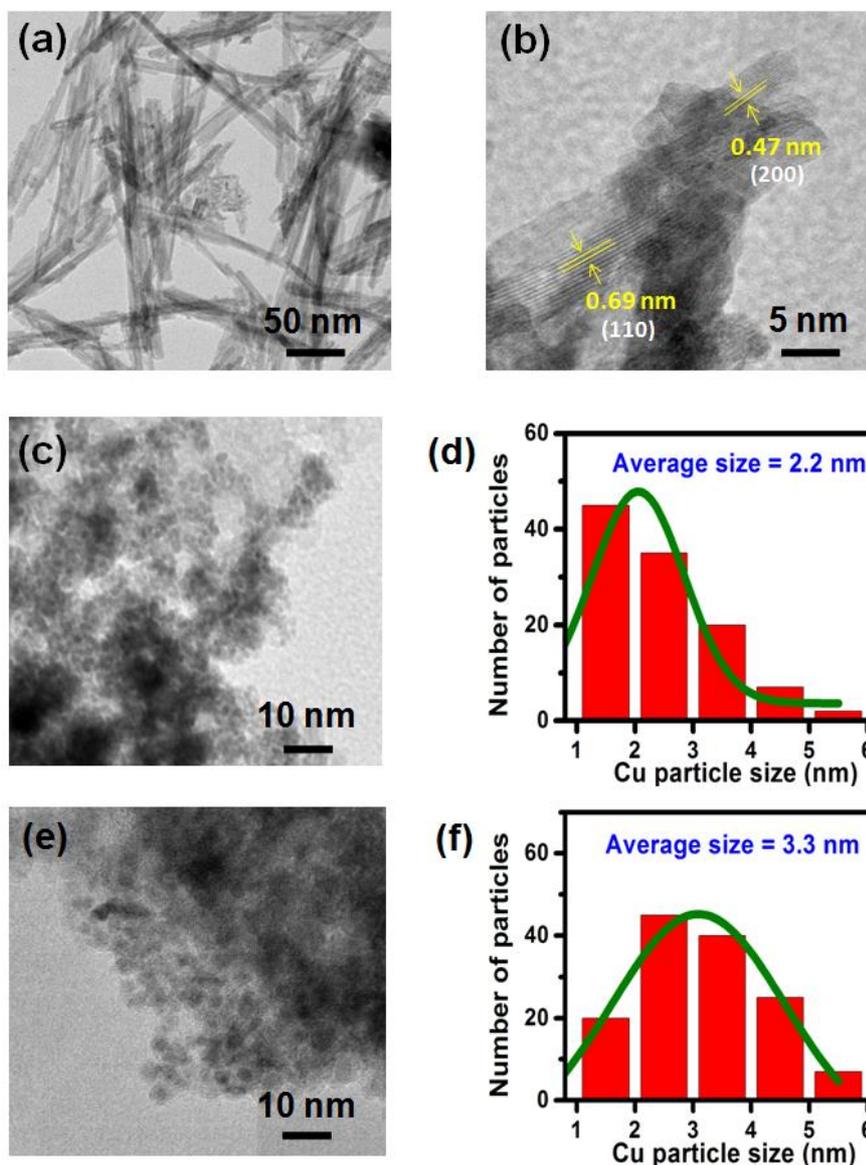
<sup>[a]</sup> Total pore volume at P/P<sub>0</sub> = 0.899. <sup>[b]</sup> Estimated by ICP-OES. <sup>[c]</sup> Measured by TEM.

### 3.1.3. Scanning electron microscopy (SEM)

The morphology of K-OMS-2 and Cu catalysts was studied by SEM and the results are given in Figure 3. The SEM micrographs clearly revealed that K-OMS-2 material is consisting of fibrous-needles like morphology with sharp tip, which crystallizes in “c-direction” leading to the formation of fibrous/nanorods structure [1-3]. The morphologies of K-OMS-2 supported Cu catalysts was found to be similar to that of K-OMS-2.



**Figure 3.** SEM images of (a) K-OMS-2 and (b) 2wt% Cu / K-OMS-2 catalyst.



**Figure 4.** 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).

#### 3.1.4. Transmission electron microscopy (TEM)

TEM images of K-OMS-2 material and K-OMS-2 supported Cu catalysts are given in Figure 4. The TEM micrograph of K-OMS-2 is consist of well defined lattice planes, confirming the good crystallinity of K-OMS-2 material (Figure 4a,b). The lattice fringes spacing of 0.47 & 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 [1-3]. 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 4c,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.

#### 4. CONCLUSION

Manganese oxide Octahedral Molecular Sieve (K-OMS-2) material was prepared by redox method. Highly dispersed Cu nanoparticles supported on K-OMS-2 were synthesized by ion-exchange method. All the materials were examined by various physico-chemical characterizations technique like XRD, N<sub>2</sub> adsorption-desorption, ICP-OES, SEM and TEM. Highly efficient Cu nanoparticles catalysts would be promising heterogeneous catalyst in chemical transformations.

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#### CONFLICT OF INTEREST:

The authors have no conflict of interest.

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