OCTAHEDRAL MOLECULAR SIEVE (K-OMS-2) SUPPORTED METAL NANOPARTICLES FOR CATALYSIS

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ABSTRACT:

Catalysis plays an important role in synthesis of many fine chemicals and fuels via numerous chemical processes like hydrogenation, oxidation, dehydrogenation, etc. Herein, we have demonstrated first time the efficiency of cryptomelane type microporous manganese oxide Octahedral Molecular Sieve (K-OMS-2) material for the preparation of highly dispersed Cu nanoparticles. The catalysts were systematically studied by X-ray diffraction (XRD), N_2 sorption and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) techniques. This K-OMS-2 supported Cu catalyst hold important potential as a good heterogeneous catalyst.

Keywords: Heterogeneous catalysts, Octahedral Molecular Sieve; Cu nano catalyst; catalysis.

1. INTRODUCTION

Catalysis is an essential part of daily life. Notably, supported metal catalysts were extensively utilized as superior catalysts in many chemical transformations. Manganese oxide octahedral molecular sieve (OMS) type materials possess highly porous structure, adsorption-desorption property, ion-exchange ability and moderate surface acidity–basicity.[1] Microporous manganese oxide OMS materials has 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. EXPERIMENTAL SECTION

2.1. Chemicals

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

2.2. Synthesis of materials

2.2.1. Preparation of K-OMS-2 material

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 mixture 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 ºC. The resulting material was washed with distilled water until the pH become neutral. Lastly, the sample was dried for 12 h at 100 ºC and was calcined at 350 ºC for 3 h to get K-OMS-2 material.

2.2.2. Preparation of Cu catalysts supported on K-OMS-2

Cu catalysts supported on K-OMS-2 were synthesized by ion-exchange method according to previous literature.[9] In a typical synthesis procedure, K-OMS-2 (1.96 g) was dispersed in 50 mL of deionized water in a round-bottomed flask (100 mL). 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 mol mol^{-1}) 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 $AgNO_3$ 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.

2.3. Material Characterization

All the samples were characterized by various physico-chemical characterization techniques like X-ray diffraction (XRD), N_2 sorption and Inductively Coupled Plasma-Optical Emission Spectrometry **(**ICP-OES).

3. RESULTS AND DISCUSSION

3.1. Structural characteristics of the catalysts

3.1.1. X-ray diffraction (XRD)

The XRD patterns of K-OMS-2 material 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 of cryptomelane K-OMS-2 material (JCPDS card 29-1020).[2] 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.

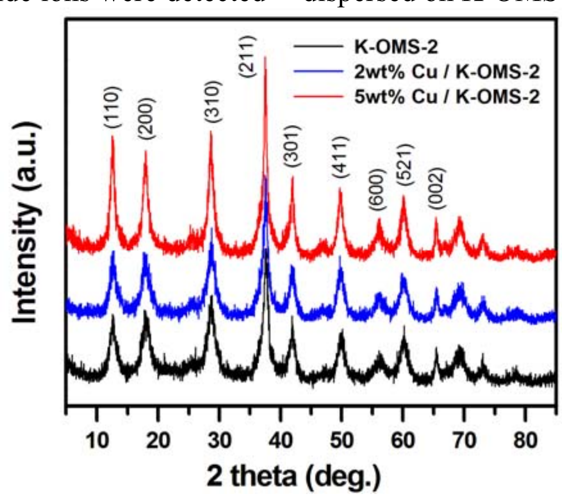

Figure 1. XRD patterns of K-OMS-2 and Cu catalysts.

3.1.2. N_2 physisorption

Figure 2 shows the N_2 adsorption-desorption isotherm of as synthesized K-OMS-2 and Cu catalysts. All the materials 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^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.

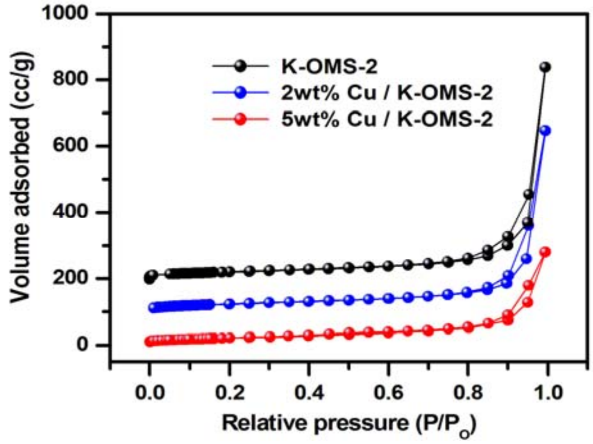

Figure 2. N_2 adsorption-desorption isotherm of K-OMS-2 and Cu catalysts.

Table 1. Chemical composition and structural characteristics of catalysts.

Catalyst	BET surface area (m^2/g)	Total pore volume [a] (cm^3/g)	Cu content [b] (wt%)
K-OMS-2	96	0.13	--
2 wt% Cu / K-OMS-2	78	0.11	1.9
5 wt% Cu / K-OMS-2	65	0.09	4.7

[a] Total pore volume at $P/P_0 = 0.899$. [b] Estimated by ICP-OES.

4. CONCLUSIONS

Manganese oxide Octahedral Molecular Sieve (K-OMS-2) material was synthesized by redox method. K-OMS-2 supported highly dispersed Cu nanoparticles catalysts were synthesized by via ion-exchange method. All the materials were examined by various physico-chemical characterizations techniques. Highly efficient Cu nanoparticles catalysts would be promising heterogeneous catalyst in numerous chemical transformations.

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CONFLICT OF INTEREST:

The authors have no conflict of interest.

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