

NANOCRYSTALLINE COPPER OXIDE HIGHLY DISPERSED ON MESOPOROUS ALUMINA BY INCIPIENT WETNESS IMPREGNATION METHOD: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

A low-cost Cu/Al₂O₃ nanocatalyst was prepared and characterized by using diverse instrumental techniques. Brunauer Emmett Teller (BET) study exhibits that the Specific surface area and pore diameter of nanocatalyst was 63.29 m²/g and 10.7 nm, respectively. X-ray Diffraction (XRD) study shows that the crystalline size of the nanocatalyst was 24.31 nm. Morphology of the nanocatalyst showed needle and plate-like structures using Field Emission Scanning Electron Microscopy (FESEM). The nanocatalyst has high stability till 700 °C was confirmed by thermogravimetric analysis (TGA).

Keywords: Mesoporous Materials, Wet Impregnation Method, X-ray Techniques, Catalyst, Thermal Analysis.

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INTRODUCTION

Nanoparticles are considered as a good resource for various chemical processes due to its best catalytic activity and used in industry and academia.¹⁻³ Copper nanoparticles are very attractive owing to its availability, cheap and the simplicity of practical ways of synthesizing Cu-based nonmaterial.^{4,5} Furthermore the wide range of oxidation states (Cu⁰, Cu^I, Cu^{II}, Cu^{III}) of copper-based materials facilitates them to undergo a variety of reactions thus they find application in nanotechnology including electrocatalysis, organic transformations and photocatalysis.⁶⁻⁸ Preparation of highly active, stable and inexpensive catalytic nanoparticles is highly challengeable.^{9, 10} Copper oxide (CuO) nanostructures have distinctive benefits with chemical stability, high specific surface area, and electrochemical activity.¹¹ Metal oxides like ceria, alumina, zinc oxide, magnesium oxide, titania and zirconia are commonly used supports for Cu-based nanoparticles.¹² Recently, various researchers are highly interested to synthesize metal oxide supported Cu-based nonmaterial since they are compatible with high temperature and pressure chemical reactions.^{13, 14} Very few studies have reported Al₂O₃ as support for copper metal by incipient wetness impregnation method due to the formation of aggregates.¹⁵ The present study solely focuses on various properties of alumina supported copper nanoparticles. In this work, industrially important Cu/Al₂O₃ catalysts were synthesized using rarely studied precursors by incipient wetness impregnation method and described by XRD, FESEM, EDX, BET and TGA methods.

EXPERIMENTAL

Apparatus and Reagents

The chemicals used in this study were acquired from Sigma-Aldrich and utilized as received. Copper (II)

Rasayan J. Chem., 13(4), 2188-2192(2020)

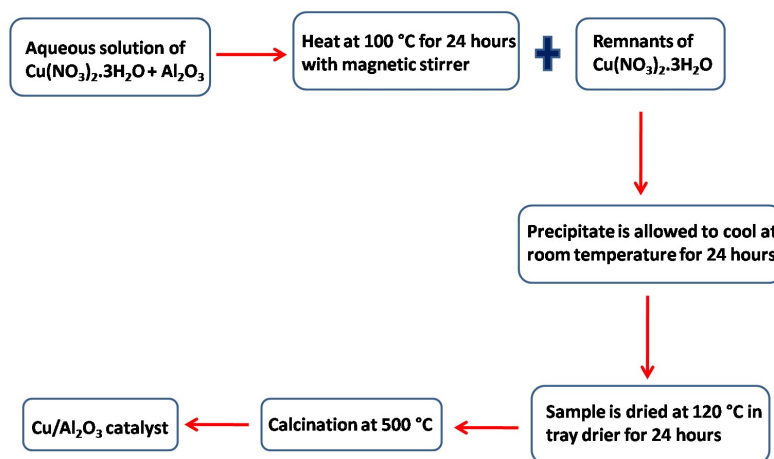
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nitrate trihydrate and aluminium oxide were the precursors used. 1 M stock solution of the precursors was prepared using double distilled water. FESEM-EDX analysis was executed by using CARL Zeis supra 55 with the oxford INCAs400. Powder X-ray diffraction was recorded on Rigaku Geiger flex X-ray diffractometer in the range of 2 theta values 20-80°. The size of the crystal was obtained using the Debye Scherer equation. The Specific surface area of the catalyst, pore volume and pore diameter were verified by nitrogen adsorption-desorption isotherms by a Micrometrics ASAP2020 automated system and Thermo Gravimetric Analysis was carried out by TGAQ500V20.10 Build 36.

Preparation of Cu/Al₂O₃

The atomic percentage of Cu/Al = 0.5 was prepared. 80 ml of copper nitrate solution was added to the 100 ml of Al₂O₃ solution, and followed by the reaction mixture was continuously stirred with heating at 90 °C, until it gets saturated. Then remaining 20 ml of the copper nitrate solution was added to the saturated solution and continuously stirred with heating till a precipitate is formed. The precipitate was allowed to cool and kept in a closed container for over 24 h at room temperature. Further, it was dried for 24 h in a tray drier until moisture content gets eliminated. The dried catalyst was introduced for calcinations in a muffle furnace at 500 °C for 20 h (Scheme-1).



Scheme-1: Synthetic Method of Cu/Al₂O₃Catalyst

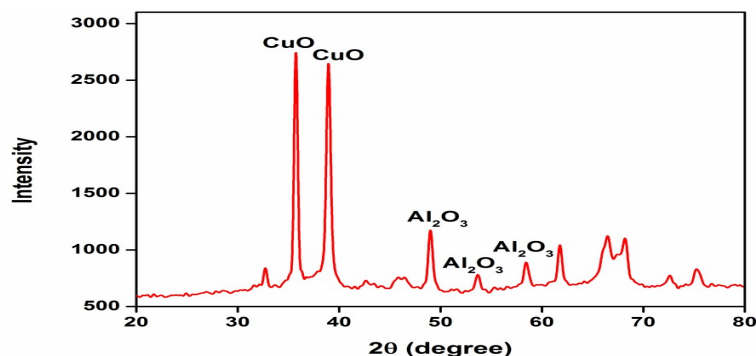
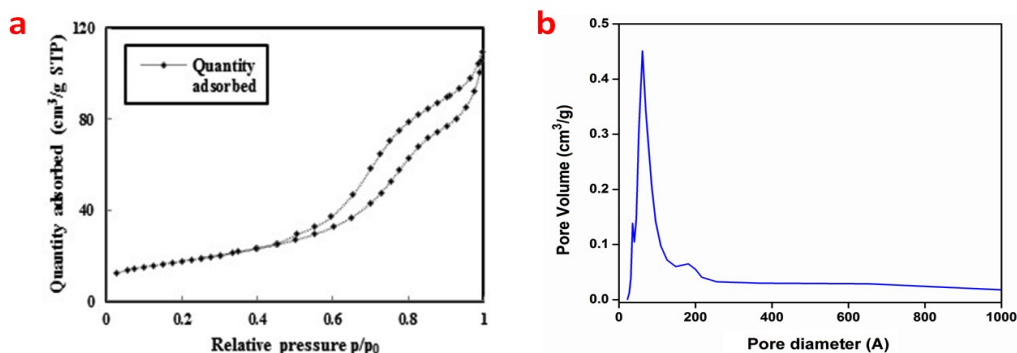
RESULTS AND DISCUSSION

XRD Analysis

XRD analysis of Cu/Al₂O₃ nanocatalyst has been exhibited in Fig.-1. All the XRD patterns exhibit narrow diffraction peaks due to good crystalline nature. The peaks appearing at $2\theta = 49^\circ, 53^\circ, 59^\circ$ in diffraction patterns were attributed to the support structure of Al₂O₃ (JCPDS 82-1468) is orthorhombic in phase. The signals relating to other oxides phases of CuO were observed at position $2\theta = 35^\circ$ and 39° corresponding to the (0 0 2) plane of end centered monoclinic structure of CuO. The average crystallite size of Cu/Al₂O₃ nanoparticles obtained was estimated to be around 24.31 nm using the Debye Scherer equation. High-intensity peaks for CuO shows the even dispersion of copper on support, which was also confirmed in BET analysis.

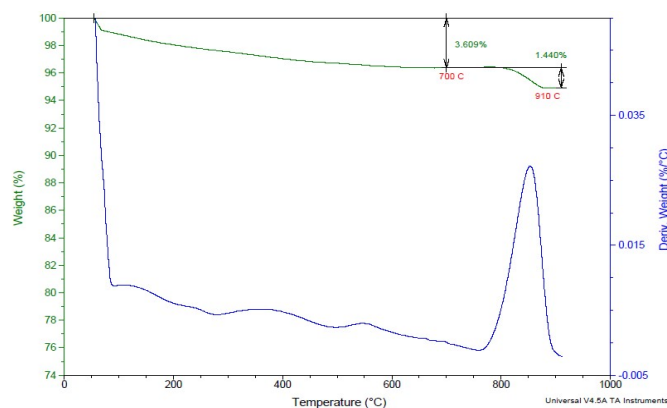
Specific Surface Area Determination

Figure-2 shows the nitrogen adsorption/desorption isotherm (class IV type of adsorption) of the synthesized nanocatalyst designating the existence of interparticle and non ordered mesoporosity in the sample. This study revealed that the isotherm undergoes abrupt changes when the relative pressure is in the medium range from 0.6 to 0.9 and the formation of hysteresis which confirms the catalyst to be mesoporous nature. The other significant findings were examined in this analysis as follows: BET specific surface area is 63.29 m²g⁻¹, the pore volume is 0.169 cm³g⁻¹. To evaluate the porous properties of the sample, BJH pore plot was recorded. Based on the BJH pore distribution curve, the major pore size is found to be 10.7 nm.

Fig.-1: XRD Pattern of Prepared Cu/Al₂O₃CatalystFig.-2: (a) N₂ Adsorption/Desorption Isotherm of Cu/Al₂O₃ Catalyst, (b) BJH Plot of Cu/Al₂O₃ Catalyst

Thermogravimetric Analysis

Thermogravimetric analysis for Cu/Al₂O₃ catalyst is given in Fig.-3. Two endothermic peaks may be observed on the DTA curve approximately at 100 °C and 760 °C. It was related to the evaporation of residual moisture and weight loss caused by the decomposition of nitrates, tenorite - alumina conversion and CuO formation.¹⁶ It was observed that a weight loss of about 3 wt. % of the synthesized catalyst was observed at 700 °C. Similarly, several exothermic peaks were observed at 220, 380, 550 °C due to the phase transformation of Al₂O₃ and the intensive increase on the TG curve was recorded approximately to 910 °C. From TGA analysis it was concluded that the catalyst was stable till 700 °C, and after that, it was showing the loss of mass in its weight. Further, maximum weight loss at 910 °C was observed from the thermal curve.

Fig.-3: TGA Analysis of Cu/Al₂O₃ Catalyst

FESEM Analysis and EDX Analysis

As shown in Fig.-4a and 4b, two different types of microstructure comprised needle-like crystallites as its major part and the remaining portion was composed of a plate or sheet-like crystallites. Further, the sheet-

like structure of the synthesized catalyst showed that the adsorption of Cu can occur on both the external surface and interlayer spaces (Fig.-4c). The elemental EDX analysis results are given in Fig.-4d and 4e. The identified peaks correspond to the elements present in the nanocomposite are Cu, Al and O and it showed that copper has high dispersion and distributed homogeneously on all the surface of alumina.

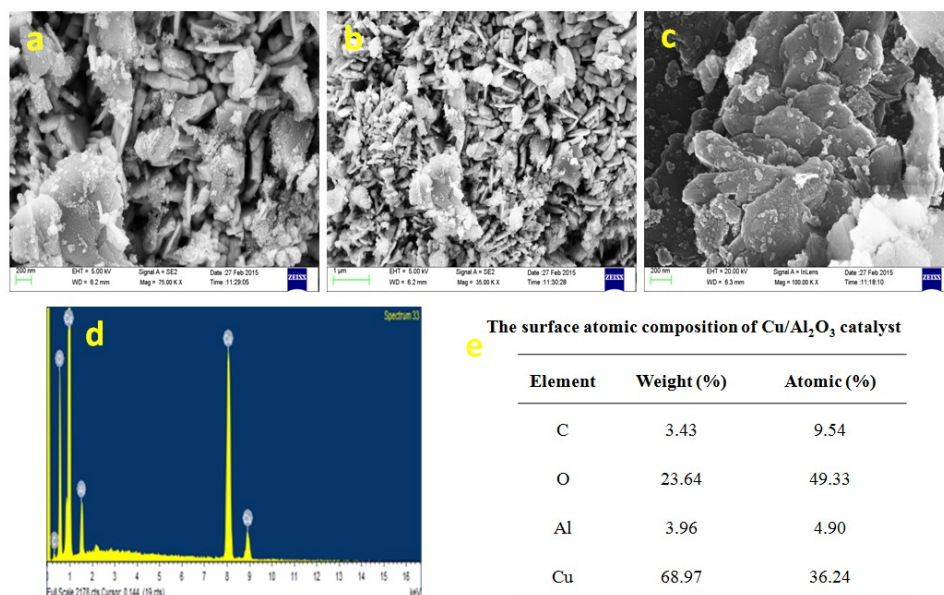


Fig.-4: (a-c) SEM Images of Cu/Al₂O₃Catalyst with Diverse Magnifications and (d and e) Elemental EDX Analysis Results of Cu/Al₂O₃Catalyst

CONCLUSION

Cu/Al₂O₃nanocatalyst was successfully synthesized using an incipient wet impregnation technique and characterized by diverse techniques. XRD result confirms the crystalline nature of the catalyst and the crystalline size of the catalyst was calculated to be 24.31 nm by the Debye Scherer equation. The morphological analysis of the catalyst shows that the needle and plate-like microstructures were observed. The surface area of the prepared catalyst was determined to be 63.29 m²/g using BET analysis. The nanocatalyst has good stability till 700 °C was confirmed by TGA method.

ACKNOWLEDGEMENT

M.A.J. thanks Sathyabama Institute of Science and Technology and Sethu Institute of Technology for providing their lab and instrumentation facilities.

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[RJC-5903/2020]