NUST Journal of Engineering Sciences, Vol. 7, No. 1, 2014, pp. 38-41

Modified Metal Catalysts with Enhanced Surface Area and their Activity

Tajamal Hussain[1]*, Adnan Mujahid[1], Munazza Ashraf[1], Farah Tufail[1]
Hamid Raza[1], Khurram Shehzad[2]
[1] Institute of Chemistry, University of the Punjab, 54590-Lahore, Pakistan.
[2] Centre for Nano and Micro Mechanics, Tsinghua University, Beijing, People's Republic of China
Corresponding Author: *tajamalhussain.chem@pu.edu.pk

Abstract

Catalysts play an important role in order to enhance the efficiency of the chemical processes. Catalysis being surface phenomena, catalytic activity mainly depends on total surface area of the active metal dispersed on supported material. Metals were often used as catalysts for electrochemical and chemical reactions. In this study, different techniques were employed to prepare/modify some of the metal based catalysts. Modification of metals, from first row of transition series and lead, was done in terms of particles size and their distribution. Electrodes of copper and zinc were modified by creating nano clusture on their surface through electro chemical deposition. More importantly these modified electrodes were employed to check their catalytic activity for the oxidation of methanol and ethanol in basic environment. That is one of the potential reactions which occur in fuel cell. Secondly, hydrothermal method was adopted for the synthesis of the metal nanoparticles of copper and lead. Synthesized materials were tested against their catalytic activity for redox reaction of organic dye i.e. methylene blue which exhibited substantial catalytic activity. Moreover, scanning electron microscopy images were used for investigating surface morphology of prepared/modified materials.

Key words: Catalyst, Electrode, Electroxidation, SEM, Copper, Zinc, Lead

Introduction

Since huge number of publications have been devoted to field of nanoscience in the last decade [1]. This field emerges as major research direction. Nanoscience has wide spread application in various fields like catalysis, sensors, model membrane systems, solubilization media and drug delivery [2-6]. Many interesting properties like large specific area and quantum size effect have been evolved when the size of the materials revolve around 100nm [7-12]. There is a considerable interest in the fabrication of high surface area metal nanostructures as thin films for a wide variety of applications including energy storage (super capacitors), energy conversion (fuel cells), separations (electrochemical chromatography) and sensors [13-16]. Towards this end, a common approach has been observed that classical materials should have been replaced with materials of nano size in order to have maximum control on the features and characteristics.

Large number of research groups are working on synthesis and characterization of the nanoparticles [17-19]. They observed that there was possibility to have the desired properties through the control over size of particles. This trend is equally frequent in the field of catalysis [20-22]. Catalytic efficiency of the catalyst mainly depends upon the surface area and dimensions of nano size catalysts. Owing to the achievements of interesting and desired properties, efficiency of the catalyst can be enhanced to make the process economical. Therefore, field of nanocatalysts looks very promising to work on. In the present work, various methodologies have been adopted for the synthesis of metallic nanoparticles as catalysts. Zinc and Copper electrodes were modified by electrochemical deposition. Then these modified electrodes were employed to check their catalytic activity for the oxidation of methanol and ethanol in basic environment. Furthermore, hydrothermal methods have been used to prepare said nanoparticles. Moreover, these prepared nanocatalysts were further investigated through their use in mineralization of organic dyes. In extension, surface analysis of the modified and prepared catalyst has been done by the scanning electron microscopy (SEM).

Experimental

Chemical and Reagents

All chemical used were of analytical grade. These chemicals were purchased from Sigma-Aldrich and used as received without further purification.

Electrochemical Method for the Modification of Nanocatalysts of Zinc and Copper

For electrochemical modification of nanocatalysts, zinc and copper nanoparticles were grown on the surface of Z_n and C_u electrode respectively, by electrochemical deposition. For this purpose Z_nSO_4 and C_uSO_4 were used as precursors of Zn and Cu, respectively, along with the other additives in reverse micro emulsion (RME). In order to avoid the problem of low conductivity of RME [23], 5mL concentrated HCl solution was added. To grow nanoparticles of mentioned metals, graphite electrode was taken as anode and respective metal electrodes were taken as cathode. All these depositions took place at 4.5 ± 0.02V for 30mins.

Hydrothermal Method to Generate Bimetallic Nanoparticles of Copper and Lead

A 0.05 M aqueous solution of $C_uSO_4 . 5H_2O$ was prepared by dissolving 0.125 gm of salt in 100 mL of water. 1.7 mg of Pb(NO3)2 was dissolved in 100mL of deionized water to prepare 0.05M solution. These solutions were transferred to the conical flask and stirred for 30 minutes. 10M solution of NaOH was prepared and added to the solution mixture and pH was adjusted at 13 under continuous stirring at room temperature for 1h. The flask was sealed and placed in the autoclave lined with teflon. The temperature of autoclave was maintained at 125°C and heated for 5h. The precipitates of nanocatalyst obtained after 5h were cooled down to room temperature and washed three times with acetone and distilled water.

Electroxidation of Methanol and Ethanol

Zinc and Copper electrodes modified through electrochemical deposition were further subjected to the investigation of their catalytic activity and compared to unmodified electrodes. For these electrodes, electroxidation of methanol and ethanol was selected as model reaction. Such reactions normally take place in fuel cell. Modified Cu and Zn electrodes were used as anode for the oxidation of ethanol and methanol in basic medium. For all these reactions, graphite electrode was taken as cathode. For this, mixture of 0.1M solution of ethanol in 0.1M NaOH in water was taken as an electrolyte. Values of the current were recorded as a function of voltage. Same procedure was adopted for methanol.

Catalytic Activity for Oxidation of Methylene Blue

Decolouration of methylene blue dye in the presence of strong oxidizing agent (H_2O_2) was selected as a model reaction to demonstrate the catalytic activity of the bimetallic synthesized nanoparticles of copper and lead by hydrothermal method. UV-Vis spectrometer (Labomed, UVD 3500) was used to analyze the catalytic activities of the nanoparticles. Spectra were recorded after a certain time period to the start of oxidation of methylene blue dye by hydrogen peroxide as an oxidizing agent without and with nanocatalyst. For this purpose, 0.8mg of methylene blue dye was dissolved in 100mL of deionized water to prepare solution of methylene blue. 0.7M H_2O_2 was used for both the cases. In this experiment, 20mL of dye solution was mixed with 15mL of H_2O_2 followed by recording of UV-Vis spectrum after certain period of time. To check the catalytic activity, same procedure was repeated with the addition of 0.02mg of catalyst. All the study was done around 660nm which is the lmax value of methylene blue [24].

Result and Discussion

A. Copper and Zinc Modified Electrodes

1. SEM Analysis: SEM images (Hitachi, S-4800) of the copper and zinc modified and unmodified electrodes are given in Fig. 1-4. These electrodes were modified through electrochemical deposition. On examination of the SEM images, it can be seen that nanoparticles are grown. Due to the growth of these nanoparticles, true surface area of the electrodes is enhanced. As ability of a catalyst mainly depends upon its available surface therefore enhanced catalytic activities are expected.

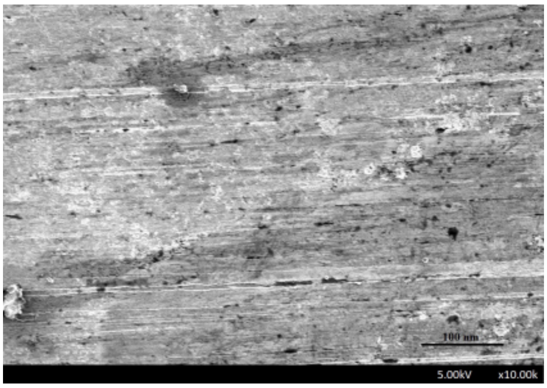

Fig. 1: SEM image of zinc unmodified electrode (Scale bar = 100 nm).

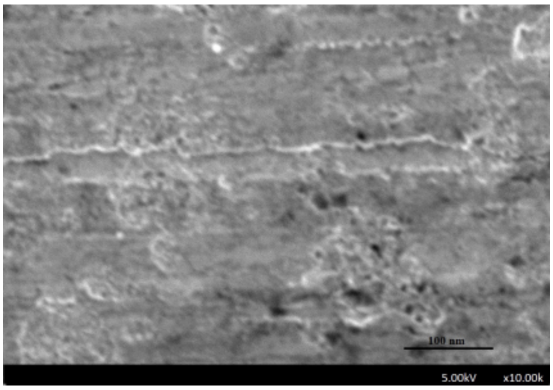

Fig. 2: SEM image of copper unmodified electrode (Scale bar = 100 nm).

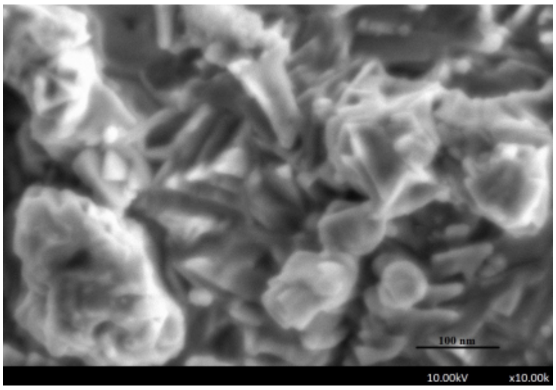

Fig. 3: SEM image of zinc modified electrode (Scale bar = 100 nm).

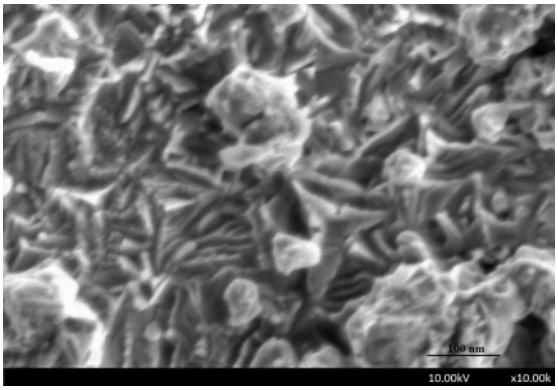

Fig. 4: SEM image of copper modified electrode.

2) Electroxidation of Ethanol and Methanol: As it is confirmed from SEM images that true surface area of the zinc and copper electrodes are enhanced after the modification through electrochemical deposition. It is believed that catalytic activity of the catalysts will be improved with the increases in surface to volume ration. To demonstrate this, modified and unmodified electrodes has been undergone for the catalytic characterization. For the said purpose modified and unmodified electrodes of copper and zinc were used as anode for electro oxidation of ethanol and methanol while for every case graphite electrode was taken as cathode. Current as function of voltage was measured and results for ethanol are given in fig. 5, when electrodes of copper were taken as anode. From the given plot, one can say that large slope is observed for modified copper electrode as compared to respective unmodified electrode. This indicates that large amount of ethanol get oxidized for given voltage by using modified electrode. Although trend is same for both the electrodes, which proves that mechanism of the oxidation is same and not responsible for large amount of current. Similar results are obtained for other combination of alcohols and electrodes.

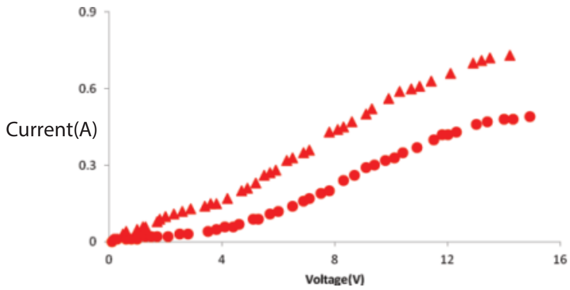

Fig. 5: Plot of electroxiadtion of 0.1M ethanol in basic environment when graphite electrode acts as cathode and modified copper electrode(▲), udmodified copper electrode (●) used as anode.

Copper and Lead Nanocatalysts from Hydrothermal Method

1) SEM Analysis: Scanning electron microscope was used to study the morphological characteristics of the prepared catalyst. Figure 6 shows SEM image of the Cu-Pb alloy catalyst synthesized at pH 13. This figure provides the evidence that Cu-Pb alloy catalyst prepared at pH 13 exhibits the dendrite like morphology. The size of this dendrite like structure is in the range of 100-200nm.

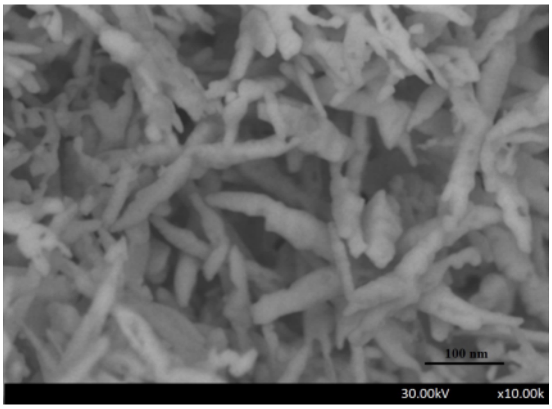

Fig. 6: SEM image of Cu-Pb catalyst

2) Catalytic Activity of Cu-Pb Nanocatalyst: Catalytic activity of the Cu-Pb bimetallic catalyst for the oxidation of methylene blue dye was studied by UV-Vis spectroscopy. λmax of methylene blue was observed around 660nm. For the oxidation of methylene blue, H2O2 was used as oxidizing agent. In first case, oxidation was done without the addition of any catalyst. In second case, same procedure of oxidation was adopted but in the presence of Cu-Pb as catalyst. In the absorption spectra, given in figure 7 recorded in the same experimental conditions, intensity of absorption peak corresponds to the amount of un-oxidized dye. Intensity of the peak, amount of un-oxidezed dye, is far less when catalyst is used as compared to when no catalyst is used. This shows the considerable contribution of the catalyst to speed up the oxidation process.

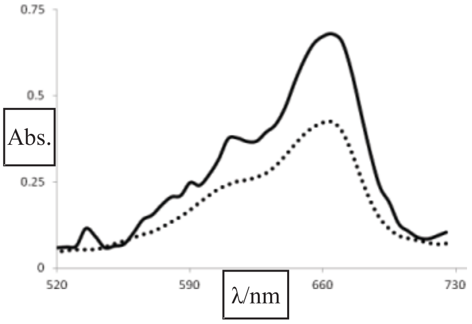

Fig. 7: UV-visible spectra for the oxidation methylene blue using H_2O_2 as an oxidizing agent without Cu-Pb nanocatalyst (solid line) and with Cu-Pb nanocatalyst (dotted line).

Conclusion

Catalyst of different metals particularly from first row of transition series and lead have been successfully modified and prepared by two different routes. SEM analysis showed that catalysts with suitable morphology i.e. enhanced surface area are obtained. This substantial increase in surface area is mainly responsible for better catalytic activity for both type of catalysts.

Acknowledgment

Tajamal Hussain would like to thank University of the Punjab, Lahore, Pakistan for funding to support this work.

Reference

1. A. C. Ferrari, and D. Basko, "Raman spectroscopy as a versatile tool for studying the properties of grephene", Nature Nanotechnology, online published on April 2013, DOI: 10.1038/NNANO.2013.46

2. T.C. Franklin, S. Mathew, K.L. Mittal (Ed.), Surfactant in Solutions, Plenum, New York, (1989).

3. J.H. Fendler, Membrane Mimetic Chemistry, Wiley-Interscience, New York, (1982).

4. E. Pelizzetti and E. Pramauro, Analytical applications of organized molecular assemblies, Anal. Chim. Acta. vol. 169, pp-1, 1985.

5. P.L. Luisi, M. Giomini, M.P. Pileni and B.H. Robinson, "Reverse micelles as host for protein and small molecule"

Biochim. Biophys. Acta. Vol. 947, pp-229, 1988.

6. K. Shinoda and B. Lindman "Organized surfactant system" Langmuir, vol. 3, pp. 134, 1987.

7. A. Manna, T. Imae, T. Yogo, K. Aoi and M. Okazaki, "Synthesis of gold nanoparticles in a winsor II type microemuslion and their characterization" J. Colloid Interface Sci. vol. 256 pp. 297, 2002.

8. M.P. Pileni, "The role of soft colloides tempates in controlling the size and shape of inorganic nanocrystals" Nat. Mater. vol. 2 pp. 145, 2003.

9. H. Zhou, C. Peng, S. Jiao, W. Zeng, J. Chen and Y. Kuang, "Electrodeposition of nanoscaled Nickel in reverse microemulsion" Electrochem. Commun. vol. 8, pp.1142, 2006

10. C. Destree, J. Ghijsen and J.B. Nagy, "Preparation of organic nanoparticles using microemuslion: Their potential use in trenasdermal delivery" Langmuir, vol. 23, pp. 1965, 2007.

11. L. Xiong and A. Manthiram, "Catalytic activity of Pt-Ru alloys synthesised by a microemulsion methods in direct methanol fuel cells" Solid State Ionics vol. 176, pp. 385, 2005.

12. X. Zhang, K. Y. Chan, "Microemulsion synthesis and elecrocatalytic properties of platinum-ruthenium nanoparticles" Chem. Mater. vol. 15, pp- 451, 2003.

13. R. Campbell, M. G. Bakker, C. Treiner and J. Chevalet, "Electrodeposition of mesoporous nickel onto foamed metals using surfactant and polymer templates" J. Porous Mater. vol. 11, pp. 63, 2004.

14. R. Campbell, M. G. Bakker, G. Havrilla, V. Montoya, E. Kenik and M. Shamsuzzoha, "Development of ordered mesoporous semiconductor and semiconductor containing thin films for advanced oxidation processes", Micro. Meso. Mater. vol. 97, pp. 114, 2006.

15. A. Seghiouer, J. Chevalet, A. Barhoun and F. Lantelme, "Electrochemical oxidation of nickel in alkaline solutions: a voltammetric study and modeling" J. Electroanal. Chem. vol. 442, pp. 123, 1998.

16. J. P. Hsu and A. Nacu, "Behavior of soybean oil-in-water emulsion stabilized by nonionic surfactant" J. Colloid Interface Sci. vol. 259, pp- 374, 2002.

17. Z. Dang, K. Shehzad, J. Zha, T. Hussain and N. Jun, "On refining the relationship between aspect ratio and percolation threshold of practical carbon nanotubes/polymer nanocomposites" J. Bai, Jpn J. Appl. Phys. vol. 50 2011, 080214.

18. Z. Dang, K. Shehzad, J. Zha, A. Mujahid, T. Hussain, J. Nie and C. Shi, "Complemntry percolation characteristics of carbon fillers based electrically percolative thermoplastic elastomer composites" Composites Science and Technology, vol. 72, pp. 28, 2011.

19. F. Wang, Multiphonon Raman scattering from individual single-walled carbon nanotubes. Phys. Rev. Lett. vol. 98, 2007, 047402.

20. F. Rasalbino, G. Scavino and M. A. Grande, "Electrocatalyric activity of Ni-Fe-M (M(=Cr, Mn, Cu) sintered electrodes for hydrogen evolution reaction in alkaline solution" J Electroanalytical Chemistry, vol. 694, pp.114, 2013.

21. S. Chatuvedi, P. N. Dave and N. K. Shah, "Application of nano-catalyst in new era" J. of Saudi Chemical Society, vol. 16 pp. 307, 2012.

22. M. A. Zolfiqol, V. Khakyzadeh, A. R. Moosavi-Zare, A. Rostami, A. Zare, N. Iranpoor, M. H. Beyzavi and R. Luque, "A highly stable and active magnetically separable Pd nanocatalyst in aqueous phase heterogeneously catalyzed couplings" Green Chemistry, vol. 15, pp. 2132, 2013,

23. H. Zhou, C. Peng, S. Jiao, W. Zeng, J. Chen and Y. Kuang, "Elecrodepsoitioin of nanoscaled nickel in reverse microemuslion", Electrochemistry Communications, vol. 8

pp. 1142, 2006.

24. N. Kannan, and M. M. Sundaram "Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study", Dyes and Pigments, vol. 51, pp. 25-40, 2001.