Synthesis and characterization of ternary Pt-Ni-M/C (M=Cu, Fe, Ce, Mo, W) nano-catalysts for low temperature fuel cells

Riaz Ahmed¹,², Rabia Jamil¹ and Muhammad Shahid Ansari¹
¹Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan
²COMSATS, Shahrah-e-Jamhuriat, G.5/2, Islamabad, Pakistan
E-mail: riaz_ecfe@yahoo.com

Abstract. Ternary metal catalysts were synthesized by impregnation method. The mixture of metal solutions was reduced slowly under inert atmosphere and the reduced metals were deposited on the Vulcan Carbon (VC). Tungsten, molybdenum, cerium, iron and copper were added to specified amounts of platinum and nickel. Addition of nickel generally improves catalytic activity of platinum. The XRD of the catalysts was done and the crystallite size and other parameters were calculated. Crystallite sizes were in the range of 5 to 16 nm. Electrochemical surface areas of the catalysts were determined by cyclic voltammetry (CV) in acidic media and are compared. Electro oxidation of methanol on the catalysts was done and peak potential, peak current, mass activity of the catalysts were calculated and are compared. These parameters were determined in acidic and basic media. It was found that mass activity increased significantly in basic media. Rate constants for the electro oxidation of methanol were also calculated in acidic and basic media and are compared and discussed. Rate constants were generally higher in basic media. Ternary catalysts showed improved catalytic activity than the binary catalyst. Nano alloying improved the catalytic activity and stability of the ternary catalysts.

1. Introduction

Demand for clean energy sources has become a strong driving force for sustainable economic development. To avoid irreversible damage to the environment as a consequence of burning fossil fuels, some viable alternatives must be harvested. Fuel cells are poised for a breakthrough into the mainstream, and offer an attractive combination of highly efficient fuel utilization and environment friendly operation. A fuel cell is an electrochemical device that continuously and directly converts the chemical energy of externally supplied fuel and oxidant to electrical energy [1]. Electro catalysts are type of heterogeneous catalysts which facilitate electrochemical reactions either functioning at the electrode surface or the electrode itself. Due to a wide range of possible combinations of metals and their composition [2], choice of appropriate electro catalysts has become difficult in fuel cell technology [3]. Like platinum catalyst, particle size and shape influence the catalytic activity of binary and ternary catalysts [4-5]. Addition of two metals shows higher catalytic activity than single platinum metal [6-7] and even higher than binary catalysts [8]. Particle size, synergistic effects on the activity due to the difference in the redox potentials of the metals and atomic scale structural and chemical ordering in Nano alloy catalysts influence the catalytic activity [9-10]. Alloy catalysts are better catalysts than platinum alone [11-12]. Ternary alloys have a potential for the fine-tuning of the electronic structures to improve the catalytic activities [13-15]. Nano and high surface area catalysts...
have been thoroughly investigated but the catalytic activities of platinum ternary catalysts have not been fully investigated.

In this study Pt-ternary catalysts have been synthesized and characterized using XRD, electrochemical surface area, specific activity and kinetics of methanol oxidation on the catalysts.

2. Materials and Methods

2.1. Chemicals and equipments:

Platinum(IV) chloride PtCl4, Nickel(II) chloride NiCl2.6H2O, Sodium tungstate dihydrate Na2WO4.2H2O, Copper(II) chloride CuCl2.2H2O, Ammonium Cerium(IV) sulphated hydrate (NH4)4Ce(SO4)4.2H2O, Ferric chloride FeCl3.6H2O, Molybdenum chloride MoCl5, Sodium borohydride NaBH4, Vulcan Carbon (VC) Trisodium citrate Na3C6H5O7.2H2O, Methanol, Ethanol, 2-Propanol C3H8O, Nafion solution, Hydrogen peroxide H2O2 35%, Hydrochloric acid, Sulphuric acid, Nitric acid, Potassium hydroxide, of analytical grades were used.

X-ray diffraction pattern of all samples were obtained at room temperature by using X-ray Diffractometer (3040/60 X’pert PRO) using Ni -filtered cu-Kα radiations (40 kV,30mA). Cyclic voltammetric measurements were carried out using Eco Chemie Autolab PGSTAT 12 potentiostat/galvanostat Netherlands, with the electrochemical software package GPES 4.9.

2.2. Synthesis of catalysts:

Vulcan carbon was purified by treating with 6M HCl. The contents were refluxed and ultra sonicated for 4 hours at 60°C. Treated VC was filtered off and washed several times with de-ionized water till neutral pH of the filtrate. Finally the purified VC was vacuum-dried for 24 hours at 110°C. Functionalization of the purified VC was done in 4:1 v/v mixture of 8M HNO3 and 35% H2O2 by ultra sonication, filtered, washed and vacuum-dried for 24 hours at 110°C.

Pt-Ni/C and Pt-Ni-M/C (M= Cu, Fe, Ce, Mo, W) catalysts were synthesized using NaBH4 as reducing agent by conventional co-reduction method under argon atmosphere at room temperature. Aqueous solutions of PtCl4, NiCl2.6H2O and solutions of different metals (M= Cu, Fe, Ce, Mo, W) were added and stirred under argon atmosphere along with VC; the mixture became colorless from golden indicating adsorption of metal ions on the VC. Freshly prepared solution of NaBH4 was added drop wise into the above dispersion. Four hours stirring resulted formation of black suspension which was filtered and washed several times with de-ionized water till neutral pH of the filtrate. The residue was vacuum-dried for 24 hours at 110 °C. Pt-Ni-M/C (M= Cu, Fe, Ce, Mo, W) catalysts were synthesized using NaBH4 as reducing agent by conventional co-reduction method under argon atmosphere at room temperature.

2.3. Electrochemical measurements:

Graphite electrode (GE) was polished with 1.0 μm alumina (CHI Inc., USA) washed in ethanol and ultra-pure water ultrasonically to remove organic and inorganic impurities from the surface of electrode. Then, 20 mg catalyst and 1 mL of solvent (water + 2-propanol) were mixed ultrasonically for 30 min in a test tube. 50 μL of the suspension was pipetted out and pasted over the tip of polished graphite electrode, dried in air. After the solvent evaporation, 10 μL binder (5% nafion solution) was spread over the tip of GE. The air dried, working electrode was ready to use.

3. Results and discussions

3.1. XRD analysis:

XRD was done to find out the crystallite size of the particles, alloy formation and other parameters. Standard XRD data for platinum (00-001-1190) was used for comparison purposes. Fig.1 shows the comparison of XRD patterns of Pt–Ni–M/C (M= W, Cu, Fe, Mo, Ce) of all the five ternary catalysts. The broad peaks located at 2 theta (θ) position 26.19°, 44.14°, 54.39° and 59.54° are associated with the (002), (100), (004) and (101) planes of the graphite-like structure of the VC. Platinum face centered
cubic peak at 2 theta position (39.67°) is prominent in all the catalysts and used as reference peak. Shift in platinum 2 theta position for different ternary catalysts shows the alloy formation.

![XRD patterns of Pt-Ni-W/C, Pt-Ni-Cu/C, Pt-Ni-Fe/C, Pt-Ni-Mo/C and Pt-Ni-Ce/C](image)

Figure 1. XRD patterns of Pt-Ni-W/C, Pt-Ni-Cu/C, Pt-Ni-Fe/C, Pt-Ni-Mo/C and Pt-Ni-Ce/C

The peaks observed at 20 position 40.10°, 39.98°, 39.82° and 39.89° are due to Pt(111) plane of fcc crystalline structure in Pt–Ni–W/C, Pt–Ni–Ce/C, Pt–Ni–Fe/C and Pt–Ni–Mo/C catalysts respectively. Maximum shift in 20 position is observed for Pt–Ni–W/C. The respective additions of Fe, Ce and Mo to Pt-Ni have caused some shift in platinum peak which indicates its alloy formation and more shift shows more alloy formation and crystalline structure of platinum has also not changed. Different parameters evaluated from XRD patterns of Pt–Ni–M/C (M= W, Cu, Fe, Mo, Ce) respectively are displayed in Table 1. There is a significant decrease in d-spacing and density. Decrease in density is due to the alloy formation of platinum with other low molecular weight metals. There is a change in lattice parameter and cell volume for all the additives. The rough estimated average crystallite sizes are 4–16 nm and is 4.5 nm for Pt-Ni-Mo/C, 8.0 nm for Pt-Ni-Fe/C, 11.9 nm for Pt-Ni-W/C and 16.0 nm for Pt-Ni-Ce/C. Shift in 2θ position shows alloy formation. This alloy formation has significant effect on catalytic activity.
3.2. Electrochemical Surface area (SESA)
Various transition metals have been incorporated to Pt-Ni in a view to further enhance the activity of bi-metallic catalysts. Table 2. shows the comparison of various tri-metallic catalysts, among them Pt-Ni-W/C shows the highest SESA followed by Pt-Ni-Fe/C, Pt-Ni-Cu/C, Pt-Ni-Mo/C and Pt-Ni-Ce/C.

Roughness factor for the catalysts can be calculated by dividing the real surface area (electrochemical surface area) by the apparent area of the electrode.

3.3. Evaluation of catalytic activity from cyclic voltammograms
Cyclic voltammograms of the catalysts were taken both in acidic media and basic media. Cyclic voltammograms in acidic media are shown in Fig. 2. For all the catalysts forward and backward anodic peaks for methanol oxidation were observed and peak heights were different for different catalysts. The height of the peaks shows the catalytic activity of the catalysts. Peak current, mass activity and current density of the catalysts were calculated from voltammograms and are given in table-3.
It can be seen that the Pt-Ni-W/C has the maximum mass activity followed by Pt-Ni-Mo/C, Pt-Ni-Ce/C and Pt-Ni-Fe/C catalysts. Catalytic activity of the ternary catalysts is considerably higher than the binary catalyst.

Table 3. Activity parameters evaluated from CVs in 1M CH₃OH in acidic and basic media

| Catalysts       | Peak Potential E_p/V | Peak current /mA | Mass activity /mA.mg⁻¹ | Mass activity /mA.mg⁻¹ |
|-----------------|----------------------|------------------|-------------------------|-------------------------|
|                 | Acidic | Basic | Acidic | Basic | Acidic | Basic | Acidic | Basic |
| Pt-Ni/C         | 0.69   | -0.18 | 1.7    | 21.8   | 17     | 218.1 |
| Pt-Ni-W/C       | 0.71   | -0.11 | 7.8    | 37.4   | 78     | 373.6 |
| Pt-Ni-Cu/C      | -      | -0.21 | -      | 3.04   | -      | 30.4  |
| Pt-Ni-Ce/C      | 0.67   | -0.20 | 1.8    | 15.5   | 18     | 154.8 |
| Pt-Ni-Fe/C      | 0.70   | -0.29 | 1.7    | 0.8    | 17     | 8.0   |
| Pt-Ni-Mo/C      | 0.68   | -0.20 | 3.0    | 24.2   | 30     | 242.0 |

It can be seen that the Pt-Ni-W/C has the maximum mass activity followed by Pt-Ni-Mo/C, Pt-Ni-Ce/C and Pt-Ni-Fe/C catalysts. Catalytic activity of the ternary catalysts is considerably higher than the binary catalyst.

Figure 2. CVs measured in 1M CH₃OH + 1M H₂SO₄ on Pt-Ni-M/C (M= Cu, W, Mo, Fe, Ce)

In Fig.3 is given voltammogram for methanol oxidation in basic media for all the catalysts. Here we also get a forward anodic peak and a backward anodic peak. In basic media the backward anodic peak is much smaller than the forward anodic peak. Specific activities of the catalysts in basic media are given in table-3. In basic media the specific activity of the Pt-Ni-W/C catalyst is highest followed by Pt-Ni-Mo/C, Pt-Ni-Ce/C, Pt-Ni-Cu/C and Pt-Ni-Fe/C catalysts. Mass activities of the catalysts have nearly the same trend in both the media but are much higher in basic media. Generally the catalytic activity of the ternary catalysts in basic media also is better than the binary catalyst.
Figure 3. CVs measured in 1M CH$_3$OH + 1M KOH on Pt-Ni-M/C (M= Cu, W, Mo, Fe, Ce)

3.4. Kinetics of methanol oxidation on catalysts

Better catalysts will show fast kinetics and rates of reaction will be higher. Rate of an electrochemical process can be calculated by the Klinger and Kochi or Nicholson and Shain methods. In this work Nicholson equation was used [16-17] which can be written as:

\[ i_p = 0.227 \, nFAC_o \exp\left(\frac{\alpha nF}{RT}(E_p - E_i)\right) \]

where \( i_p \) is the peak current, \( n \) is the number of electrons transferred, \( A/cm^2 \) is the area of the electrode, \( C_o/mol/cm^3 \) is the bulk concentration of the reactant and \( k_s/cm^3s^{-1} \) is the standard heterogeneous rate constant. \( F \) and \( R \) are the Faraday and gas constants. \( E_i \) is the potential at the root of the wave. A graph is plotted between \( \ln(I_p) \) vs. \( E_p - E_i \) to get a straight line and from the value of the slope, \( k_{het} \) was calculated. The values of heterogeneous rate constants for the MO on the catalysts in acidic and basic media have been calculated and are listed in Table.4. It can be seen that the rate constants are better on ternary catalysts as compared to binary catalyst and generally rate constants are higher in basic media.
3.5. Comparison of catalytic activities:
In Fig.4 are compared the catalytic activities of different ternary catalysts both in acidic and basic media. Pt-Ni-W/C is the best catalyst followed by Pt-Ni-Mo/C and others. Catalytic activity is much better in basic media for all the catalysts except for the Pt-Ni-Fe/C catalyst. Basic binary catalyst used here Pt-Ni/C has also better catalytic activity in basic media (Table-3). Decrease in catalytic activity in basic media due to iron may be its tendency for hydrolysis in basic media.

| Catalysts     | Rate constant $k_{\text{net}}$ \(/\text{cm.s}^{-1} \times 10^{-5}\) | Rate constant $k_{\text{net}}$ \(/\text{cm.s}^{-1} \times 10^{-5}\) |
|---------------|-------------------------------------------------|-------------------------------------------------|
| Pt-Ni/C       | 1.7                                             | 4.1                                             |
| Pt-Ni-W/C     | 4.3                                             | 15.3                                            |
| Pt-Ni-Cu/C    | -                                               | 0.8                                             |
| Pt-Ni-Ce/C    | 1.7                                             | 3.7                                             |
| Pt-Ni-Fe/C    | 1.6                                             | 0.2                                             |
| Pt-Ni-Mo/C    | 2.8                                             | 4.1                                             |

**Table 4. Rate constants of CH₃OH oxidation**

4. Conclusions
Ternary catalysts were prepared by adding different metals to the binary catalyst Pt-Ni. The addition of non noble metals to the binary catalyst has improved the catalytic activity of the ternary catalyst. Electrochemical surface area is higher for the ternary catalysts. Catalytic activity both in the acidic and basic media has improved in the ternary catalysts. Similarly rate of reaction both in acidic and basic media are also better in ternary catalysts. Alloying of the metals have improved the catalytic activity of the catalysts. Nano alloys through better structural and chemical ordering has improved the catalytic activity of the ternary catalysts. It can be concluded that the ternary catalysts are better than the...
binary and single platinum catalysts and addition of non noble metals will also reduce the costs of the catalysts.

5. References

[1] Zang J.(Ed.) 2008, PEM fuel cell Electrocatalysts and catalysts layer fundamentals and applications, Springer-Verlag, London

[2] Ferrando, R.; Jellinek, J. Johnstons R.L.C. 2008, Revs. Lett. 3, 108-119.

[3] Perry, M. L.; Fuller, T. F.; 2002, J. Electrochem. Soc149.59–67.

[4]. Stamenkovic, V. R.; Mun, B. S.; Mayrhofer, K. J. J.; Ross, P. N.; Markovic, N. M. 2006, J. Am. Chem. Soc., 128 (27), 8813.

[5] Fang, B.; Luo, J.; Chen, Y.; Wanjala, B. N.; Loukrakpam, R.; Hong, J.; Yin, J.; Hu, X.; Hu, P.; Zhong, C. J. 2011, ChemCatChem, 3, 583.

[6] Wanjala, B. N.; Fang, B.; Luo, J.; Chen, Y.; Yin, J.; Engelhard, M.; Loukrakpam, R.; Zhong, C. J. 2011, J. Am. Chem. Soc., 133, 12714.

[7] Loukrakpam, R.; Luo, J.; He, T.; Chen, Y.; Xu, Z.; Njoki, P. N.; Wanjala, B. N.; Fang, B.; Mott, D.; Yin, J.; Klar, J.; Powell, B.; Zhong, C. J. 2011, J. Phys. Chem. C, 115, 1682.

[8] Koh, S.; Leisch, J.; Toney, M. F.; Strasser, P. J. Phys. Chem. C 2007, 111, 3744.

[9] Greco, G.; Witkowska, A.; Minicucci, M.; Olivi, L.; Principi, E.; Dsoke, S.; Moretti, A.; Marassi, R.; Cicco, A. D. 2012, J. Phys. Chem. C,116, 12791.

[10] Wanjala B. N., Fang B., Shan S., Petkov V., Zhu P., Loukrakpam R., Chen Y., Luo J., Yin J., Yang L., Shao M., Zhong C.-J, Chem. Mater. 2012, 24, 4283–4293

[11] Wang C., Li  D., Chi M., Pearson J., Rankin, R. B. Greeley J., Duan Z., Wang, G. van der Vliet D., More K. L., Markovic N. M., Vojislav R. Stamenkovic, J. 2012, Phys. Chem. Lett., 3, 1668–1673.

[12] Stamenkovic, V. R.; Mun, B. S.; Arenz, M.; Mayrhofer, K. J. J.; Lucas, C. A.; Wang, G. F.; Ross, P. N.; Markovic, N. M. 2007, Nat. Mater., 6, 241–247.

[13] Antolini, E. 2007, Appl. Catal., B, 74, 337–350.

[14] Mani, P.; Srivastava, R.; Strasser, P. 2011, J. Power Sources, 196, 666–673.

[15] Wanjala, B. N.; Loukrakpam, R.; Luo, J.; Njoki, P. N.; Mott, D.; Zhong, C. J.; Shao, M. H.; Protsailo, L.; Kawamura, T. 2010, J. Phys. Chem. C, 114, 17580–17590.

[16] Nicholson, R.S., and Shain. I. Anal. Chem; 1964, 36, 70,

[17] Reinmuth, W.H., Anal. Chem. 1960, 32, 1891.