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# Study on single step solid state synthesis of WC@C nanocomposite and electrochemical stability of synthesized WC@C & Pt/WC@C for alcohol oxidation (methanol/ethanol)

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WC@C nano composite was prepared by a single step solid–state reaction through *in situ* reduction and carburization of $WO_3$ in the presence of Mg and activated charcoal. The XRD results and thermodynamics analysis showed that the optimization of reaction temperature facilitates the reduction as well as carburization of tungsten oxide(s) at different reaction temperature. Thermogravimetric analysis of the product was done to assess the thermal stability in air. The Raman spectroscopy was used to find out the nature (amorphous/graphitic) of carbon in the obtained phase. The $N_2$ adsorption–desorption measurement showed a narrow pore size distribution from 3 to 4 nm with BET surface area of up to 522.5 $m^2/g$. TEM/HRTEM images confirmed formation of the WC nano particles with spherical morphology. Electrochemical stability of pure and platinized carbide sample (Pt/WC) has been investigated using cyclic voltammetry in acidic media for alcohol (methanol and ethanol) oxidation.

## 1. Introduction

In the current era of 21st century, a lot of emphasis is given to enhance the performance of fuel cell to reduce the petroleum consumption which is in diminishing stage. Among the non conventional energy resources, fuel cell is an environmental friendly energy conversion system. This is an electrochemical device similar to battery, which consists of anode, cathode, catalysts and electrolyte. In fuel cell, electricity is generated by electrochemical reaction between hydrogen and oxygen through charge movement and also generates pure water ($2H^+ + O^{2-} \rightarrow H_2O$) [1]. The performance of this device mainly depends upon the properties of materials used in it. To enhance the charge transport through the cell in this electrochemical device, a necessary support (electrocatalyst) is required. This electrocatalyst should be electrically conductive but at the same time must be resistant to corrosion in the extreme electrochemical environment in the fuel cell. Although platinum (Pt) nanoparticles have been regarded as the best electrocatalyst for energy conversion in fuel cells, but it has been restricted because of high cost, CO deactivation and limitation in resources [2].

Now, WC has emerged as a new electrocatalyst which can replace Pt as WC has similar properties to that of noble metals like Pt, Pd, Au, etc. [3–5]. Hence, the cost of fuel cell can be minimized by reducing the usage of noble metals while maintaining the electrochemical performance of electrocatalyst. The catalytic activity of WC depends upon the preparation conditions like the reactions by which the carbides are produced. Apart from this, the reaction temperature, composition of the reaction atmosphere, carbon deficiency and surface composition of synthesized powder also play an important role to improve its chemical activity [6–8]. Apart from the electrochemical activity, the mixture of WC and Co is used as cermet (WC–Co) for machining, cutting, drilling, mining, and wear resistant parts, due to their excellent high hardness, wear resistance and improved toughness [9,10].

Because of unusual properties of materials at nano range different methods like chemical processing method [9], thermal processing [10], mechanical alloying method [11], combustion synthesis method [12], chemical vapor condensation (CVC) [13], solvothermal route [14], ion exchange method [15], single step pyrolysis method [16] etc. have been adopted to prepare nano WC by taking tungsten, tungsten oxide, tungsten hexacarbonyl, tungsten hexachloride, ammonium metatungstate (AMT) as the starting

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materials. Among different tungsten sources, tungsten oxide has been found to be better one for single step synthesis of tungsten carbide [14]. Moreover, the carbon Supporting materials, such as carbon nanotubes (CNT), carbon nanofibers (CNFs), mesoporous carbon (MC) and graphene are also frequently used as catalyst supports to improve the electro catalytic reaction in the fuel cells [17–20]. So, the stability and activity of WC can be further improved by formation of WC@C nanocomposite prepared by microwave heating method [21], solution synthesis [22], surface decoration and *in situ* reduction carburization [23], solution plasma synthesis method [24], direct carburization method [25] etc. However, the existing difficulties for each process have put the limitations of above-mentioned methods for producing highly active electrocatalyst in a more economical way. Moreover, synthesis of highly pure WC nano powder at low reaction temperature will further cut the cost of production to considerable extent. This has led to explore the new processes. In this work, we report a new efficient single step solid state synthesis route to develop WC@C by taking tungsten oxide ($WO_3$), activated charcoal and magnesium (Mg). Because of fast thermite reaction of magnesium (Mg) during synthesis [26], temperature as well as time for getting pure transition metal is minimized. It makes Mg as better reducing agent and is widely used in the synthesis of carbides [14,27–32]. The developed process is single step, economical and of commercial importance.

## 2. Experimental procedure

### 2.1. Preparation

#### 2.1.1. Synthesis of tungsten carbide

For the synthesis of nano tungsten carbide (WC), $WO_3$ (1.157 g), Mg (2 g) and activated charcoal AC (2 g) were added into a specially designed stainless steel autoclave. The autoclave was sealed from the top, and the entire assembly was put inside the electric furnace at room temperature. The temperature of the furnace was raised to different temperature (500, 600, 700 and 800 °C) slowly at a heating rate 5 °C/minute and maintained at these temperatures for 10 h in the absence of inert atmosphere. After that the autoclave was allowed to cool to room temperature. The resultant product was collected and washed by dilute HCl (1:1) to remove MgO. After leaching, the powder was washed with distilled water several times to remove HCl. Finally, the obtained product was washed with acetone and then dried in vacuum at 100 °C. The sample so obtained are denoted as C5, C6, C7 and C8 corresponding to their reaction temperature of 500, 600, 700 and 800 °C.

#### 2.1.2. Deposition of Pt

Pt nano particles were deposited on synthesized WC by dispersing 40 mg of WC powder in 20 ml of ethanol in ultrasonic bath and then 100 μL hexachloroplatinic acid ($H_2PtCl_6$) aqueous solution was added to ultrasonicated solution. In the mixture of metal salt and WC support, appropriate amount of 0.05 M NaOH/ethanol was added to maintain the pH ~10. The precipitate was washed with high purity water and then dried at 80 °C.

### 2.2. Characterization of synthesized nano powder

#### 2.2.1. Physical characterization of synthesized powder

The X-ray diffraction study of the product phase was done to identify crystalline phases. The XRD of the samples was performed using PANalytical Xpert-Pro with CuKα radiation ($\lambda = 1.54$ Å) obtained from the copper target using an inbuilt Ni filter. During XRD experiment, scan speed was 5 °C $\text{min}^{-1}$. Crystallite size of synthesized WC was determined by XRD profile technique. The Williamson–Hall equation as given in Equation (1) was used to calculate the crystallite size.

$$\beta_{hkl} \cos\theta_{hkl} = [K\lambda/t] + [4\varepsilon \sin\theta_{hkl}] \quad (1)$$

Where $\beta_{hkl}$ is the integral breadth ($A/I_o$, $A$: area of the peak, $I_o$: maximum intensity), $\lambda$ is the X-ray wavelength, $t$ is the crystallite mean size and $\varepsilon$ is strain. Thermogravimetric analysis (TGA) was done to find out the thermal stability of the samples. The TGA experiment was done at heating rate of 5 °C $\text{min}^{-1}$ from room temperature to 800 °C in air atmosphere. Raman spectra of powder sample was recorded using Renishaw via Raman spectrometer with the 514.5 nm line of an $Ar^+$ laser at 20 mW power. The morphology, particle size and distribution of the samples were studied by high-resolution transmission electron microscope (HRTEM, JEOL 2100F) operating at 200 kV. The energy dispersive X-ray spectra (EDS) attached to the (JEOL JSM-6510 LV; INCA) were also used to investigate the surface chemical composition of the powder sample. The $N_2$ adsorption/desorption studies to determine the BET surface area were conducted using at TriStar 3000 V6.05 A. Before the measurement, all the samples were degassed at 200 °C for 2 h in vacuum.

#### 2.2.2. Electrochemical characterization of WC@C powder

The electrochemical measurement was performed at Bio-Logic EC Lab SP300. A standard three compartment electrochemical cell was used with glassy carbon electrode (GCE), Pt wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. All the measurement was carried out at room temperature in 0.5 M $H_2SO_4$.

The top surface of GCE rod having 3 mm diameter was pre cleaned with emery paper. Typically 4 mg of synthesized powder sample was mixed with 1 mL of ethanol. The mixture was treated ultrasonically for 20 min for uniform dispersion. 10 μL of mixture was then dropped onto the surface of the GCE. Finally a drop of 10 μL of Nafion® 117 solution (Sigma Aldrich) was dropped onto the top surface and left in air for overnight drying. Before the CV measurement the electrolyte solution is purged with argon gas for 5 min to deoxygenate the solution. The electrochemical testing of the sample has been done by cycling the potential from −0.2–1.2 V at a sweeping rate of 30 mV $s^{-1}$ in the presence of 0.5 M $H_2SO_4$. Thereafter, the alcohol (methanol and ethanol) electrolyte was added and cyclic voltammogram tests were carried out for oxidation from −0.2–1.2 V at sweeping rates of 30 mV $s^{-1}$. The influence of alcohol concentration on the catalyst catalytic performance was tested with concentrations 0.4 M, 0.6 M and 0.8 M.

## 3. Results and discussion

### 3.1. X-ray diffraction analysis (XRD)

The X-ray powder diffraction data were collected for all the samples at room temperature between $20° \leq 2\theta \leq 80°$. Fig. 1 shows the XRD pattern of carbon source (AC: activated charcoal), and the product phase(s) synthesized at different temperatures for 10 h after leaching the samples. The appearance of $WO_3$, $WO_{2.72}$, $WO_2$ and W peaks in XRD pattern at 500 °C gives a path way for the reduction of $WO_3$ as ($WO_3 \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$). The intermediate lower oxide ($WO_{2.72}$) known as Magneli phase clearly indicates that this kind of reduction will be very fast and multi step reaction [33]. The broadened nature of XRD peaks of tungsten carbide indicates that the particles are of nanometer scale. The peak position ($2\theta$), integrated intensity, the peak maximum position and the peak width of the individual reflections was obtained through fitted Gaussian function. The result of the curve fit routine for the