SYNTHESIS OF ZINC OXIDE BY FLAME SYNTHESIS METHOD – ITS APPLICATION FOR HYDROGEN STORAGE

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ABSTRACT

This paper reports the synthesis of zinc oxide by flame synthesis method using zinc acetate as a starting precursor by maintaining the flow rates and temperatures. It also includes the studies of hydrogen adsorption at various pressures and constant temperature. They are characterized for the XRD, SEM and BET surface area. The obtained hydrogen storage results were 0.8 1.0, 1.2 and 2.4 wt % at a pressure of 25, 50, 75 and 100 bar respectively.

Keywords: Zinc acetate, Hydrogen, Storage, Precursor, Flame Synthesis.

INTRODUCTION

Hydrogen is a renewable and environmentally friendly energy source and has been considered an ideal energy medium for replacing fossil fuel such as coal and oil. A major focus has been placed on improving the hydrogen production and storage. Generally, there are four storage methods of hydrogen such as compression, liquefaction, and metal hydride storage. However to apply these technologies to vehicular applications storage materials should meet the DOE targets and satisfy the requirement. The DOE, USA has set goals for hydrogen storage capacity of 9wt% for 2015 and 5.5 wt% for 2017 in gravimetric capacity, operating temperature 40-60^{0}C under a maximum delivery pressure of 100 atm [2] .The interests in hydrogen as an energy efficient was initiated in the late 1960s and many research scientists came forward working on the storage materials . Besides the storage methods got their own advantages and disadvantages. More suitably storage on solid materials turned out to be the best way for storing of hydrogen and research focused on developing new materials and interest carried towards tailoring the pore size and surface area by coming with new synthesis procedures. A solid hydrogen material should have few commandments like:

1. Storage capacity to be least 6.5 wt%
2. Desorption temperature to be 60-120^{O}C
3. Low cost
4. Low toxicity

Among the various hydrogen storage materials compound like zinc oxide is a well known substance to physicists and chemists due to its electrical, optical and catalytic properties. Zinc oxide has been chosen because of its high surface area, low cost, easy synthesis procedure and less toxicity. In this paper, we report the synthesis of zinc oxide by flame synthesis, a promising technique for the synthesis of high purity zinc oxide particles with controlled size and crystallinity in a single step. The recorded results obtained are 0.8, 1.0, 1.2 and 2.4 wt % at 25, 50 75and 100 bar. Our novelty lies in the preparation of zinc oxide indigenously designed by flame reactor and its hydrogen storage application. Only few Works on hydrogen adsorption of zinc oxide were studied by Nagarjunan et al and Atul Gupta et al.

MATERIALS AND METHODS

All the chemicals used for zinc oxide are purchased from M/s. Sigma Aldrich India Pvt. Ltd and SRL chemicals are of highest purity. Zinc acetate, LPG (domestic, Bharat Gas), and oxygen and nitrogen gas were purchased from Industrial gas Agency of Pvt. Ltd. India. All experiments were carried out in a flame reactor indigenously by JNTU, Hyderabad.

Preparation of zinc oxide: Zinc acetate was purchased from SRL Chemicals India, LPG (domestic, Bharat Gas), and oxygen and nitrogen gas were purchased from Industrial gas Agency of Pvt. Ltd. India. All experiments were carried out in a flame reactor indigenously by JNTU, Hyderabad as shown. The reactor operates under atmospheric pressure. The measured quantity of the LPG and the oxidant reaches the ignition chamber. During the process we have observed the dark orange flame color which is perfect in a spindle form. Along the entire length of the flame, its temperature was recorded using a K-type thermocouple. In this study, zinc oxide was synthesized in diffusion flame by using zinc acetate as the zinc precursor. In this experiment, flame is ignited in the burner with LPG and oxygen, nitrogen gas is bubbled through a reagent vessel containing zinc acetate to deliver vapor to the burner. In order to prevent any condensation of the precursor, all gas line downstream and the burner were wrapped with heating tapes to maintain them at 125^{0}C. The zinc oxide produced is captured on a glass fiber filter (Axiva GF/A), and is scrapped carefully and weighed. Later, it was heat treated at 350 ^{O}C in the presence of air for 60 min to remove any traces of amorphous carbon impurities and then the samples were characterized by SEM and XRD for morphology and crystallinity.

Hydrogen adsorption unit: The high-pressure hydrogen adsorption/desorption experimental setup as given in consists of two adsorber assembly units (AAU). Each AAU consists of measuring section, heater and sample cell assembly. The measuring section is attached to the main frame unit used to monitor the hydrogen pressure is connected to the pressure transducers of range (0 – 148 bar) procured from Keller, USA. A heater attached to the main frame to remove any undissolved gases and for the activation of the pores of the sample taken in the quartz tube is provided with water circulation to avoid the O- ring from overheating. Sample cell assembly comprises of a cylindrical outer SS-block into which a cylindrical copper block is fitted. To allow the sample to be placed inside the copper block, it has a drill with 10 mm diameter. The sample is taken in a quartz tube of 6 mm inner diameter, which is inserted into the sample cell. The sample cell is kept inside a vertical tube furnace for studying the hydrogen storage properties at different Pressures. The main frame consists of stainless steel tubes, tees, elbow joints and needle valves are procured from Swagelok USA which can withstand up to a maximum pressure of 350 bar. It also consists of piping and reference vessels which are used for passage

of gas and calibration purposes. A turbo molecular pump attached to the main frame is used for complete evacuation of the system up to 10–9 mbar. A K-type thermocouple is introduced into the AAU to monitor the temperature of the furnace. The unit is tested for leaks at high pressures using nitrogen and leaks were arrested by tightening the bolts.

Hydrogen – storage measurement: The specific surface area and pore volume are two factors that govern the hydrogen storage in MOF materials. Before we start our experiments the leaks should be arrested by carrying out the leak test with gases and the bolts were tightened. The experiments are performed using a volumetric setup that had been tested for leaks. Initially, a known volume of hydrogen gas is inserted and it is taken as initial pressure (P_1) for regular interval of time the pressure drop is noted and at a certain point the pressure gets stable it is noted down as (P_2). Hydrogen adsorption and desorption studies are carried out at 25, 50, 75, 100 bar respectively. The hydrogen adsorption capacity is expressed in terms of wt%. For the calculation of hydrogen concentration present in the material, the Vander Waals equation of state is used.

It is defined as:

$$Wt\ \% = \frac{Weight\ of\ the\ hydrogen\ molecules}{Weight\ of\ the\ material} \times 100$$

RESULTS AND DISCUSSION

Zinc oxide is synthesized by using a pilot Scale Diffusion Flame reactor, using inexpensive fuel, LPG as fuel and oxygen as oxidant. The XRD pattern and SEM image of the zinc oxide material synthesized at flow rate of 0.4 and 0.8 slpm of LPG and oxygen.

Scanning electron microscope (SEM) analysis: The surface morphology was being investigated by SEM method using Hitachi S-3400N variable vacuum SEM at an accession voltage of 15.0 KV, using a carbon conducting tape adhered on aluminum stub. The zinc oxide was a white powdery material. The SEM image clearly indicates the presence of higher specific surface area and probably better adsorption material.

X-ray diffraction analysis (XRD): The XRD image demonstrates the XRD patterns of the synthesized ZnO particles. The X- ray diffraction data were recorded by using Cu Kα1 type of radiation with a wavelength of 1.5406 A˚. The intensity data were collected over a 2θ range of 20-80^0 using the XRD (7000 Schimadzu). XRD graph of zinc oxide material produced using LPG-Oxygen at flow rates of 0.2 slpm and 0.7 slpm is shown in Fig. The step size was 0.02 8/step and step time was 0.2 s/step. It can be observed that majority of the phases appear at 30.0 and 35.0 respectively. X- ray diffraction studies confirmed that the synthesized materials were ZnO and all the diffraction peaks agreed with the reported JCPDS data no characteristic peaks were observed other than ZnO.

Fourier Transform Infrared Spectroscopy (FT-IR): The FT IR of the ZnO particles synthesized by flame synthesis which was acquired in the range of 4000-4000 cm$^{-1.}$ The band between the 450-500 cm^{-1} correlated to metal oxide bond ZnO. The peaks in the range of 1452.34 cm -1 corresponds to the C=O bonds. The peak at 1318 cm $^{-1}$ corresponds to C=O and O-H bending vibrations respectively. The FTIR data can be compared with the Panigrahi et al work.

Nitrogen sorption measurements: The BET (Brunauer, Emmett, and Teller) measurements from these crystals yield a surface area of 890 m^2 /g and a pore size of 1.3 m^3/g. The high surface area confirms the formation of zinc oxide structure. The pore size mainly determines the interaction between hydrogen and the zinc oxide. The recorded results can be compared to the obtained to the results of Nittaya Tamaekong et al, 2010 work.

Hydrogen storage results: After few leak tests performed the reported results for zinc oxide are 0.8, 1.0, 1.2 and 2.4 wt % at 25, 50 75 and 100 bar.

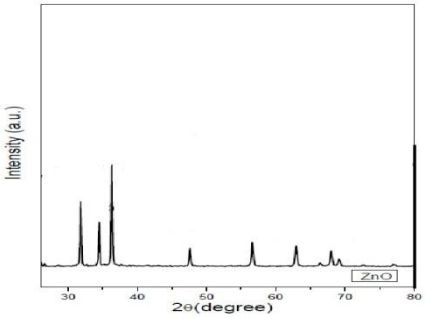

Figure.1.XRD Image of zinc oxide

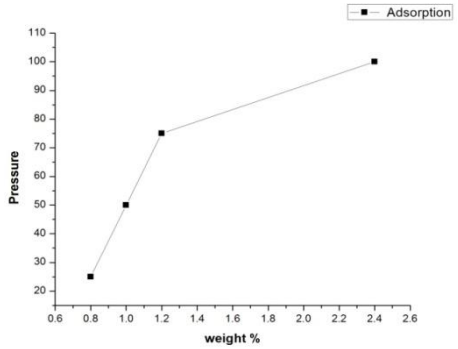

Figure.2.Isotherm of zinc oxide

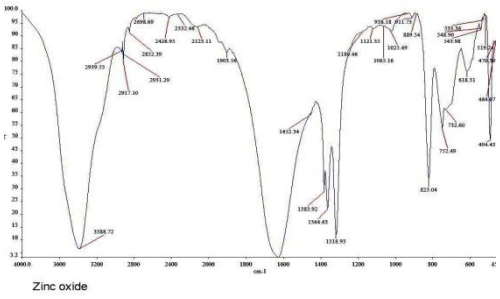

Figure.3.FTIR of zinc oxide

CONCLUSION

Global warming and reduction in fossil fuels are the main issues to be covered as per hydrogen economy and thrown a light upon hydrogen storage for vehicular application. Among the various adsorbents studied zinc oxide got its own advantages over other materials. In summary, we have shown that flame reactor synthesis is a promising technique an inexpensive method for the synthesis of high purity zinc oxide materials with controlled size and crystallinity in a single step. The present study discusses about the synthesized zinc oxide its morphology and hydrogen adsorption capacities. The hydrogen capacities of zinc oxide are 0.8, 1.0, 1.2, 2.4 wt % at 25, 50, 75 and 100 bar at 297 K. The calculations of the adsorbed hydrogen are done using the standard Vander Waals equation and cubic equation software respectively.

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