BINIVOX catalyst for hydrogen production from ethanol by low temperature steam reforming (LTSR)

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Abstract. Nickel doped bismuth vanadate \([\text{Bi}_4(\text{V}_{0.90}\text{Ni}_{0.10})_2\text{O}_{11-\delta};\text{BINIVOX}]\) calcined at 800°C (BINIVOX-800) catalyst is prepared by a solution combustion method. The catalytic activity study is carried in the temperature range of 250–400°C, and with the molar feed ratios of water: ethanol at 23:1 and 2.5:1. The study reveals an increase in the ethanol conversion and selectivity of carbon dioxide & hydrogen but a decrease in the selectivity of carbon monoxide and methane with an increase in temperature and water: ethanol mole ratio. Fresh and used catalysts are characterized using DTA, TGA, XRD and FTIR. XRD results reveal that the fresh catalyst is phase pure \(\gamma\)-BINIVOX. The phase purity and crystallinity of the catalyst is retained after 30 h of activity study.

Keywords. BINIVOX catalyst; catalytic activity; phase transition; crystal structure; thermal analysis.

1. Introduction

International Energy Outlook (IEO 2016) has predicted that the world energy demand will rise from 540.5 to 815.0 quadrillion BTU by 2014, as the projection for world population indicates that the 8 billion marker will be reached in 2025 which is 7 billion in 2012. Conventional energy sources, in addition to their non-renewable nature, pose various problems such as environmental pollution (ozone depletion, global warming, acid rain, radioactive discharge) and health hazards (bronchial diseases, malignancy, infant mortality), effects on human health, agriculture, economy, and society are detrimental. Thus renewable energy sources, that are sustainable and economic at the same time, are the need of the hour.

Out of all the renewable energy sources, hydrogen is garnering attention among environmental enthusiasts, industrial and scientific community because of its non-toxic nature, zero emission of a pollutant, high calorific value (3100 kcal/kg) and a wide range of flammability. Hydrogen is industrially manufactured by various processes like catalytic partial oxidation, steam reforming, dry reforming, decomposition of hydrocarbons, petroleum gasification, electrolysis, fermentation (biological ways), etc. Steam Reforming is a widely practised synthesis route owing to its high process efficiency and economic viability. Steam reforming is usually carried out at temperatures higher than 550°C. Low Temperature Steam Reforming (LTSR) is preferred due to it incurring lower operational and fixed costs, while, simultaneously offering high energy efficiency.

The renewable feedstock for hydrogen production for steam reforming is usually lighter hydrocarbons (methane, natural gas) and oxygenated hydrocarbons (alcohols, bio-oils, organic acids), out of which, we have used ethanol owing to its wide availability in India. Most common catalysts used for steam reforming are nickel (Ni), cobalt (Co), iron (Fe), copper (Cu) (transition metals), silver (Ag), gold (Au), platinum (Pt), rhodium (Rh), ruthenium (Ru), palladium (Pd) (noble metals) as active phase. Alumina, ceria, zirconium oxides are used as supports usually.

This work focuses on an individual group of catalysts called BIMEVOX which are complex oxides of bismuth, a metal (different transition metals such as Ni, Cu, Co, Mg, Zn, Fe, etc.) and vanadium. These catalysts have high oxide ion conductivity.
been used earlier for partial oxidation of propylene in the vapour phase. This is the first time we are reporting the application of these catalysts for hydrogen production via steam reforming. The high oxygen conductivity can help in reduction of carbon deposition and increase water gas shift reaction and thus decrease the deactivation rate.

This work centres on preparation, characterization and activity study of BINIVOX \([\text{Bi}_4(\text{V}_{0.90}\text{Ni}_{0.10})_2\text{O}_{11}]_{1-\delta}\) catalyst. The catalytic activity study has been performed at different temperatures and the varied composition of feed consisting of ethanol and water. The catalytic activity study is carried out by collecting and analyzing gaseous and liquid samples with the help of GC and HS-GC, respectively. Physical and chemical properties of BINIVOX-800 catalyst (BINIVOX calcined at 800 °C) are determined by characterizing the powders using XRD, DTA, TGA, and FTIR.

2. Experimental

2.1 Catalyst Preparation

BINIVOX-800 (\([\text{Bi}_4(\text{V}_{0.90}\text{Ni}_{0.10})_2\text{O}_{11}]_{1-\delta}\)) catalyst is synthesized by a solution combustion synthesis (SCS) method. Stoichiometric amount of bismuth nitrate (\([\text{Bi(NO}_3]_3.5\text{H}_2\text{O}\) (Rankem, LR grade, purity > 99\%) (34.9 g), vanadium pentoxide (\([\text{V}_2\text{O}_5]\) (Himedia, LR Grade, purity > 98\%) (2.9 g), nickel nitrate (\([\text{Ni(NO}_3]_2.6\text{H}_2\text{O}\) (QLS, AR Grade, purity > 99\%) (1.04 g) as oxidizer and glycine (\([\text{C}_2\text{H}_5\text{NO}_2]\) (Rankem, LR Grade, purity > 99\%) (9.3 g) as fuel (with oxidizer to fuel ratio as 1:1) are mixed thoroughly with ethanol in a 500 cc beaker. The mixture is left overnight for drying at room temperature. The homogenous paste is heated to 300 °C over a heating plate inside the fume hood to ensure security. The mixture is self-ignited in one place and spread throughout the beaker eventually, turning it into a black fluffy mass. The obtained mass is washed three to four times with DI water to remove the un-reacted salts and fuel and dried at 60 °C for 12 h. Finally, it is calcined at 800 °C for 2 h. This catalyst from now on is called as BINIVOX-800. The SCS method has been explained as a flowchart in Figure 1.

2.2 Catalyst Characterization

Simultaneous thermogravimetric and differential thermal analysis (S-DTG; Shimadzu, DTG-60H) of the dried powder is carried out in the presence of air from 30 to 800 °C at a rate of 5 °C per min rise in temperature. DTA data of the catalyst is also collected during the cooling cycle from 800 to 200 °C.

The X-ray diffraction data of the fresh and used BINIVOX-800 is acquired by Rigaku Miniflex II with the help of CuKα radiation (1.5 Å, 15 mA, 30 kV). The sample is scanned at 2°/min from 20 to 60°.

2.3 Catalyst Activity Study

Catalytic activity studies are conducted in a custom-made U-tube packed bed reactor (inner diameter of 3/8 inch) sited inside a muffle furnace. 2 g of the catalyst powder is loaded into the reactor. Water: ethanol mixture of 2.5:1 and 23:1 mole ratio is preheated to 110 °C. Pure nitrogen gas (99.99 %) swept through the preheater and carries vapour to the reactor. The vapour conducting ducts are maintained at 110 °C. An ice cooled phase separator is used to separate liquid and gaseous parts of the product coming out of the reactor. The gaseous products are analyzed at an interval of each hour for 6 h. A gas chromatograph instrument (Shimadzu gas chromatograph (GC - 2014)) with porapak as reference column and carbosphere as sample column with thermal conductivity detector (TCD) is used for the purpose. The liquid products are collected at the end of 6 h and are analyzed by a GC- HS (Shimadzu model no.10) equipped with Flow Ionization Detector (FID). The schematic of the experimental setup is shown in Figure 2.
3. Results and Discussion

3.1 Characterization Results

3.1a S-DTG Analysis: Figure 3 show the DTA and TGA profiles of the dried powder. Thermogravimetric analysis shows that there is a \( \sim 0.8\% \) decrease in weight at \( \sim 305^\circ C \) accompanied by an endothermic DTA peak. This could be attributed to the loss of surface moisture, volatile organic materials and/or some Bi-V-O related phase change.\(^{17}\) The exothermic DTA peak at \( \sim 640^\circ C \) may correspond to some phase change in the sample. The DTA cooling spectrum devoid of any phase reversal peak indicates the stability of the catalyst. Figure 4 shows the DTA and TGA spectra for BINIVOX-800 (a) fresh and (b) used catalyst. DTA spectra show that there is no change in phase during heating and cooling both, after 30 h of the experiment. TGA analysis shows that there is a \( \sim 0.24\% \) and \( \sim 0.26\% \) decrease in weight for the fresh and used catalyst, respectively. The change in weight is observed only minimal (\( \sim 0.02\% \)), which could be attributed to C deposition (DTA has no peak) on the catalyst. This indicates the stability (in terms of phase content and activation) of the catalyst.

3.1b XRD Analysis: From the X-Ray diffraction spectra of the fresh and used samples (Figure 5), it could be inferred that the heat treated (800 °C for 2 h) catalyst...
3.2 Catalytic Activity Study

Gaseous products obtained by steam reforming of ethanol consist of hydrogen, carbon monoxide, carbon dioxide and methane. The percentage (%) selectivity of the individual products is calculated using the following equations.\(^{21,22}\)

\[
\text{H}_2 \text{ selectivity} (\%) = \frac{x_{H_2}}{3x_{CO_2}} \times 100 \tag{1}
\]

\[
\text{CO}_2 \text{ selectivity} (\%) = \frac{x_{CO_2}}{x_{CO_2} + x_{CH_4} + x_{CO}} \times 100 \tag{2}
\]

\[
\text{CO selectivity} (\%) = \frac{x_{CO}}{x_{CO_2} + x_{CH_4} + x_{CO}} \times 100 \tag{3}
\]

\[
\text{CH}_4 \text{ selectivity} (\%) = \frac{x_{CH_4}}{x_{CO_2} + x_{CH_4} + x_{CO}} \times 100 \tag{4}
\]

Ethanol conversion = \((\text{mol EtOH}_{in} - \text{mol EtOH}_{out})/\text{mol EtOH}_{in}\) \times 100 \tag{5}

Experimental results indicate that the selectivity of the products attains steady state after five hours and almost remains constant for next 20 h indicating that the catalyst is stable over 25 h which is in accordance with the X-ray Diffraction and DTA/TGA results.

Figure 7 shows the changes in ethanol conversion (%), product selectivity (%) in the gaseous phase and carbon (%) in the gas phase with temperature. As temperature and the feed composition of water: ethanol (2.5:1 and 23:1 mole ratio) increase ethanol conversion increases. The similar results have been established by Romero-Sarria F et al.\(^{23}\) With the increase in steam content in the feed to the reactor, there is enhanced C-C and C-O bond cleavage. The lowest and the highest ethanol conversion (42% and 75%) is observed at 250 °C, H\(_2\)O: EtOH = 2.5:1 and 23:1 mole ratio, respectively.

Figures 7(b), 7(c), 7(d) and 7(e) reveal the rise of the hydrogen and carbon dioxide selectivity and drop in carbon monoxide and methane selectivity with respect to the temperature for both feed concentration. At the feed composition of H\(_2\)O: EtOH = 23:1, the highest hydrogen and carbon dioxide selectivity are recorded.
BINIVOX catalyst for hydrogen production

Figure 7. Catalytic activity as a function of temperature for the BINIVOX-800 powder for low temperature steam reforming of ethanol-H₂O mixture at two different mol ratio; (a) ethanol conversion (%), (b) H₂ selectivity (%), (c) CO₂ selectivity (%), (d) CO selectivity (%), (e) CH₄ selectivity (%), and (f) C in gas product (%).

to be 50 and 35%, respectively at 400 °C, which are, 140 and 600%, respectively, larger than the selectivity observed at the lowest reaction temperature (250 °C). The lowest selectivity values of carbon monoxide and methane are noticed to be 16 and 48%, respectively, at 400 °C and water: EtOH = 23:1 mole ratio. Supplementary word file is provided to show the carbon balance.

Reportedly, at lower steam reforming temperature (200 to 500 °C), ethanol undergoes the direct decomposition yielding carbon monoxide, methane and hydrogen (eq. 6).

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2; \quad \Delta H^\circ = 49 \text{ kJ/mol} \quad (6) \]

That can be followed by methane steam reforming reaction to produce carbon dioxide and hydrogen (eq. 7).

\[ \text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow 4\text{H}_2 + \text{CO}_2; \quad \Delta H^\circ = 164.5 \text{ kJ/mol} \quad (7) \]

At the similar low temperature, water gas shift reaction can also take place (eq. 8).

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2; \quad \Delta H^\circ = -40 \text{ kJ/mol} \quad (8) \]

Higher reaction temperature (550 °C) favours direct ethanol steam reforming to produce carbon dioxide (and/or CO) and hydrogen (eqs. 9 and 10).

\[ \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \leftrightarrow 6\text{H}_2 + 2\text{CO}_2; \quad \Delta H^\circ = 173.3 \text{ kJ/mol} \quad (9) \]
\[ \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \leftrightarrow 4\text{H}_2 + 2\text{CO}_2; \quad \Delta H^\circ = 260 \text{ kJ/mol} \quad (10) \]

Here, our results show that higher water: ethanol ratio favours methane reforming and water gas shift reaction, as expected.

4. Conclusion

BINIVOX catalyst annealed at 800 °C can be used for the production of hydrogen by low temperature steam reforming of ethanol. The preliminary catalytic activity study shows the significant formation of hydrogen and carbon dioxide in the product gas. Carbon dioxide is observed to be produced at temperatures as low as 250 °C. There is an increase in the selectivity of hydrogen, carbon dioxide and a decrease in the selectivity of methane and carbon monoxide with the increase in reaction temperature and water: ethanol mole ratio. This probably indicates methane steam reforming and water gas shift reaction capacity of the catalyst at low temperature. According to XRD and S-DTG analysis, the fresh catalyst is a phase pure γ- BINIVOX and retains its crystallinity and phase purity till after 30 hours of activity study.
Supplementary Information (SI)

The comparative peak width data of the fresh and used catalysts are demonstrated in Table S1. The detailed carbon balance related calculation procedure (flow rate, Ethanol conversion and Carbon in gas and liquid phases, etc.) is provided in SI available at www.ias.ac.in/chemisci.

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