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# Low temperature steam reforming of ethanol over cobalt doped bismuth vanadate $[Bi_4(V_{0.90}Co_{0.10})_2O_{11-\delta}$ (BICOVOX)] catalysts for hydrogen production

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#### ABSTRACT

The atmospheric pressure low temperature steam reforming of ethanol over  $Bi_4(V_{0.90}Co_{0.10})_2O_{11.6}$  (BICOVOX) catalysts, synthesize by a solution combustion synthesis method and calcined at 400, 600 and 800 °C, has been investigated at different reactor temperatures, H<sub>2</sub>O: EtOH molar ratios and feed flow rates. For fresh catalysts amount, crystallinity and particle size of pure  $\gamma$ -BICOVOX phase is observed to increase with increasing calcination temperature. Phase purity and crystallinity of the catalysts are almost retained till 30 h of activity study with some amount of carbon formation as derived from XRD, XPS, FESEM and simultaneous DTA-TGA study. Catalyst calcined at 600 °C (BICOVOX-600) exhibits the highest ethanol conversion (100%) with maximum H<sub>2</sub> selectivity (80%) under reaction conditions of 400 °C, 23:1H<sub>2</sub>O: EtOH molar ratio and 0.35 cc min<sup>-1</sup> feed flow rate. The maximum O<sup>2-</sup> vacancy present in lattice and lowest coke deposition could explain the best performance of BICOVOX-600 catalyst.

# 1. Introduction

Continuous growth in population, urbanization, and industrialization are major responsible factors for the constant consumption of fossil fuel leading to their depletion and emission of greenhouse gases [1]. In order to solve the energy & economy crises and environmental pollution problems related to this, governments of different countries are looking for the proper utilization of renewable energy resources. Hydrogen (H<sub>2</sub>) is considered as one of the promising renewable energy carriers with high heating value (34 kcalgm<sup>-1</sup>) to replace fossil fuels and fulfill the requirements of the clean energy [2,3].

Challenges regarding  $H_2$  production technology are lowering the cost of production, at least by a factor of 3–4, and improving the production rate. Ethanol has been chosen for the present study, because, it is less toxic and can be produced from different renewable biomass waste sources, bagasse or molasses (waste product after the extraction of sugar from sugar cane), different agricultural wastes (rice husk & straw, wheat straw, etc.) and forests debris like grass, wood, etc., by many diverse biochemical processes [4,5].

Although there are several catalytic reactor systems (such as aqueous phase reforming, combustion, partial oxidation, etc.) for H<sub>2</sub> production,

steam reforming has shown great potential. High temperature steam reforming, a well-known process, operates at 600–900 °C. In recent times, researchers have reported low temperature steam reforming (200–600 °C) of hydrocarbons for H<sub>2</sub> production. The success of this technology would lead to energy savings. Additionally, the longevity of the system is expected to be high, while reactor materials and operational costs would be lower compared to the conventional high temperature steam reforming.

Many works on low temperature (200–600 °C) & atmospheric pressure steam reforming of ethanol over inorganic catalyst powders have been reported. Most of these are on unary (Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, etc.) or mixed ceramic oxide supported single (Ni, Pt, etc.) or mixed metal (bi-, tri-etc.) catalysts [6,7]. Moraes et al. investigate low temperature steam reforming (LTSR) of ethanol over Ni(10 wt%)/CeO<sub>2</sub> and Pt(1 wt%)-Ni(10 wt%)/CeO<sub>2</sub> catalyst at 400 °C, under atmospheric pressure with H<sub>2</sub>O: EtOH molar ratio of 3:1 [8]. With only Ni, the EtOH conversion is found to be 54% with high H<sub>2</sub> (47–56%) and CO<sub>2</sub> (10–22%) selectivity values, while, with the addition of Pt to Ni the ethanol conversion increases to 69% with drops in H<sub>2</sub>(41–44%) and CO<sub>2</sub> (8–12%) selectivity values. Sahoo et al. perform steam reforming of ethanol over Co (15 wt%)/Al<sub>2</sub>O<sub>3</sub> catalyst, prepared by wet

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Received 3 May 2020; Received in revised form 6 September 2020; Accepted 7 September 2020 Available online 12 September 2020 0022-3697/© 2020 Elsevier Ltd. All rights reserved. impregnation, to investigate the effect of reaction temperature (350–600 °C), contact-time (3–10 kg cat./(mol/s)) and H<sub>2</sub>O: EtOH molar ratio (1:1–8:1) on H<sub>2</sub> production. The maximum H<sub>2</sub> (~78%) with minimum CO (~5%) and CH<sub>4</sub> (~2%) yield are achieved at 500 °C, H<sub>2</sub>O: EtOH molar ratio = 3:1–5:1 and contact-time 15–17 kg cat./(mol/s) [9]. Banach et al. study the effect of potassium inclusion (1–2 wt%) on Co–ZnO–Al<sub>2</sub>O<sub>3</sub> catalysts for ethanol steam reforming [10]. The reforming is carried out at 420 °C, atmospheric pressure, and H<sub>2</sub>O: EtOH mole ratio 21:1, 15:1 and 12:1. The catalyst with 2 wt% potassium and 28 wt% Co shows the maximum H<sub>2</sub> yield (5.5–5.3 mol H<sub>2</sub>/mol EtOH) along with 1.8–1.7 mol CO<sub>2</sub>/mol EtOH.

So far, most of the catalysts (including those mentioned above) used for steam reforming are in reduced form, in which the active phases are metal. However, few researchers have used simple and complex oxide catalysts for H<sub>2</sub> production without reduction as well. Ethanol steam reforming over  $\text{CeNi}_xO_v$  (0 < x < 5) mixed oxide catalysts has been demonstrated at 200-480 °C, atmospheric pressure and H2O: EtOH molar ratio of 3:1 by Duhamel et al. [11]. Catalyst without reduction shows the production of H<sub>2</sub> (70% selectivity) with 15% EtOH conversion at 300 °C. In the case of reduced catalyst, 62% H<sub>2</sub> selectivity and 17% EtOH conversion at the same reaction temperature have been reported. Lee et al. investigate the ethanol steam reforming over unreduced MgAl<sub>2</sub>O<sub>4</sub> and Zn<sub>0.3</sub>Mg<sub>0.7</sub>Al<sub>2</sub>O<sub>4</sub> oxide catalysts, at 300-600 °C, atmospheric pressure, and gas hourly space velocity (GHSV) of 6000  $h^{-1}$ [12]. For MgAl<sub>2</sub>O<sub>4</sub> catalyst the occurrence of H<sub>2</sub> (50% selectivity) happens at 350 °C and maximum H2 selectivity (78%) with 89% EtOH conversion is obtained at 550 °C. In case of Zn<sub>0.3</sub>Mg<sub>0.7</sub>Al<sub>2</sub>O<sub>4</sub> catalyst, H<sub>2</sub> (58%) starts to be produced at 300 °C and the maximum H<sub>2</sub> selectivity of 88% with 94% EtOH conversion is achieved at 550 °C.

Clearly, the development of efficient and stable catalysts, which can lead to high H<sub>2</sub> yield and ethanol conversion, is a critical step [4]. It has been found in the literature that supports with higher  $O^{2-}$  ion conductivity may play a very important role in the reforming. A comparative study shows the higher activity of Ni/CeO<sub>2</sub> system over Ni/Al<sub>2</sub>O<sub>3</sub> for aqueous-phase reforming of n-BuOH and this behavior is explained on the basis of higher  $O^{2-}$  ion mobility through the CeO<sub>2</sub> lattice [13,14]. Oxygen mobility through ceria and other oxide related catalysts is discussed by many other researchers [15,16].

The metal-doped bismuth vanadate (BIMEVOX) systems could be considered as potential catalysts (or supports for catalysts) for H<sub>2</sub> production due to high O<sup>2-</sup> ion conductivity. The Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> (BIVOX) is the parent compound, where, V<sup>5+</sup> ion is partially substituted (10–15 at%) with other metallic ions (Me = Li<sup>+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Ti<sup>4+</sup>, Sn<sup>4+</sup>, Pb<sup>4+</sup>, Nb<sup>5+</sup>, etc.) to acquire BIMEVOX.  $\alpha$  (face-centered orthorhombiczh),  $\beta$  (orthorhombic), and  $\gamma$  (tetragonal), the three main polymorphs of BIVOX are shown below with sequential phase transition temperatures [17].

$$\alpha \xrightarrow{\approx 450^{\circ}\mathrm{C}} \beta \xrightarrow{\approx 570^{\circ}\mathrm{C}} \gamma \xrightarrow{\approx 890^{\circ}\mathrm{C}} Liquid \tag{1}$$

The subvalent substitution of vanadium may stabilize the highest conductive  $\gamma$ -phase and leads to the formation of additional O<sup>2-</sup> vacancies in the significantly deformed vanadate octahedral, giving rise to enhanced oxygen ion mobility at low temperature [17,18].

Some of the BIMEVOX systems are used as catalysts in a fixed bed reactor and in a dense membrane catalytic reactor for the oxidation of hydrocarbons. Chetouani et al. report the application of BICOVOX and BICUVOX for vapor phase oxidation of propene in a stainless-steel fixed bed reactor in the temperature range of 300–550 °C. For both of the catalysts, up to 450 °C, propene ( $C_3H_6$ ) is mostly converted to CO<sub>2</sub>, while from 450 to 550 °C zone, oxidative dimerization of  $C_3H_6$  to 1,5-hexadiene ( $C_6H_{10}$ ) is increased at the expense of CO<sub>2</sub>. The detailed study shows that BICOVOX is more active and selective to the formation of 1,5-hexadiene than BICUVOX [19,20]. Löfberg et al. use polycrystalline BICOVOX and BICUVOX membranes in a catalytic dense membrane reactor for the oxidation of propene and propane. The conversion rate is

observed to depend on the number of available active sites on the surface of membranes [21,22].

Based on the above discussion, BICOVOX could be considered as a catalyst for low temperature (200-400 °C) atmospheric pressure steam reforming of ethanol. In our previous paper, limited study of BICOVOX (Bi<sub>4</sub>(V<sub>0.90</sub>Co<sub>0.10</sub>)<sub>2</sub>O<sub>11-δ</sub>) powder, calcined at 800 °C, for steam reforming of ethanol has been reported [23]. Here our interest is to present elaborate catalytic activity of BICOVOX powders (calcined at 400, 600 and 800 °C) at different reactor temperatures, feed concentrations and feed flow rates and correlate the performance of the catalysts with their physicochemical properties. X-ray diffraction (XRD) analysis has been used to explain the phase composition, while an electron microscopy technique with EDX is useful to understand the powder morphology and particle size and elemental distribution of the samples. X-ray photoelectron spectroscopy (XPS) helps to characterize the chemistry of the powder surface. S-DTGA is used to study the thermal decomposition behavior and Fourier transport infrared spectroscopy (FTIR) is utilized for surface analysis of the samples.

# 2. Experimental

#### 2.1. Catalyst preparation

BICOVOX catalysts are synthesized by a self-propagating solution combustion synthesis (SCS) method. Stoichiometric (O:F = 1:1) amounts of bismuth nitrate [Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O, > 99%; Rankem, Gurgaon, India], vanadium oxide [V<sub>2</sub>O<sub>5</sub>, >98%; Himedia, Mumbai, India], cobalt nitrate [(Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, > 99%; Rankem, Gurgaon, India] and glycine [C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, >99%; Rankem, Gurgaon, India] are mixed thoroughly with 10 ml ethanol in a mortar with a pestle for about 30 min. The mixture is transferred to a crystallization disk, allowed to air dry for overnight, and ignited on a hot plate at  $\sim$ 300 °C inside a fume-hood. The tip of a sheathed type-K thermocouple is placed just on the top of the mixture in an attempt to measure the temperature change with time during combustion. The mixture is kindled at a spot and the flame wave propagates throughout the volume instantaneously. Thus, a transient reddish flash appears over the entire area of the disk and a voluminous black smoke is produced. After cooling down, the foamy and porous mass is ground to obtain the powder sample, which is washed four to five times with deionized water to remove unwanted impurities. The powder sample is dried at 60 °C for a period of 12 h and named as 'BICOVOX-wash'. For the catalytic study, the powder is heat-treated in a muffle furnace at 400, 600 and 800 °C for a period of 2 h each, and then is designated as 'BICOVOX-400\_F', 'BICOVOX-600\_F' and 'BICOVOX-800\_F' catalysts, respectively [24].

# 2.2. Characterization of the catalysts

Simultaneous thermo-gravimetric and differential thermal analysis are carried out (DTG-60H, SHIMADZU) under atmospheric air, from 50 to 800 °C with a ramping rate of 10 °C min<sup>-1</sup> to understand the decomposition behavior of the catalyst. The DTA data is also collected during cooling from 800 to 200 °C in order to study the phase stability.

XRD (Rigaku miniflex II system with CuK $\alpha$  radiation, operated at 30 kV and 15 mA) study is accomplished over the 2-theta range from 10 to 90° at a scan rate of 0.5°/minute in order to characterize the phase content/composition and crystalline nature of the powder samples.

The BICOVOX catalysts are investigated using the IR probe in the mid-infrared region (Frontier, PerkinElmer, India) equipped with attenuated total reflection (ATR) attachment (GladiATR, PIKE Technologies, Inc.) to identify the presence of different chemical bonds and groups. A diamond crystal is used as an internal reflection element. The data is averaged over 20 scans.

The particle size distribution, morphology, and microstructure of the washed catalyst powder are studied with a field emission scanning electron microscope (FESEM Hitachi S-800, Krefeld, Germany),

operated at 15 kV with an energy-dispersive x-ray spectroscopy (EDX) detector (Inca Penta Fetx3). For other powders, the FESEM instrument from Carl Zeiss Merlin with EDX detector (EDX Ametek) is used. In order to prepare the FE-SEM specimen, a pinch of powder is sprinkled over carbon tape mounted on top of an aluminum stub.

The XPS data are collected by a Kratos Axis Ultra DLD X-ray photoelectron spectrometer with monochromatic Al Ka source operating at 13 kV AC voltage and 9 mA emission current. The operating pressure is maintained at  $\sim 10^{-9}$  torr. Charge compensation is achieved by the technique of charge neutralization using low energy electrons. After a wide-range survey of each, high-resolution C (1s), V (2p), Bi (4f), Co (2p) and O spectra of the samples are acquired in order to quantify the C/ coke deposition and to identify the oxidation states of the different metal/metal-oxides. Both BICOVOX\_F and BICOVOX\_30Hrs\_U (after using a catalyst for 30 h in the reactor at best operating parameters) catalysts are examined to understand the catalyst stability and changes with use. The deconvolution of all spectra is performed with the XPSPEAK 4.1 program using a Voigt function.

# 2.3. Catalyst activity test

Catalytic activity is performed by using a custom-designed continuous flow fixed bed stainless still reactor placed in a muffle furnace under atmospheric pressure. 2 gm batch of the BICOVOX catalyst, sandwiched in between two layers of quartz wool, is loaded in the reactor and preheated at 150 °C for 30 min with flowing nitrogen (10 ml  $\min^{-1}$ ) for the removal of the adsorbed moisture from the surface. The performance of the catalyst is evaluated at atmospheric pressure, for 23:1 and 2.5:1H<sub>2</sub>O: EtOH molar ratios, reactor temperature range of 200–400  $\,^\circ\text{C},$  and 0.1 and 0.35 cc  $\,\text{min}^{-1}$  feed flow rates (GHSV = 5097.9–17,318  $h^{-1}$  at STP). The liquid mixture of ethanol and water is

(a)

BICOVOX

preheated at 110 °C and N<sub>2</sub> gas (>99.99%) is swept through the preheater to carry the vapor mixture to the reactor. The tubing connecting the preheater to the reactor is heated at 110 °C to prevent condensation. The effluent from the reactor is passed through an ice-cooled phase separator in order to separate the gaseous and liquid phase products. The gaseous products from the phase separator are analyzed by using gas chromatography (SHIMADZU-2014) instrument equipped with a thermal conductivity detector (TCD) and liquid product is analyzed with a headspace gas chromatography (HSGC; Shimadzu-HS10) equipped with a flame ionization detector (FID). The schematic of the LTSR experimental set-up is shown in the supplementary file (S-Fig. 1).

In the present study, ethanol conversion (X<sub>EtOH</sub> (%)) and the selectivity of C-containing products are calculated by using the following equations [14]:

$$X_{EtOH} (\%) = [(mol EtOH_{in} - mol EtOH_{out}) / mol EtOH_{in}] * 100$$
(2)

$$S(\%) = [(C \text{ in CO}, CO_2 \text{ or CH}_4)/(\text{total C present in the out flow gas})] * 100$$
(3)

H<sub>2</sub> selectivity is calculated as the number of moles of H<sub>2</sub> present in the outflow gas, normalized by the number of moles of H<sub>2</sub> that would be formed if each mole of C in ethanol is considered to participate in the reforming reaction ideally to give 3 mol of  $H_2$  according to equation (4) [14]:

$$S_{H2}(\%) = [ (mol\% H_2 \text{ in out flow gas}) / (3* mol\% CO_2 \text{ in out flow gas})]*100 \tag{4}$$

The selectivity of CH<sub>3</sub>CHO, CH<sub>3</sub>OH, and CH<sub>3</sub>COCH<sub>3</sub>, in the liquid effluent, is calculated similarly to equation (3):

> Fig. 1. XRD spectra of the (a) BICOVOX-wash and BICOVOX\_F catalysts calcined at 400, 600, and 800 °C, (b) BICOVOX catalysts calcined at 400, 600, and 800 °C and used in reactor for 30 h at 400 °C, 0.35 cc min<sup>-1</sup> feed flow rate, and 23:1H<sub>2</sub>O: EtOH molar ratio. The symbols \* and \$ represent tetragonal (amcsd-0010069) and monoclinic (amcsd-0011925) Bi<sub>2</sub>O<sub>3</sub>, and # represents (amcsd-0014281) BiVO4 -related phases, respectively. FTIR spectra of (c) BICOVOXwash and BICOVOX\_F catalysts calcined at 400, 600, and 800 °C, and (d) BICOVOX catalysts calcined at 400, 600, and 800 °C and used in reactor for 30 hrs at 400 °C, 0.35 cc min<sup>-1</sup> feed flow rate, and 23:1 H<sub>2</sub>O: EtOH molar ratio.



S (%) = [(C in CH<sub>3</sub>CHO, CH<sub>3</sub>OH, or CH<sub>3</sub>COCH<sub>3</sub>)/(total C present in liquid products)] \* 100

#### 3. Results

BICOVOX catalysts have been testes at different reactor temperatures, feed flow rates, and feed concentrations. Among all, the best activity is obtained at 400 °C, 0.35 cc min<sup>-1</sup>, and 23:1H<sub>2</sub>O: EtOH molar ratio. Accordingly, the physicochemical characterization of the catalysts corresponding to this reaction condition is performed in detailed and reported here.

#### 3.1. Microstructural and related analysis

XRD spectra (Fig. 1(a) & (b)), shown in layer lines, illustrate the effects of heat treatment and reactor conditions on phase composition and crystallinity of the BICOVOX fresh and used catalysts. BICOVOX-Wash sample (Fig. 1(a)) shows a multiphase combination, containing tetragonal β-Bi<sub>2</sub>O<sub>3</sub> (\*; American mineralogist crystal structure data base 0010069 or amcsd-0010069), monoclinic  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (\$; amcsd-0011925), BiVO<sub>4</sub> (#; amcsd-0014281) along with the desired pure γ-BICOVOX (amcsd-0016748). The fresh sample calcined at 800 °C, can be indexed

to be mostly pure  $\gamma$ -BICOVOX (around 93 wt% with average crystallite size 20.4 nm) phase with the presence of the small amount of tetragonal-BiVO<sub>4</sub> (7.2 wt%; peaks at ~ 18.8, 28.9 and 30.5°) [17,25]. For BICOVOX-400 F (around 75 wt% pure y-BICOVOX with crystallite size 45 nm) and BICOVOX-600\_F (pure γ-BICOVOX around 83.0 wt% with crystallite size 46.8 nm) samples, little amount of BiVO<sub>4</sub> phase is observed (around 15 and 7 wt%, respectively) and two more extra peaks, at  $\sim 28.0$  and  $\sim 46.3^{\circ}$ , indicate the presence of tetragonal  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> related secondary phases. However, in BICOVOX-600\_F, besides β-Bi<sub>2</sub>O<sub>3</sub> monoclinic (~1 wt%)  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> peaks at ~25.8 and ~27.4° is also observed [24]. After use in a reactor, for BICOVOX-600 30Hrs U sample, amount of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> increases slightly, while for BICOVOX-400\_30Hrs\_U sample a new  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> is appeared (Fig. 1(b)). No phase change occurs in BICOVOX-800\_30Hrs\_U catalyst and it retains good crystallinity. XRD patterns for parent compound BIVOX (wash and calcined at 600 °C) depicts the presence of more amount of secondary phases even after calcination (supplementary file (S-Fig. 2)).

FT-IR spectra (Fig. 1(c) & (d)) of washed, fresh and used catalysts reveal a broad and strong band at  $\sim$ 710 cm<sup>-1</sup> which could be assigned to V–O stretching mode, corresponds to the variation of the V–O bond length in the range of 1084–1079 Å for VO<sub>4</sub> tetrahedra and/or VO<sub>6</sub>



Fig. 2. DTA/TGA spectra for (a) BICOVOX-wash, (b) BICOVOX-400\_30Hrs\_U, (c) BICOVOX-600\_30Hrs\_U and (d) BICOVOX-800\_30Hrs\_U catalysts used in reactor at 400 °C, 0.35 cc min<sup>-1</sup> feed flow rate, and 23:1H<sub>2</sub>O: EtOH molar ratio.

literature [30,31].

octahedra [25]. In addition, the Bi–O symmetric vibrations due to β-Bi<sub>2</sub>O<sub>3</sub> are observed at 609, 510 and 418 cm<sup>-1</sup> [26]. Peaks captured in the region of 477 to 440 cm<sup>-1</sup> could be ascribed to doping metal-oxygen bond Co–O [27]. Additionally, an extra peak at 823 cm<sup>-1</sup> could be assigned to asymmetric V–O stretching [25]. BICOVOX-600\_F and BICOVOX-400\_30Hrs\_U show additional bands in the region of 516–422 cm<sup>-1</sup>, which could be attributed to α- Bi<sub>2</sub>O<sub>3</sub> [26,28], and supported by XRD results. In the case of all BICOVOX\_30Hrs\_U catalysts one peak at ~1369 cm<sup>-1</sup> signifies the presence of C=C stretching and confirms the carbon deposition (Fig. 1(d)) [29]. One band is observed (only in used samples) at 1204 cm<sup>-1</sup>, corresponds to an asymmetric V–O stretching [30]. Our observations are consistent with the results reported in the

S-DTGA profiles of BICOVOX-wash and BICOVOX\_30Hrs\_U catalysts are unveiled in Fig. 2. The DTA profile of the BICOVOX-wash catalyst (Fig. 2(a)) contains two peaks-the first one, endothermic at ~ 270 °C and corresponds to weight loss of ~1.7%, could be attributed to chemisorbed moisture and ethanol, carbon left from glycine, and/or some Bi–V–O (such as  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> to  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>) related phase change. The second one, exothermic in nature at ~650 °C and observes only during heating (without weight loss), could be due to the Bi–V–O (secondary phases ( $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>) to pure  $\gamma$ -BICOVOX) related phase transformation [32]. The exothermic DTA peak, at ~600 °C for BICOVOX-400\_30Hrs\_U and BICOVOX-600\_30Hrs\_U catalysts (Fig. 2(b–c)) with ~0.3% weight



Fig. 3. FESEM images with particle size distribution and EDX spectrum for (a) BICOVOX-wash. Catalysts calcined at 400 °C (b) & (c), 600 °C (d) & (e), and 800 °C (f) & (g) show the variation of particle size and elemental distribution for catalysts in fresh stage and after use in reactor for 30 h at 400 °C, 0.35 cc min<sup>-1</sup> feed flow rate, and 23:1H<sub>2</sub>O: EtOH molar ratio, respectively.

loss, could be attributed to both C deposited on samples and phase transformation [32]. However, for BICOVOX-800\_30Hrs\_U catalyst (Fig. 2(d) small weight loss (due to deposited carbon to  $CO_2$  formation), without any DTA peak (indicating no phase decomposition during reforming) is observed. The featureless DTA profile during cooling shows the phase stability of the catalysts. The TGA spectra of BICOVOX-wash shows that most of the residual carbon burned out within 400 °C. In used samples, the TGA spectra extended till 700-750 °C implies that the nature of C formed during sample preparation (amorphous) is different from the C-deposited (mixed amorphous and graphitic nature) in the course of reforming reaction. These results are in accordance with the XRD and FTIR analysis. The endothermic peak at ~623 °C in the DTA cooling spectrum of BIVOX-wash powder (supplementary file; S-Fig. 3) suggests the reverse transition of  $\gamma$ -BIVOX which indicates the instability of the undoped parent phase. Here, it is important to mention that DTGA is a standard method for detecting C deposited on used catalysts [32,33].

The porous and flaky network of interconnected particles is a common morphology for the solution combustion synthesized BICOVOX powders and well evident in the FESEM images (Fig. 3 (a), (b), (d) and (f)) along with the particle size distribution and EDX spectra of the wash and fresh catalysts. EDX data show the presence of Bi, V, Co, C and O elements. Table 1 includes the particle size distribution and elemental analysis, obtained from FESEM-EDX, for wash, fresh, and 30 h used BICOVOX catalysts.The average particle size for the fresh catalysts increases with calcination temperature, as expected, and some particle agglomeration is observed after using these catalyst for 30 h in the reactor (Fig. 3(c), (e) and (g)). No clear carbon structure is evident in the FESEM images but EDX indicates coke deposition on the used catalysts. Which implies the formation of a thin layer of carbon. EDX shows some what higher amount of carbon deposition on the BICOVOX-800\_30Hrs\_U catalyst compared to the others.

As reported, most of the research works on BIMEVOX powders use the standard solid state reaction (SSR) technique for the sample preparation and average particle size of the synthesized power lies in the range of ~15–25 µm [34,35]. The particle size distribution of the fresh catalysts (0.1–13.6 µm) indicates that SCS could be a useful method for the preparation of BIMEVOX powder of smaller particle size leading to highly effective materials of application. Roy et al. synthesize the Bi<sub>4</sub>(V<sub>0.85</sub>Cu<sub>0.15</sub>)<sub>2</sub>O<sub>11-δ</sub> catalyst by SCS and calcined at 600, 700 and 800 °C [24]. Reported particle sizes for as-combusted, 600, 700 and 800 calcined catalysts are 0.1–1, 0.2–5.8, 0.5–6.5 and 1–10 µm, respectively which is in the same line of our results.

#### 3.2. Surface chemistry analysis

Wide range XPS spectra of the washed and fresh (supplementary file (S-Fig. 4 (a))) and used (supplementary file (S-Fig. 4 (b))) catalysts, presented in layer lines, show the presence of all essential elements; Bi, V, O, and Co, along with adventitious C. The peaks at ~27.0, 93.0, 163.0, 440.0, 460.0, 680.0, and 940.0 eV could be assigned to Bi5d, Bi5p, Bi4f, Bi4d<sub>5/2</sub>, Bi4d<sub>3/2</sub>, Bi4p, and Bi4s, respectively [36,37]. Peaks at ~284.0, ~530.0, ~515.0, and ~779.0 eV correspond to C1s, O1s, V2p, and Co2p, respectively [36]. Binding energies of all the elements

are calibrated by carbon i.e. 284.4 eV as it is found to be the maximum intensity peak for C1s.

High resolution XPS spectra of the V2p, for fresh and used catalysts calcined at different temperatures, are depicted in Fig. 4(a-c). For all the BICOVOX\_F catalysts, the deconvoluted V2p3/2 peak at ~517.0 eV, corresponds to the  $V^{5+}$  oxidation state and the  $V2p_{3/2}$  peak at ~516.2 eV could be attributed to  $V^{4+}$  oxidation state [37]. After catalytic activities, the intensity and area of the lower binding energy peak (for  $V^{4+}$ oxidation state) is found to reduce and intensity of high binding energy peaks, indicating the presence of  $V^{5+}$  state, are found to increase [38]. The V<sup>5+</sup>:V<sup>4+</sup> ratio for BICOVOX-400 F, BICOVOX-600 F and BICOVOX-800 F is calculated to be 0.65, 0.33 and 0.63, respectively which reflects that BICOVOX-600 F catalyst contains the maximum amount of V<sup>4+</sup> oxidation state. Clearly, Co dopant incorporated in structure is responsible for the formation of dual oxidation states, as supported by the literature. Kim et al. and Khaerudini et al. study and report the V2p spectra for  $Bi_4V_2O_{11}$ ,  $Bi_4(V_{0.90}Co_{0.10})_2O_{11-\delta}$  and  $Bi_4(V_{0.90}Nb_{0.10})_2O_{11-\delta}$  powder, prepared by SSR method [37,39].  $Bi_4V_2O_{11}$  shows only  $V^{5+}$  oxidation state, however, both  $V^{5+}$  and  $V^{4+}$ oxidation states are seen for the other two, reflecting the formation of more anionic vacancies.

The high-resolution C1s core level XPS data, as shown in Fig. 4(d–f), indicates the variation of coke present on the surface of the fresh and used catalysts. For all fresh catalysts, C1s profile comprises adventitious carbon at ~284.0 and ~285.6 eV ascribe to  $\text{sp}^2$  and  $\text{sp}^3$  hybridized C–C bonding, respectively with C=O at ~288 eV. It is observed that peak area and intensity reduces with calcination temperature, from BICOVOX-400\_F to BICOVOX-800\_F catalysts, as expected [40,41]. C1s spectrum of all used catalysts is noticed to increase in intensity and area of all the peaks, indicating deposition of C during reforming. Calculated fresh:30Hrs\_U carbon ratio is 1:2.2, 1:1.9 and 1:2.8 for BICOVOX-400, BICOVOX-600, and BICOVOX-800\_addet, respectively. The maximum amount of carbon is seen for BICOVOX-800\_30Hrs\_U catalyst, and it is supported by FESEM results [40].

The high resolution Bi4f spectra of BICOVOX-wash and all BICO-VOX\_F catalysts (Fig. 5(a–c)) exhibit two peaks centered at ~164.2 and ~159.1 eV, which might be ascribed to Bi4f<sub>5/2</sub> and Bi4f<sub>7/2</sub> of Bi<sup>3+</sup> in Bi<sub>2</sub>O<sub>3</sub> [42]. Two more peaks at ~163.7 and ~158.4 eV, corresponding to the Bi4f<sub>5/2</sub> and Bi4f<sub>7/2</sub> of Bi metal (Bi<sup>0</sup>), are observed in general, except for BICOVOX-800\_F catalyst [42]. After using the catalysts in the reactor, intensity and area of the lower binding energy peaks are observed to increase, suggesting the reduction of Bi<sup>3+</sup> to lower oxidation states Bi<sup>0</sup> [42]. Obtain an order of reduction (Bi<sup>3+</sup> to Bi<sup>0</sup>) is BICOVOX-400\_30Hrs\_U > BICOVOX-800\_30Hrs\_U>BICOVOX-600\_30Hrs U.

Fig. 5(d–f), representing the high resolution XPS spectra for O1s, indicates the presence of two sites of oxygen. The deconvoluted peaks at  $\sim$ 529.2 and  $\sim$ 531.2 eV confirm the presence of lattice oxygen (O<sub>L</sub>) and O<sup>2-</sup> vacancies (O<sub>V</sub>) with -2 and +2 oxidation state, respectively, in all catalysts [43]. The O<sub>L</sub>: O<sub>V</sub> ratio for BICOVOX-400\_F, BICOVOX-600\_F, and BICOVOX-800\_F are calculated to be 5.7, 1.7 and 2.7, respectively which reflects that BICOVOX-600\_F catalyst contains the maximum amount of O<sup>2-</sup> vacancies. Spectra of Co2p for all BICOVOX catalysts are depicted in Fig. 5(g–i). The five deconvoluted peaks at  $\sim$ 780.0(Co<sup>3+</sup>),

# Table 1

Particle size distribution from FESEM and elemental analysis from EDX and XPS of wash, fresh, and 30 h used BICOVOX catalysts.

Catalysts	Particle size Dist. (FESEM)	Elemental Analysis-EDX (at%)					Elemental Analysis-XPS (at%)				
		Bi	v	Со	С	0	Bi	V	Со	С	0
BICOVOX-WASH	0.1 - 1.1	30.8	14.9	1.7	15.5	37.1	13.3	6.6	0.7	47.1	32.3
BICOVOX-400_F	0.2–4.9	34.7	16.6	1.5	12.2	35.0	20.0	9.8	1.1	43.2	25.9
BICOVOX-400_30HRS_U	0.3-8.3	35.9	16.4	1.9	16.5	29.3	12.9	6.3	0.7	49.9	30.2
BICOVOX-600_F	0.4–7.8	35.9	16.8	1.9	10.5	34.9	15.4	7.5	0.8	39.6	36.7
BICOVOX-600_30HRS_U	0.5–10.9	38.5	16.8	1.9	14.7	28.1	11.7	5.5	0.6	48.7	33.5
BICOVOX-800_F	0.4–13.6	36.9	17.5	1.9	8.5	35.2	16.2	8.1	0.9	33.9	40.9
BICOVOX-800_30HRS_U	0.7–15.8	35.2	15.8	1.9	18.7	28.4	12.0	5.8	0.6	52.3	29.3



**Fig. 4.** High resolution XPS spectra of V for the catalysts calcined at (a) 400 °C, (b) 600 °C, (c) 800 °C, and C for the catalysts calcined at (d) 400 °C, (e) 600 °C, and (f) 800 °C showing the variation of oxidation states for fresh, and 30 Hrs\_U BICOVOX catalysts.

 ${\sim}782.6({\rm Co}^{2+}),~786.5({\rm satellite}),~797.2({\rm Co}^{2+})$  and 804.8({\rm satellite}) eV denote the presence of Co in the lattice in Co^{3+} and Co^{2+} oxidation states [44]. However, no certain trend of doping metal oxidization state with heat treatment or reactor conditions are observed. High resolution XPS spectra of V2p and O1s for BIVOX-600 (fresh and used) are reported in the supplementary file (S-Figure 4 (c) and (d)). Calculated V^{5+}:V^{4+} (2.4) and O\_L: O\_V (8.6) ratio for fresh catalyst shows a small amount of O^{2-} vacancy and for used catalyst, only V^{5+} oxidation states and O\_L are detected.

Table 1 shows the elemental analysis of BICOVOX fresh and used catalysts obtained from XPS profile. Atomic % of the elements is determined using CasaXPS-2.3.17 software and considering the core shell peaks for each element. The Bi: V and V: Co atomic ratios, calculated from both EDX and XPS data, are  $\sim$ 2 and  $\sim$ 9 (taking ±0.5 error) for all BICOVOX catalysts, which suggest that proper stoichiometry is maintained in the compositions.

#### 3.3. Catalytic activity study

The catalytic activity is presented in terms of ethanol conversion (%), C in the gas product (%), selectivity (%) of gaseous ( $H_2$ ,  $CO_2$ , CO, and  $CH_4$ ) and liquid ( $CH_3CHO$ ,  $CH_3OH$ , and  $CH_3COCH_3$ ) products for various temperatures, feed concentrations and flow rates.

Irrespective of reactor temperature, feed concentration, and flow rate, for all the BICOVOX catalysts, EtOH conversion, C in the gas phase and selectivity values of  $H_2$  and  $CO_2$  increases and CO and  $CH_4$ 

selectivity reduces with time, attain the steady-state within 5–6 h and remain stable till ~30 h. Fig. 6 shows an example, where the activity is carried out at 400 °C, 23:1H<sub>2</sub>O: EtOH molar ratio and 0.35 cc min<sup>-1</sup> feed flow rate. For BIVOX steady state is obtained within 6 h, but H<sub>2</sub> and CO<sub>2</sub> selectivity values (~12.0 and ~5%, respectively) detected to be much smaller compared to BICOVOX catalysts (supplementary file; S-Fig. 5).

In the following sections, the effect of temperature, flow rate, and feed concentrations on steady-state EtOH conversion, C-in gas, the selectivity of gaseous and liquid products of BICOVOX catalysts are discussed.

### 3.4. Effect of temperature

EtOH conversion, C in the gas phase and selectivity values of  $H_2$  and  $CO_2$  increase with temperature irrespective of feed concentration and flow rate, while CO and CH<sub>4</sub> show an opposite trend as shown in Fig. 7 (a–f) and Table 2. Maximum EtOH conversion of 100% with highest  $H_2$  (80%),  $CO_2$  (72%) selectivity, and C in gas phase (97%), and lowest CO (0%) and CH<sub>4</sub> (28%) selectivity is obtained for BICOVOX-600 catalyst at 400 °C, 0.35 cc min<sup>-1</sup>, and 23:1H<sub>2</sub>O: EtOH molar ratio.  $H_2$  and  $CO_2$  selectivity of BICOVOX-600 are noticed to be 30.0 and 23.6% higher with respect to BICOVOX-400 and 23.7 and 12.5% higher with respect to BICOVOX-800 catalysts, respectively. The temperature at which 1st  $CO_2$  is formed, called crossover point. Only CO is detected below 200 °C, in general and  $CO_2$  is started to form (crossover point) at ~200 °C for the catalysts calcined at 600 and 800 °C and for the catalysts calcined at 400



**Fig. 5.** High resolution XPS spectra of the elements present in the BICOVOX catalysts calcined at 400 °C (a) Bi, (d) O, and (g) Co; 600 °C (b) Bi, (e) O, and (h) Co; and 800 °C (c) Bi, (f) O, and (i) Co show the variation of oxidation states and chemistry in fresh state and after use in reactor for 30 h at 400 °C, 0.35 cc min<sup>-1</sup> feed flow rate, and 23:1H<sub>2</sub>O: EtOH molar ratio.

 $^{\circ}$ C crossover point is at ~225  $^{\circ}$ C. Fig. 7(g–i) show that selectivity of CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> increases with an increase in reaction temperature and CH<sub>3</sub>OH selectivity shows an opposite trend. Similar trends have been observed in our last paper [23].

Steam reforming of ethanol over BIMEVOX catalysts has not been reported till date. Research works reported in the scientific literature for LTSR over various other catalysts have been considered for analyzing our results. Dai et al. perform LTSR over Pt nano-particles encapsulated





**Fig. 6.** Variation of EtOH conversion, and selectivity of the gaseous products as a function of time under steam reforming conditions of 400  $^{\circ}$ C, atmospheric pressure, 23:1H<sub>2</sub>O:EtOH molar ratio and 0.35 cc min<sup>-1</sup> feed flow rate of (a) BICOVOX-400, (b) BICOVOX-600, and (c) BICOVOX-800 C catalysts.

in hollow zeolite microreactor catalyst at atmospheric pressure, weight hourly space velocity (WHSV) of 8.5 h<sup>-1</sup>, H<sub>2</sub>O: EtOH mole ratio of 4:1 and temperature range from 200 to 400 °C [45]. Catalytic activity results show the increase in EtOH conversion from 68 to almost 100% and an increase in H<sub>2</sub> and CO<sub>2</sub> selectivity from ~42.0 to 72.0% and ~15.0–23.0%, respectively on increasing temperature from 200 to 400 °C. CO and CH<sub>4</sub> selectivity show an opposite trend with temperature. Lee et al. perform ethanol steam reforming over mesoporous Sn-incorporated SBA-15 catalyst at atmospheric pressure, GHSV 6600 h<sup>-1</sup>, H<sub>2</sub>O: EtOH molar ratio of 1:1, and temperature varying from 200 to 400 °C [46]. The maximum EtOH conversion and H<sub>2</sub> selectivity of 92.0 and 70.0%, respectively, are achieved at 400 °C. Results reported in the literature with respect to the effect of temperature on product distribution and EtOH conversion, are in the same line of our experimental outcomes.

#### 3.4.1. Effect of ethanol concentration in the feed

The effect of feed concentration on the catalytic activity is reported in Fig. 7 and (supplementary file (S-Fig. 6)). As a general trend, ethanol conversion, C in gaseous products, and  $H_2$  & CO<sub>2</sub> selectivity reduce and on the contrary CO and CH<sub>4</sub> selectivity increase with increasing EtOH concentration from 23:1 to 2.5:1H<sub>2</sub>O: EtOH molar ratio for all the catalysts. EtOH conversion,  $H_2$  and CO<sub>2</sub> selectivity reduces from 100 to 86%, 80.0 to 66.0% and 72.0 to 54.0%, respectively and CO and CH<sub>4</sub> selectivity increases from 0.0 to 13.0% and 28.0 to 33.0%, respectively with increasing EtOH concentration, at 400  $^{\circ}$ C, and 0.35 cc min<sup>-1</sup> for BICOVOX-600 catalyst. Obtain trends for liquid products shows that selectivity of CH<sub>3</sub>COCH<sub>3</sub> and CH<sub>3</sub>OH increases and CH<sub>3</sub>CHO decreases with increasing EtOH concentration from 23:1 to 2.5:1H2O: EtOH molar ratio. In our last paper we have also seen the similar trends [23]. These are consistent with the effects of feed concentration on product distribution reported by other researchers. Comas et al. perform ethanol steam reforming over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at 1 atm, 400 °C, and H<sub>2</sub>O: EtOH molar ratio varies from 6:1 to 1:1 [47]. Results show that with increasing EtOH concentration, the H<sub>2</sub> and CO<sub>2</sub> selectivity reduces 90.0 to 55.0% and 42.0 to 30.0%, respectively and CO and CH<sub>4</sub> selectivity increases from 15.0 to 38.0% and 21.0 to 23.0%, respectively. Mulewa et al. shows that EtOH conversion, H<sub>2</sub> and CO<sub>2</sub> yield reduces from 98.9 to 88.9%, 54.6 to 28.8% and 21.4 to 13.3%, respectively, with the increase in feed concentration from 10:1 to 1:10 H<sub>2</sub>O: EtOH molar ratio at 1 atm, 400 °C and GHSV =  $13200 \text{ ml/gcat} \cdot h$  [48]. On the contrary, CO (2.5–14.3%) and CH<sub>4</sub> (12.6-13.3%) yield increases with an increase in feed concentration.

# 3.4.2. Effect of feed flow rate

In general, EtOH conversion, CO and CH<sub>4</sub> selectivity reduce with an increase in flow rate from 0.1 to 0.35 cc min<sup>-1</sup>, but H<sub>2</sub> and CO<sub>2</sub> selectivity show an opposite trend, as shown in Fig. 7. H<sub>2</sub>, CO<sub>2</sub> selectivity



**Fig. 7.** Steady state variation of (a) EtOH conversion,(b) C in gaseous phase, selectivity of the gas products; (c)  $H_2$ , (d)  $CO_2$ , (e) CO, (f)  $CH_4$ , and liquid products; (g)  $CH_3CHO$ , (h)  $CH_3OH$ , and (i)  $CH_3COCH_3$  as a function of reactor temperature, for  $H_2O$ :EtOH molar ratio of 23:1 and feed flow rates 0.1 & 0.35 cc min<sup>-1</sup> over the BICOVOX catalysts calcined at different temperatures. Legend is represented as: catalyst calcination temperature  $-H_2O$ : EtOH molar ratio-feed flow rate.

increases from 73.0 to 80.0%, and 63.0 to 72.0% respectively and CO and CH<sub>4</sub> selectivity reduces from 2.0 to 0.0% and 35.0 to 28.0%, respectively with increasing flow rate from 0.1 to 0.35 cc min<sup>-1</sup> at 23:1H<sub>2</sub>O: EtOH molar ratio and 400 °C for BICOVOX-600 catalyst. EtOH conversion reaches 100.0% at 400 °C for BICOVOX-600 catalyst and remains unaffected with the change in flow rate further. The selectivity of CH<sub>3</sub>COCH<sub>3</sub> and CH<sub>3</sub>OH reduces and CH<sub>3</sub>CHO increases with an increase in flow rate. Hongbo et al. perform ethanol steam reforming over

Ni/Y<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst at H<sub>2</sub>O:EtOH = 13:1 molar ratio, temperature 300–500 °C , and feed flow rate varies from 0.01 to 0.3 ml min<sup>-1</sup> [49]. At 400 °C, complete conversion of EtOH happens and remains unaffected as feed flow rate changes from 0.01 to 0.3 ml min<sup>-1</sup>, and H<sub>2</sub> yield increases from 32.1 to 38.5% with increasing feed flow rate, which is in the same line with our results. The effect of feed concentration and flow rate on gaseous and liquid products at 400 °C is reported in Table 2 for all catalysts.

#### Table 2

Steady state catalytic activity data for LTSR of EtOH over BICOVOX catalysts at 400 °C reactor temperature under different feed concentration and flow rates.

Catalysts	BICOVOX-400				BICOVOX-600				BICOVOX-800			
Feed flow rate (cc min <sup><math>-1</math></sup> )	0.1		0.35		0.1		0.35		0.1		0.35	
H <sub>2</sub> O:EtOH (molar ratio)	23:1	2.5:1	23:1	2.5:1	23:1	2.5:1	23:1	2.5:1	23:1	2.5:1	23:1	2.5:1
EtOH conv. (%)	83	71	78	68	100	96	100	86	88	75	83	69
C in gas (%)	83	78	85	80	90	79	97	82	90	75	96	83
H <sub>2</sub> selectivity (%)	50	38	56	44	73	59	80	66	55	43	61	51
CO <sub>2</sub> selectivity (%)	48	38	55	42	63	48	72	54	55	46	63	50
CO selectivity (%)	16	28	10	22	2	19	0	13	13	16	8	14
CH <sub>4</sub> selectivity (%)	36	34	35	36	35	33	28	33	32	38	29	36
CH <sub>3</sub> CHO selectivity (%)	50	35	57	44	65	51	75	60	59	44	65	52
CH <sub>3</sub> OH selectivity (%)	31	40	28	35	16	25	15	20	23	30	20	25
CH <sub>3</sub> COCH <sub>3</sub> selectivity (%)	19	25	15	21	19	24	10	20	18	26	15	23

#### 4. Discussion

Several research works have been published in the field of ethanol steam reforming over various catalysts with the aim of improving the catalytic activity and less carbon formation [50-55]. Martinelli et al. study the effect of Na (2.5 wt%) addition on the performance of Pt(2.0 wt%)/ZrO2 catalyst for ethanol steam reforming at 250-400 °C, atmospheric pressure, and GHSV of 381000  $h^{-1}$ . Na enhances the CO<sub>2</sub> selectivity and H<sub>2</sub> selectivity by promoting C–C scission. The maximum H<sub>2</sub> and CO<sub>2</sub> selectivity are obtained to be 68 and 47%, respectively, with almost 100% ethanol conversion [50]. Dai et al. investigate low temperature ethanol steam reforming over dragon fruit-like engineered structure Pt–Cu (Pt/Cu = 2.5/1)/mesoporous SiO<sub>2</sub> catalyst at 250–450 °C, and atmospheric pressure. Almost 100% ethanol conversion with maximum H<sub>2</sub> and CO<sub>2</sub> selectivity values of 71 and 22%, respectively, are achieved at 450 °C [51]. Riani et al. compare the activity of unsupported Co nanoparticles prepared by borohydride reducing route with that of prepared via thermal decomposition for ethanol steam reforming at 250-500 °C. Co nanoparticles prepared from the borohydride reducing route, contain borate and boride impurities, show 82% H<sub>2</sub> yield, 77% CO2 selectivity, and almost 100% ethanol conversion at 500 °C. Whereas, the Co nanoparticles prepared via thermal decomposition and free form boron show lower catalytic activity; maximum 51% H<sub>2</sub> yield, 61% CO2 selectivity, and 77% ethanol conversion at 500 °C [52]. Gharahshiran et al. develop yttria and/or zirconia promoted mesoporous carbon-Ni-Co catalysts for ethanol steam reforming at 200-400 °C, H<sub>2</sub>O:EtOH molar ratio 3:1 and atmospheric pressure [53]. Addition of Y<sub>2</sub>O<sub>3</sub> reduces the active phase particle size compare to that of the ZrO<sub>2</sub>. The Y<sub>2</sub>O<sub>3</sub>-promoted catalyst show 39% H<sub>2</sub> yield, 49% CO<sub>2</sub> selectivity, and 58% ethanol conversion, where as the  $\rm ZrO_{2^{-}}$  promoted catalyst show 29% H<sub>2</sub> yield, 60% CO<sub>2</sub> selectivity with 40% ethanol conversion [54]. Hence, it is clear that the activity results obtained in the present study for BICOVOX catalyst are consistent and comparable with those reported recently in the literature.

# 4.1. Reaction pathway

A set of possible reaction pathways, which can be drawn based on the gas and liquid phase products acquired, is schematically presented in Fig. 8 (a) and described below. Here, the standard heat of reactions is calculated by considering the gaseous state of the reactant and products as these are present in gaseous form at the reaction temperature. The overall steam reforming reaction is

$$C_2H_5OH(g) + 3H_2O(g) \Longrightarrow 2CO_2(g) + 6H_2(g); \Delta H^0_{298K} = 174 \text{ kJmol}^{-1}$$
 (6)

Reaction step 1: dehydrogenation leading to the formation of  $\mathrm{CH}_3\mathrm{CHO}$ 

$$C_2H_5OH(g) \Leftrightarrow CH_3CHO(g) + H_2(g); \Delta H^0_{298K} = 68.9 \text{ kJmol}^{-1}$$
 (7)

CH<sub>3</sub>CHO can undergo to various pathways:



**Fig. 8.** (a) Possible reaction path ways and (b) possible mechanisms for the LTSR reaction over the BICOVOX catalyst. Numbers are showing the possible reaction step sequentially. The arrows are showing the incoming reactants (arrow tail) and outgoing products (arrow head). where shows the oxygen vacancies.

Pathway 1: reaction step 2: C-C bond breakage in acetaldehyde

$$CH_{3}CHO(g) \leftrightarrows CH_{4}(g) + CO(g); \Delta H^{0}_{298K} = -19 \text{ kJmol}^{-1}$$
(8)

 $CO(g) + H_2O(g) \leftrightarrows CO_2(g) + H_2(g); \Delta H^0_{298K} = -41.2 \text{ kJmol}^{-1}$  (9)

Reaction Steps 4 and 5: Formation of methane via Fischer-Tropsch reactions (FTR)

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g); \Delta H^0_{298K} = -205.8 \text{ kJmol}^{-1}$$
 (10)

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g); \Delta H^0_{298K} = -165 \text{ kJmol}^{-1}$$
 (11)

Reaction Steps 6 and 7: Steam reforming of methane (either created by C–C bond breaking or via FTR)

$$CH_4(g) + H_2O(g) \leftrightarrows CO(g) + 3H_2(g); \Delta H^0_{298K} = 205.8 \text{ kJmol}^{-1}$$
 (12)

$$CH_4(g) + 2H_2O(g) \Rightarrow CO_2(g) + 4H_2(g); \Delta H_{298K}^0 = 165 \text{ kJmol}^{-1}$$
(13)

Reaction step 8: formation of CO via reverse WGSR

$$CO_2(g) + H_2(g) \cong CO(g) + H_2O(g); \Delta H_{298K}^0 = 41.2 \text{ kJmol}^{-1}$$
 (14)

Reaction step 9: formation of CH<sub>3</sub>OH

$$CO_2(g) + 3H_2(g) \Longrightarrow CH_3OH(g) + H_2O(g); \Delta H^0_{298K} = -48.9 \text{ kJmol}^{-1}$$
 (15)

Pathway 2: reaction step 10: formation of CH<sub>3</sub>COCH<sub>3</sub>

$$CH_{3}CHO(g) + CH_{3}OH(g) \Rightarrow CH_{3}COCH_{3}(g) + H_{2}O(g); \Delta H_{298K}^{0}$$
  
= -93.4 kImol<sup>-1</sup> (16)

Pathway 3: reaction step 11: hydration of CH<sub>3</sub>CHO to CH<sub>3</sub>COOH

$$CH_3CHO(g) + H_2O(g) \Rightarrow CH_3COOH(g) + H_2(g); \Delta H^0_{298K} = -30.1 \text{ kJmol}^{-1}$$
(17)

Reaction step 12: C–C bond breakage in acetic acid to form CO<sub>2</sub>

 $CH_{3}COOH(g){\leftrightarrows}\ CO_{2}(g)+\ CH_{4}(g); \\ \Delta H^{0}_{298K}=-29.9\ kJmol^{-1} \eqno(18)$ 

However, in our case CH<sub>3</sub>COOH is not comprehended in liquid product, presumably because the amount present could very small or the survival time of the intermediate is too short as both the reaction steps 11 and 12 are exothermic with almost same amount of heat of reaction and therefore this step-in Fig. 8 (a) is showed with dash line.

At low temperatures, below 250  $^{\circ}$ C, along with high EtOH concentration in the feed mixture, the predominant reaction could be the decomposition of ethanol [56].

$$C_2H_5OH(g) \hookrightarrow CH_4(g) + CO(g) + H_2(g); \Delta H_{298K}^0 = 50 \text{ kJmol}^{-1}$$
 (19)

At lower temperatures with small amounts of water in the feed, the contribution of the WGSR (path 3, equation (9)) is small. Therefore, no CO2 is observed at a temperature of 200 °C and 2.5:1H2O: EtOH molar ratio for BICOVOX-800. The presence of large amount of CO and CH<sub>4</sub> indicates the dehydrogenation of ethanol to CH<sub>3</sub>CHO (path 1, equation (7)) as the most probable, which is followed by C-C bond breakage (path 2, equation (8)) along with the formation methane via FTR (path 4 and 5, equations (10) and (11)). An increase in temperature, ethanol reforming reaction (equation (6)) and the WGSR (path 3, equation (9)) become dominant and lead to an increase in the selectivity of H2 and CO<sub>2</sub>. Meanwhile, the low selectivity of by-products (CO and CH<sub>4</sub>) are also exhibited in the gas products, suggesting that the acetaldehyde decomposition reaction (path 1, equation (7) followed by path 2, equation (8)) is occurred in parallel with the methane steam reforming (path 6 and 7, equations (12) and (13)) and WGSR (path 3, equation (9), [57].

As the amount of water increases, water inhibits the ethanol decomposition reaction by channeling ethanol reactivity towards the main ethanol steam reforming reaction (equation (6)) [58]. An increase in the amount of water also has the effect of increasing the extents of the WGSR (path 3, equation (9)) and methane steam reforming reactions (path 6 and 7, equations (12) and (13)) and consequently, a reduction in the amounts of the undesired products, CO and CH<sub>4</sub> which leads to increasing overall H<sub>2</sub> selectivity [47].

Ethanol conversion is found to decrease with increasing flow rate, as flow rate increases, residence time reduces. High residence time allows subsequent promotion of all possible and feasible reactions along with enough time for complete conversion of ethanol and vice versa. On contrary to this, longer residence time (low flow rate) decreases H<sub>2</sub> and CO<sub>2</sub> selectivity due to methane formation reaction between CO<sub>2</sub> and H<sub>2</sub> (path 4 and 5, equations (10) and (11)), which further responsible for a high amount of carbon formation [59].

The BICOVOX catalysts are organized on the basis of EtOH conversion, amount of C in gas, and the selectivity of H<sub>2</sub> at the best operating parameters (400 °C, 23:1H<sub>2</sub>O: EtOH molar ratio, atmospheric pressure, and 0.11 cc min<sup>-1</sup> feed flow rate) as follow:

The decreasing order of the EtOH conversion is: BICOVOX-600>BICOVOX-800> BICOVOX-400; The decreasing order of the Amount of C in gas: BICOVOX-600>BICOVOX-800> BICOVOX-400. The decreasing order of the H<sub>2</sub> selectivity is: BICOVOX-600>BICOVOX-600>BICOVOX-600>BICOVOX-400

# 4.2. Possible mechanisms over oxide catalyst

Most of the steam reforming catalysts are based on metal-related active centers on ceramic oxide supports. The ethanol or feed electronically attaches to the active center and high oxygen ion mobility of the support helps in WGSR. Only a few works have been reported on the mechanism of ethanol steam reforming over unreduced oxide catalysts.

Lee et al. perform ethanol steam reforming over unreduced Zn-doped (Zn<sub>0.3</sub>Mg<sub>0.7</sub>Al<sub>2</sub>O<sub>4</sub>) and Zn-Pb doped (Pd<sub>0.01</sub>Zn<sub>0.29</sub>Mg<sub>0.7</sub>Al<sub>2</sub>O<sub>4</sub>) MgAl<sub>2</sub>O<sub>4</sub> catalysts. The proposed mechanism path of reaction indicates attachment of ethanol molecules on the basic active sites of Zn-O-Mg surfaces to produce intermediate CH<sub>3</sub>CHO, followed by decarboxylation on Mg-O-Al acidic surfaces to give CO and CH<sub>4</sub> [12]. Further, the CH<sub>4</sub> reforming reaction takes place over Mg-O-Al/Zn-O-Al-O-Mg surfaces to give H<sub>2</sub> and CO. At this point, the exact reaction mechanism for LTSR of ethanol on BIMEVOX is not clear, but a possible process could be that similar. This is proposed and represented in Fig. 8(b) as 'Possible Mechanism-I'. Accordingly, ethanol might be activated sequentially on the acidic or basic sites of oxide catalyst (electronegativity difference between the metals present in the oxide could create acidic and basic active sites) to produce the intermediate products. Ethanol would be attached to the localized basic sites to form acetaldehyde by C-H bond cleavage which can undergo further decomposition through C-C bond cleavage on the acidic sites of catalyst to produce CH<sub>4</sub> and CO species [57,58]. 'Later, oxygen mobility on V(Co)–O( $\Box$ ) layer ( $\Box$  indicates O2- vacancy) is expected to act as a promoter in CH4 reforming and WGSR [60]. The creation of  $O^{2-}$  vacancies in the V<sub>2</sub>O<sub>5</sub> layer doped with a Co metal ion could be represented through Kroger-Vink equation as [61]:

$$V_2 O_5 \to 2V' + V_0^{"} + 4O_X^0$$
 (20)

$$2CoO \xrightarrow{V_2O_5} 2Co_V'' + 3V_O^{"} + 2O_X^{O}$$
(21)

Where  $2Co_V^{"}$  represents the occupancy of a V<sup>5+</sup> site by a Co<sup>2+</sup> with three negative charge,  $V_O^{~}$  represents positively charged O<sup>2-</sup> vacancies, and  $O_X^o$  represents neutral lattice oxygen. Singh et al., explains the ion conduction mechanism of vanadium polyhedral in BIMEVOX, starting with 3:1 tetrahedral to octahedral ratio in the initial stage [61]. Oxide ion leaves the original position in vanadium octahedral (coordination number 6) to occupy equatorial vacancy. The coordination number of vanadium octahedra changes from 6 to 5 thereby creating an intermediate state of two 4 coordination number and two 5 coordination vanadium polyhedra. Finally, second oxide ion from 5 coordination vanadium polyhedra leaves to occupy another vacancy resulting to the starting situation of 3:1 tetrahedra to octahedral. The vanadium octahedral and tetrahedral is in the changing state leading to the mobility of oxide ion in the vanadate layer.

Zhu et al. study the role of  $O^{2-}$  vacancy in methane reforming over unreduced  $CeO_2-Fe_2O_3$  catalyst at 850 °C [13]. Under a reductive atmosphere in the methane-conversion (CH<sub>4</sub> to CO/CO<sub>2</sub>) step, Fe<sub>2</sub>O<sub>3</sub> partially reduced to metal/oxide (Fe/FeO) system and CeFeO<sub>3</sub> is formed, via 3CeO<sub>2</sub> + Fe<sub>2</sub>O<sub>3</sub> + Fe  $\rightarrow$  Ce<sup>4+</sup>Fe<sup>2+</sup>O<sub>3</sub> and/or CeO<sub>2</sub> + FeO  $\rightarrow$  Ce<sup>4+</sup>Fe<sup>2+</sup>O<sub>3</sub> reactions. CeFeO<sub>3</sub> formation causes the generation of additional O<sup>2-</sup> vacancies, which enhances the WGSR and reduces the

carbon deposition. It is also seen in the literature that  $O^{2-}$  vacancies are able to accept hydride species and enhances the ability to abstract  $H_2$  from ethanol during dehydrogenation step  $(O^2 – M^{n+} \square + H_2 \rightarrow OH – M^{n+} H^-$  with  $\square$  anionic vacancy) [11]. Thus,  $O^{2-}$  vacancies present in BICOVOX catalyst favor the CH<sub>4</sub> reforming and WGSR as mentioned in 'Possible Mechanism-I'.

Another probable mechanism for ethanol steam reforming over BICOVOX oxide catalyst could involve the reduced bismuth metal (generated in the reducing atmosphere (CH<sub>4</sub>, CO, H<sub>2</sub>, N<sub>2</sub>) during the reforming reactions) as the active metal center. XPS (XPS analysis, Fig. 5 (a–c)) also shows a small amount of Bi metal on the surface of the fresh catalysts. Mutual interaction between ethanol and basic sites of catalysts could create acetaldehyde as an intermediate product, which undergoes the decarbonylation reaction over Bi-metal to form CO and CH<sub>4</sub> as depicted in Fig. 8 (b) as 'Possible Mechanism-II'. A similar reaction has already been reported in the literature majorly in the field of oxidative C–C cleavage of epoxides over Bi-mandelate catalysts to give carboxylic acid [62,63]. Later, oxygen mobility, via  $O^{2-}$  vacancies, plays its role in CH<sub>4</sub> reforming and WGSR as discussed above. However, more detailed experimental and/or modeling work need to be conducted to realize the actual path way of the LTSR of ethanol on BIMEVOX.

#### 4.3. Effect of heat treatment on the catalysts

The lower catalytic activity of the powders heat treated at 400 and 800 °C compared to that of the BICOVOX-600 sample could be explained in terms of phase composition, particle size distribution, and coke deposition on the surface, as studied by XRD, DTGA, FESEM, EDX, and XPS. Correspondingly, these catalysts are arranged in decreasing order as follows:

Phase composition (amount of  $\gamma$ -phase, both in fresh and used): BICOVOX-800 > BICOVOX-600 > BICOVOX-400.

Particle size distribution (largest to smallest, both in fresh and used): BICOVOX-800 > BICOVOX-600 > BICOVOX-400.

Coke deposition (highest to lowest, in used): BICOVOX-800 > BICOVOX-400 > BICOVOX-600.

While a higher amount of  $\gamma$ -phase could enhance the activity, larger particle size reduces WGSR and increases C deposition in BICOVOX-800 [11,12,48,57,58]. Reportedly, during high-temperature steam reforming, carbon may enwrap the surface as filamentary strands, surface films, or graphitic species and reduces the catalytic activity [64,65]. Rate of WGS reaction and coke deposition phenomena are interconnected and significantly depend on the particle size distribution of the catalysts. Zhou et al. investigate the behavior of decreasing CeO<sub>2</sub> particle size and report that O<sup>2-</sup> vacancies increased by 2 orders of magnitude when particle size is reduced from 60 to 4 nm [66]. Additionally, large particles could decrease the density of active centers and be responsible for reduced overall activity.

The BICOVOX-400\_F contains the smallest particle size, which could stabilize the disordered  $\gamma$ -phase, lower the activation energy for oxygen ion transition and helps in high ionic conductivity [17]. But the least amount of  $\gamma$ -phase and presence of a maximum amount of carbon in the fresh catalyst deteriorate its performance.

In terms of the amount of  $\gamma$ -phase and average particle size BICOVOX-600 is in the middle position, but contains the maximum amount of  $V^{4+}$  oxidation state (i.e. more amount of  $O^{2-}$  vacancies), as unveiled from XPS analysis. This, besides particle size, could help to minimize the C deposition on the catalysts and leads to maximum performance.

#### 5. Conclusion

It is demonstrated that BICOVOX catalysts can be useful for  $H_2$  production by steam reforming of ethanol at low temperatures (200–400 °C). Effect of time on stream data shows that the catalysts attain steady state within 5–6 h and remain stable till ~30 h. EtOH

conversion, C in the gas phase, and H<sub>2</sub> and CO<sub>2</sub> selectivity is found to increase with increasing reactor temperature and decreasing EtOH concentration in the feed for all the BICOVOX catalysts. Selectivity for CO and CH<sub>4</sub> shows an opposite trend with increasing temperature and decreasing EtOH concentration. With increasing flow rate EtOH conversion is found to decrease, however, C in the gas phase, and H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub> selectivity values are observed to increase. Maximum H<sub>2</sub> selectivity of 80% for BICOVOX-600, with almost 100% EtOH conversion at reactor conditions of 400 °C, 23:1H<sub>2</sub>O: EtOH molar ratio and 0.35 cc min<sup>-1</sup> feed flow rate is observed.

XRD study reveals that the BICOVOX-400\_F and BICOVOX-600\_F samples contain higher amount of secondary phases ( $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>,  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -BiVO<sub>4</sub>) compare to BICOVOX-800\_F catalyst, as it shows mostly pure  $\gamma$ -BIMEVOX phase.

FESEM analysis shows the growth in particle size with calcination temperature from 400 to 800 °C. After using a catalyst for 30 h in the reactor, the scale of agglomeration is increased. XPS spectra analysis of the BICOVOX catalysts show maximum  $V^{4+}:V^{5+}$  ratio for the BICOVOX-600\_F sample, indicating higher oxygen mobility in BICOVOX-600 catalyst compared to BICOVOX-800\_F and BICOVOX-400\_F catalysts. XPS data confirms the carbon deposition in used catalysts and it also confirms the deposition of the maximum amount of C in used BICOVOX-800 catalyst. The carbon deposition during reaction arises question regarding the stability of catalysts. The study on the catalyst stability and carbon deposition is on progress and the following part of this paper will present it elaborately.

# CRediT authorship contribution statement

**Shweta Sharma:** Methodology, Data curation, Writing - original draft, Writing - review & editing. **Shampa Aich:** Methodology, Visualization, Investigation. **Banasri Roy:** Conceptualization, Methodology, Supervision, Resources, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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