Ethanol condensation to butanol and higher alcohols over nickel and cobalt decorated Ce-Al mixed oxide catalysts

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Abstract

n- butanol is considered as a potential future biofuel since its fuel characteristics are better than ethanol's and closer to those for gasoline. In this context, the processes for direct conversion of abundantly available bio-ethanol to n-butanol and C_{4+} alcohols have gained prominence. Ni (8% w/w) supported on CeO_2 (5% w/w)-Al_2O_3 mixed oxide displays high activity of 52.6 % ethanol conversion, 29.2% selectivity to n-butanol and 46.4% selectivity to C_{4+} alcohols at 200°C in batch mode. In order to improve the metal function and achieve higher ethanol conversion and selectivity, cobalt is added as the second metal. A new series of bimetallic Ni-Co catalysts were prepared by step wise substitution of Ni (8% w/w) by Co, to get active phase compositions of 6%Ni-2%Co, 4%Ni-4%Co, 2.5%Ni-5.5% Co and 8% Co, supported on CeO_2(5 % w/w) -Al_2O_3 mixed oxide phase. XRD, TPR and XPS studies reveal the formation of Ni-Co alloys at specific compositions which modifies the electronic structure of bimetallic catalysts. DRS studies indicate that majority of Co^{2+} ions are located in tetrahedral sites, while Ni^{2+} ions in octahedral sites. Maximum ethanol conversion of 55.1 % is achieved with the composition 4%Ni-4%Co, with C_{4+} alcohols selectivity of 50.2%, which is higher than those realized for mono metallic Ni and Co catalysts. Slightly lower conversion of 52.8% and higher C_{4+}alcohols selectivity (53.4%) is observed with the composition 2.5% Ni-5.5% Co. The catalytic process follows classical

Guerbet alcohol chemistry pathway. Primary surface reaction involving of dehydrogenation of ethanol to acetaldehyde and hydrogenation of C_4 and higher carbon number aldehydes to the corresponding alcohols are crucial steps for ethanol conversion to butanol higher alcohols. Ni-Co alloys in Ni-Co bimetallic catalysts function as efficient dehydrogenation-hydrogenation catalysts, thereby increasing ethanol conversion and C_{4+} alcohol selectivity vis-a-vis the mono metallic catalysts.

Key words; Ethanol, Butanol, Guerbet alcohols, Co-Ni bimetallic catalysts, hydrogenation, Ceria-alumina

1. Introduction

Bioethanol, classified as carbon neutral fuel [1], is produced on large scale by the fermentation of different biomass feed-stocks [2]. Global production of bioethanol, estimated at 27050 Mill. gallons in 2017 [3], is expected to grow at a CAGR of 5.3 % during 2018-2024. Besides its use as bio-fuel, highly useful and value-added chemicals, like, acetic acid, ethyl acetate, ethylene, hydrogen, isobutene, acetaldehyde, 1,3-butadiene and butanol could be produced from abundantly available bioethanol [4]. Especially, the process for the conversion of ethanol to butanol has received global attention, since butanol has superior fuel characteristics compared to ethanol, and is widely accepted as the future biofuel. The process is based on the classical Guerbet chemistry [5], that involves condensation of a primary or secondary alcohol, either with itself or another alcohol, to yield higher carbon number alcohol. Various types of heterogeneous [6] as well as homogeneous catalysts [7] have been reported for the synthesis of Guerbet alcohols. Catalysts based on solid bases, basic zeolites, hydroxyapetite, hydrotalcite and alumina and carbon supported metal catalysts have been explored extensively [6-8]. Dehydrogenation of ethanol to acetaldehyde, aldol condensation of acetaldehyde to crotonaldehdye, followed by its hydrogenation to yield butanol, are the key reaction steps involved in the Guerbet process. Accordingly, dehydrogenation, hydrogenation, acidity and basicity are the requisite functionalities for the catalysts. Alumina supported metal (Co, Ni, Cu) catalysts possess an unique combination of these functionalities and hence have been studied in detail [9-23]. While the metal (Co, Ni, Cu, Ru, Pd, Rh) function facilitates dehydrogenation and hydrogenation steps, inherent basicity and acidity in the alumina phase catalyze aldol condensation and subsequent dehydration reaction respectively, to yield C_4 and C_{4+} aldehydes, the crucial intermediates in the formation of butanol and higher alcohols. In this respect, alumina as a versatile support, is amenable for tuning the acidity basicity and the metal function by addition of suitable promoter oxides. Detailed studies on nickel catalysts supported on modified (with lanthana, ceria, zirconia, magnesia and titania) alumina support has been reported earlier [24].

Investigations by Riittonen et al.[11a,11b] on various alumina supported metal catalysts have revealed that Ni Co and Cu based catalysts display superior performance compared to other metal (Ru, Pd, Rh, Ag and Au) based catalysts. Earlier studies by Yang et al. [10] on comparative evaluation of Fe, Co and Ni supported on alumina catalysts, have shown that Fe displayed very low ethanol conversion (2%) while Co and Ni, moderate and nearly same activity (17-19%). While the selectivity for butanol was significantly high at 64.3 % with Ni, it was considerably less with Co, at 22.7%, due to the formation of side products/intermediates, like, ethyl acetate (29.2%) butyraldehyde (15.9%) and acetaldehyde (14.1%). The product patterns thus indicate that, while both Ni & Co are almost equally active for ethanol dehydrogenation, aldol condensation of acetaldehyde and hydrogenation of butyraldehyde are relatively slower with Co. Among alumina supported Cu, Ni and Co catalysts, Ni/Al_2O_3 displays high activity and selectivity for butanol, while on Co/Al_2O_3 formation of ethyl acetate is favoured and is attributed to the presence of Co^{2+} ions in tetrahedral environment (11b). Selectivity on Cu/Al_2O_3 is reported to be dependent on loading of Cu, with lower loading resulting in higher selectivity for butanol and higher loading, ethyl acetate [11b]. It is proposed that for the dehydrogenation of different alcohols, the use of transition metals in the reduced form (Co, Ni, Cu, Fe, Ir, etc) lower the activation energy of the α-CH bond scission. In addition, reduced metals could also alter the acid/base sites distribution.

Another approach by Zhang et al [25] using commercial cobalt (Co) metal powder as a recyclable catalyst yielded butanol selectivity of 69% and yield of 2.89 mol %, but the process required long reaction time of 3 days.

Besides the active metals like Ni, Co and Cu, the support characteristics play crucial role in controlling activity and selectivity for ethanol conversion. Quesada et al observed that Mg-Al mixed oxides function as active and stable supports for ethanol conversion [26] and with Co, Ni [27] and Ru [28,29] as active metals, displays substantial increase in selectivity towards butanol. Wu et al [30] reported a series of activated carbon (AC) supported M-CeO_2 catalysts (M= Cu, Co, Ni, Pd and Fe) for catalytic upgrading ethanol to n-butanol highlighting inherent capabilities of metals for dehydrogenation, hydrogenation. Co, Ni and Pd-CeO_2 /AC catalysts exhibit higher selectivity towards n-butanol (47.6, 50.6 and 67.6%, respectively), but lower ethanol conversions. It was proposed that since the selectivity to n-butanol mainly depends on the formation and hydrogenation of crotonaldehyde steps, the trend in selectivity to n-butanol ($Fe < Cu < Co < Ni < Pd$) should be ascribed to the difference in the capability of hydrogen activation over active metals, as well as the aldol condensation of acetaldehyde over basic sites. However, ethanol conversion displays the opposite trend ($Cu > Co > Ni > Fe > Pd$) since dehydrogenation and hydrogenation is a pair of reverse catalytic processes [29].

It is clear that the selection of suitable metal and support functions are crucial for ethanol conversion and selectivity to higher alcohols. Only a few reports on the application of bimetallic catalysts, namely, Au-Ni and Au-M, with M=Fe, Co, Ag and Zr (16) and Cu-Ni and Cu-Ni-Mn (13,31), for ethanol conversion have been published so far. In the present work, we have attempted to study the importance of bimetallic Ni-Co catalysts with varying Ni and Co contents, supported on ceria modified alumina. Considering their crucial role in dehydrogenation and hydrogenation functions, catalysts with different Ni and Co contents have been investigated to bring out possible synergistic effects between the two metals.

2. Experimental

2.1. Chemicals

Boehmite (AlOOH) (Pural SB, Sasol, Germany), Nickel acetate $Ni(CH_3COO)_2.4H_2O$, Cobalt acetate $Co(CH_3COO)_2.4H_2O$, Cerium nitrate hexahydrate ($Ce(NO_3)_2.6H_2O$) (99.9%, CDH), were used as such. Absolute alcohol (99.9%) from Changshu Hongsheng Fine Chemical Co. Ltd., China, was used as such for carrying out reactions.

2.2. Preparation of support and catalysts

Gamma alumina (γ-Al_2O_3) was prepared by calcination of boehmite (AlOOH) at 450^{o}C for 4hrs. Al_2O_3 was impregnated separately with required quantity of cerium nitrate $Ce(NO_3)_3.6H_2O$, (to obtain 5% w/w of ceria in alumina) dissolved homogeneously in 20mL of distilled water. After evaporation of excess water, the slurry was dried in air at 120^{0}C for 12 hrs and then calcined at 600^{0}C for 12 hrs in N_2 atmosphere. Ni (2.5% to 8% w/w) and Co (2% to 8% w/w) as nickel acetate and cobalt acetate respectively, were loaded on modified alumina by wet impregnation, dried at 120^{0}C for 12 hrs, followed by reduction in H_2 flow at 500^{0}C for 12 hrs

2.3 Characterization of catalysts

Powder XRD diffraction patterns for the catalysts were recorded using Rigaku Corporation, Japan, Model Miniflex IIX-ray diffractometer, with Cu-Kα (λ =0.15418 nm) radiation in the 2θ range of 10º to 80º and at a scan rate of 3º/min. Ni crystallite size of the catalysts were calculated by X-ray line broadening analysis, using Debye-Sherrer equation.

N_2 adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 unit. Surface area of the catalysts were measured by BET method and pore volume and pore size distribution by BJH method.

Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) of ammonia and carbon dioxide were performed on Chem. BET TPR/TPD Chemisorption Analyzer (Quanta Chrome Instruments, USA) equipped with a thermal conductivity detector (TCD). For TPR measurements, the catalysts were calcined in air at 300°C, prior to TPR experiments. 50 mg of calcined catalyst was pre-treated at 300ºC in high purity Ar gas (25cc/min) for 1 h and then cooled to room temperature in Ar flow. The gas was changed to 10 % H_2 in Ar (25cc/min) at room temperature. After the stabilization of the baseline, TPR patterns were recorded from room temperature to 800º C with a heating rate 10º C/ min.

For TPD of ammonia, 50 mg of the reduced catalyst was pretreated at 300°C in helium flow of 20mL/min for 1 hour and cooled to room temperature in helium flow. The sample was saturated with ammonia by passing 10% NH_3 in helium gas over the catalyst for 20min. After flushing out weakly adsorbed ammonia with helium flow at 373K, the base line was established. TPD of adsorbed ammonia was then recorded by heating the sample in helium flow up to 650 ºC with a heating rate of 10°C per min. For TPD of CO_2 similar procedure was adopted using CO_2 as probe molecule instead of ammonia.

X-ray photoelectron spectra of the reduced catalysts were recorded using Omicron Nanotechnology, Oxford Instruments, UK, instrument with Mg K_α radiation. The base pressure of the analysis chamber during the scan was $2*10^{-10}$ millibar. The pass energies for individual scan and survey scan are 20 and 100 eV, respectively. The spectra were recorded with step width of 0.05 eV. The data were processed with the Casa XPS software.

Diffuse reflectance spectra of the catalysts were recorded using JASCO Model V-650 UV-Visible spectro photometer.

2.4 Evaluation of catalysts for ethanol conversion

Reactions were carried in batch mode, using 100 ml Parr reactor with Model 4848 controller unit (Parr instruments, Chicago, USA). 1.83 g of catalyst was dispersed in 20 g of ethanol. After purging three times with N_2 to remove air, the reactor was filled with nitrogen up to 10kg/cm^2 and sealed. The reaction was carried out under autogenous pressure at 200°C for 8hrs with an agitator speed of 350 rpm. During the reaction, the reactor pressure increased gradually with time and stabilized at 45-50 kg/cm^2 after 4 hrs. After the completion of 8 hrs, the reactor was cooled to room temperature and a sample of gaseous products for GC analysis was collected in a gas sampling bulb by controlled de-pressurization of the reactor. Weight of the liquid product after cooling and depressurization was noted so that mass fractions of liquid and gaseous products could be arrived at. Liquid and gaseous products were analysed by gas chromatography. Details on the analysis of product stream and computation of product stream composition are described in the Supporting Information.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1 X-ray diffraction (XRD)

Fig. 1 shows X-ray diffractograms of reduced catalysts. XRD for 8%Ni/5%CeO_2- Al_2O_3 (Fig.1a) displays major d-lines due to gamma alumina phase, with the characteristic d-lines (JCPDS 46-1131) at 2θ values of 36.8°, 45.8° and 66.8°corresponding to (111), (400) and (440) planes respectively. Besides, d-lines due to CeO_2 at 2θ values of 28.3° (111), 33.1° (211), 56.4° (311), 76.6°(420) (JCPDS 34-0394), are also observed. In addition, a weak d-line observed at 52.1° is due to (200) plane in Ni metal (JCPDS-04-0850). The major d-line (111) due to Ni metal at 44.4° is very close to the broad d-line of alumina at 45.8º and hence not observed distinctly in Fig.1a. However, expanded diffraction pattern in the 2θ range 43º-48º presented in Fig.S1a shows a weak line at 44.3º due to Ni metal. Similarly, in the case of 8%Co/5%CeO_2-Al_2O_3 catalyst (Fig.1e) all major d-lines due to alumina and ceria phases are observed, besides the major d-line due to Co metal at 2θ-44.3º (JCPDS 15-0806) as observed in Fig.S1e. In both cases, formation of Ni/Co aluminate with spinel structure is possible but is not observed distinctly, since gamma alumina and the aluminates are iso-structural. In the diffractograms of other three Co-Ni mixed metal catalysts, all major d-lines due to alumina and ceria are displayed (Fig.1b to Fig.1d). Corresponding XRD patterns in expanded mode (Fig.S1b to Fig.S1d) show d-lines at, 44.1º,44.4º and 44.6º respectively, shifted slightly from those due to Ni and Co metals, indicating possible formation of Ni-Co alloys [32,33]. Ni/Co crystallite size (8-10 nm) have been calculated using d-lines at 2θ= 52.1 to 52.5 corresponding to (200) planes, by applying Debye Scherrer equation (Table S1).

3.1.2. Textural properties

The N_2 adsorption/desorption isotherms and pore size distribution profiles of reduced catalysts are shown in Fig. S2. The catalysts display Type IV N_2 adsorption/desorption isotherms, and

Type H2 hysteresis loops, indicating mesoporous characteristics. As expected, no significant variations in the surface area, pore volume and mean pore diameter are observed. (Table S1).

3.1.3 Temperature programmed reduction (H_2-TPR)

H_2-TPR profiles of the catalysts are shown in Fig.S3 and a compilation of the reduction maxima observed for all the catalysts is presented in Table 1. Seven reduction maxima indicating H_2 consumption are observed (Fig.S3a) for the base catalyst, 8%Ni/5%CeO_2-Al_2O_3. Based on the literature data (34) on the reduction patterns for alumina supported Ni catalysts, the first two maxima at 239ºC, 325ºC, indicate the reduction of free and weakly bound NiO. Next three maxima at 403ºC, 459ºC and 507ºC are due to the reduction of well dispersed NiO species with weak interaction with the support. The maxima observed at 639ºC and 669ºC are attributed to the reduction of Ni^{2+} in nickel aluminate lattice. Partial replacement of Ni towards the composition 2%Co-6%Ni/5%CeO_2-Al_2O_3 results in multiple reduction maxima due to the presence of reducible Ni and Co oxides in free or weakly bound state (211ºC, 300ºC, 360ºC), well-dispersed over the support (426ºC, 448ºC) and as Ni/Co aluminates due to strong interactions with the support (665ºC and 759°C). Essentially, Ni and Co oxidic species undergo reduction separately, with little interaction between the species. When Co and Ni are present in equal proportions (4%Co-4%Ni/5%CeO_2-Al_2O_3), perceptible changes are observed in the reduction pattern. Reduction maxima at 360°C 426°C and 448°C for lower Co content sample are shifted to higher temperatures, 391°C,473°C and 532°C, indicating simultaneous reduction of Ni and Co oxide species, possibly leading to the formation of Ni-Co alloys. Significantly, the intensities of the low temperature reduction peaks at 266ºC and 329ºC, due to free oxides and high temperature peaks at 651ºC and 686°C, for Ni^{2+}/Co^{2+} in the aluminate phases, are relatively lower, indicating that simultaneous reduction of Ni and Co oxidic species is the dominant process. Similar reports involving simultaneous reduction of Ni and Co oxidic species leading to the formation of Ni-Co alloys have been published earlier (32,35,36). Reduction pattern observed for 5.5%Co-2.5%Ni/5%CeO_2-Al_2O_3 catalyst, also involves simultaneous reduction of Ni^{2+} and Co^{2+} involving alloy formation, along with reduction of dispersed Ni and Co oxides. The catalyst 8% Co/CeO_2-Al_2O_3 displays multiple reduction maxima due to the presence of different reducible phases of Co in +2 and +3 oxidation states. Reduction maxima in the range 200°C-300°C are due to weakly bound Co oxides. Different forms of oxidic cobalt in mixed valence states (+2 and +3) and dispersed with varying degree of interaction with the support, undergo reduction in the temperature range 300-600ºC, leading to multiple reduction maxima, while Co^{2+} in aluminate phase gets reduced at temperature >600°C.

3.1.4 X-ray photoelectron spectroscopy (XPS)

XPS profiles for the typical bi-metallic catalyst, 4%Co-4%Ni/5%CeO_2-Al_2O_3, are presented in Fig.2. Binding energy (BE) values observed for Co $2p_{3/2}$ (779.1eV) in Fig.2a and Ni $2p_{3/2}$ (853.9 eV) in Fig.2b, are close to the values reported (37-40) for clean metallic Co (778.2eV) and Ni (852.6 eV) thus confirming that in the catalyst, both Co and Ni are in metallic state. The shifts in BE values, with respect to those for clean metals, are due to the ceria modified alumina support effect and the electronic interactions between Co and Ni in metallic state, arising out of nano scale alloy formation, as indicated in the TPR studies. XPS line observed at 860.8eV (Fig.2b) is attributed to Ni2p for nickel aluminate phase (41). The satellite peak observed at 784.6 eV (Fig.2a) is due to the presence Co^{2+} in cobalt aluminate. XPS lines due to $Ce^{4+}3d_{3/2}$ core level are reported at 900.8 eV, 907.2 eV and 916.7 eV and $3d_{5/2}$ core levels at 882.4 eV, 888.8 eV and 898.1 eV (42-45). Corresponding XPS lines for Ce^{3+} are expected at 903.7 eV, 884.7 eV, 899.2 eV and 880.1 eV (42,45,46). In the present work, XPS lines (Fig 2c) observed at 902.4 eV, 915.7

eV and 898.2 eV could be assigned to Ce^{4+} state and the lines at 880.3 eV, 884.2 eV and 899.2 eV to Ce^{3+} state indicating the presence of Ce in mixed valence states.

3.1.5 Acidity and basicity of the catalysts

NH_3-TPD profiles for the catalysts in reduced state are given in Fig.S3 and the compilation of acidity and acid sites distribution in Table 2. All catalysts are characterized by the presence of weak (<250ºC), medium (300-400 ºC) and strong (>400ºC) acid sites. No significant variations in the total acidity or acid sites distribution is observed when Ni and Co contents are varied. Weak and medium strength acid sites are predominant over the strong acid sites.

CO_2 TPD profiles for the catalysts in reduces state are shown in Fig. S4 and Table 3 gives total basicity and basic sites distribution data. Weak (<250ºC), medium (300-400 ºC) and strong (>500ºC) basic sites are observed in all the catalysts. While very little variations in total basicity is observed along the series, basic sites of medium strength are predominant over weak and strong acid sites. The catalysts thus possess balanced acidic and basic sites required for condensation of ethanol to butanol and higher alcohols.

3.1.6 Diffuse reflectance spectroscopy

Diffuse reflectance spectra of the catalysts in reduced state are presented in Fig. 3. In accordance with XRD, and XPS data, part of Ni and Co are present as Ni^{2+} and Co^{2+} in aluminate phase. In the case of 8% Ni/CeO_2-Al_2O_3 absorption maxima observed at 320 nm is due to the presence of Ni^{2+} in octahedral co-ordination in nickel aluminate phase [47]. Presence of this maxima in all Ni containing samples show that Ni^{2+} in the catalysts is present in octahedral sites. Introduction of Co in the place of Ni results in additional three distinct absorption maxima in the region 530-630 nm which are attributed to the presence of Co^{2+} in tetrahedral sites [48]. Absorption maxima due to Co^{2+} in octahedral sites, expected in the region 400-700 nm [48] are possibly merged with maxima due to Co^{2+} in tetrahedral sites. DRS studies thus reveal that Ni^{2+} ions in all the catalysts are present in octahedral sites while majority of Co^{2+} ions are present in tetrahedral sites.

3.2 Catalytic activity for condensation of ethanol

3.2.1. Distribution of products

Graphical representation of the data on the conversion of ethanol and selectivity to butanol and higher carbon number alcohols at 200°C on Ni-Co series of bimetallic catalysts supported on ceria modified alumina is presented in Fig.3 and the respective values are compiled in Table S2 for easy reference. Detailed distribution of all compounds identified in the product streams for all the five catalysts are presented in Table S3. Butanol, hexanol and octanol are the major desired products and ethylene is the major by product along with small amounts of C_1-C_5 hydrocarbons and oxides of carbon. Besides C_2-C_8 aldehydes, ketones and esters are observed in trace amounts. Overall product patterns for the five catalysts indicate that the process follows typical Guerbet chemistry pathway.

3.2.2 Ethanol conversion and selectivity trends

Ethanol conversion in the range 42% to 55% is realized on all catalysts, with bimetallic Ni-Co catalysts of specific compositions displaying higher selectivity towards butanol and higher alcohols vis-à-vis mono metallic catalysts (Fig.3, Table S2). While mono metallic Ni displays butanol selectivity of 29.2% and higher alcohol selectivity of 46.4%, corresponding values for mono metallic Co catalyst are lower, at 17% and 20.7% respectively. These observations are in line with the earlier work reported for alumina supported Ni and Co catalysts (10,11a,11b). Formation of ethyl acetate (Table S3) is higher (5.23%) with mono metallic Co and the catalyst with higher Co content, $Ni_{2.5}Co_{5.5}/CeO_2$-Al_2O_3 (1.06%) in comparison with that on mono metallic

Ni (0.69%), which is attributed to the presence of Co^{2+}in tetrahedral sites (11b). Diffuse reflectance spectra for Co containing catalysts (Fig.3) reveal that majority of Co^{2+} ions in cobalt aluminate phase are in tetrahedral sites, while Ni^{2+} in nickel aluminate in octahedral sites. Presence of Ni leads to substantial decrease in the formation of ethyl acetate and increase in butanol and higher alcohol selectivity with respect to mono metallic Co catalysts (Table S3). While earlier studies (10,11a,11b) on alumina supported mono metallic Ni and Co catalysts have reported nearly same level of ethanol conversion on both catalysts, lower conversion observed for Co (43.6%) Vs Ni (52.6%) in the present work (Table S2) could be due to the alumina support used and the consequent differences in metal-support interactions therein.

Substitution of Ni by Co up to 2% results in a decrease in ethanol conversion, from 52,6% to 42.2%, along with substantial increase in selectivity towards butanol and higher alcohols, from 46.4% to 51.4% and 29.2 % to 34.2% respectively. In the case of the catalyst with equal loading of Ni and Co (4% each), further increase in ethanol conversion to 55.1% is observed, while higher alcohol selectivity is more or less maintained. With all the four Ni-Co catalysts butanol selectivity of 32 ± 2% is observed. Further increase in cobalt content to 5.5% leads to a slight decrease in conversion due to higher Co content and increase in higher alcohols selectivity.

3.2.3. Role of Ni-Co alloys

Bimetallic Ni Co catalysts, especially with compositions 4%Ni-4%Co and 2.5% Ni-5.5%Co display higher ethanol conversion and higher alcohol selectivity with respect to mono metallic catalysts. XRD, H_2 TPR and XPS studies (Section 3.1) support the formation of nano scale bi-metallic alloys of Ni and Co, which could play a pivotal role in this aspect. Formation of nano scale alloys in supported Ni-Co bimetallic catalysts and its influence on the activity for reactions like, steam methane reforming [49], dry reforming of methane with CO_2 [50, 51], steam reforming of alcohols [52] and acetic acid [53], hydrogenation of CO [54–56], methane partial oxidation [57], hydrogenation of furfural [58] and hydrogenation of benzaldehyde [59] have been documented in literature. Ni–Co alloys are known to generate active hydrogen, which suppress coke formation and retard deactivation, possibly by hydrogenation of coke precursors. Ni-Co alloy formation in titania supported catalysts and generation of active hydrogen as indicated by H_2 TPD studies (60), leads to higher activity for hydrogenation of cinnamaldehyde vis-à-vis mono metallic catalysts.

In the present work, ethanol conversion on ceria-alumina supported Ni-Co catalysts follows Guerbet chemistry pathway, wherein, dehydrogenation of ethanol to acetaldehyde, followed by aldol condensation to crotonaldehyde, butyraldehyde and higher carbon number aldehydes and their subsequent hydrogenation to butanol and higher alcohols, are the crucial steps. (Scheme 1) Acidity and basicity (for aldol condensation) and dehydrogenation-hydrogenation (for ethanol dehydrogenation to acetaldehyde and hydrogenation of C_4 and higher carbon number aldehydes) are the essential catalytic functionalities. While acidity-basicity originate from the support and Ni/Co aluminate phases, dehydrogenation-hydrogenation from the metal sites. Role of metal sites is thus crucial, since they are involved in the initial dehydrogenation and final hydrogenation steps. Compared to the monometallic (Ni/Co) catalysts, bimetallic Ni-Co catalysts are known to exhibit higher activity due to the synergetic interactions and alloy formation. In this context, formation of Co-Ni nanoscale alloys in Ni-Co bimetallic catalysts with higher activity for dehydrogenation and hydrogenation reactions are responsible for the observed higher activity and selectivity for butanol and higher alcohols. Thus, the choice of bimetallic catalysts with specific composition range seems to be a good strategy for achieving higher ethanol conversion and selectivity for higher alcohols

Sun et al. (13) have reported ethanol conversion of 56% and butanol yield of 22% on bimetallic Ni-Cu catalysts supported on Mg-Al-O mixed oxides, but at higher temperature of 320ºC. Au based bimetallic catalysts, Au-Ni and Au-M, with M= Fe, Co, Ag and Zr, studied by Chistyakov et al, and Nikolev et al (16) respectively, display good activity and higher alcohol selectivity, again at higher temperature, at 275ºC, under super critical conditions. Another recent publication on the application of tri-metallic Cu-Ni-Mn catalysts for ethanol conversion reports lower activity and selectivity. In comparison, the Ni-Co bimetallic catalysts reported in the present work display better activity and selectivity at lower temperature of 200ºC.

4. Conclusions

A new series of Ni-Co bimetallic catalysts with varying nickel and cobalt contents and supported on CeO_2 (5% w/w)-Al_2O_3 mixed oxide has been prepared and evaluated for activity for condensation of ethanol and selectivity for butanol and higher alcohols. XRD, TPR and XPS studies reveal the formation of nickel-cobalt alloys, especially with compositions, 4% Ni-4%Co and 2.5% Ni-5.5%Co. Higher ethanol conversion and selectivity for higher alcohols are observed with the same catalyst compositions. Dehydrogenation of ethanol to acetaldehyde and hydrogenation of C_4 and higher aldehydes are the key steps in ethanol condensation process. Ni-Co alloys promote both dehydrogenation and hydrogenation steps, thus leading to improvements in ethanol conversion and higher alcohols selectivity. Selection of bimetallic catalysts with specific composition seems to be the right strategy to improve ethanol conversion and higher alcohols selectivity,

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