Conversion of ethanol to higher alcohols on Ni/M$_x$O$_y$-Al$_2$O$_3$ (M=La, Ce, Zr, Mg and Ti) catalysts: Influence of support characteristics

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A new series of alumina supported nickel (8% w/w) catalysts, modified with promoters, La$_2$O$_3$, CeO$_2$, ZrO$_2$, MgO and TiO$_2$, highly active for the conversion of ethanol to butanol and higher alcohols, at 200°C-220°C, in batch mode, under autogenous pressure, has been investigated. XRD and XPS results indicate the presence of metallic Ni and Ni aluminate as the active phases. H$_2$-TPR studies reveal that the introduction of promoters improves nickel dispersion, reducibility and moderates the metal-support interactions. TPD of ammonia and CO$_2$ studies establish the strong influence of the promoter oxides on the strength and population of acidic and basic sites. Ethanol conversion at 200°C varies in a narrow range, 36-42%. CeO$_2$ and MgO modified catalysts display maximum selectivity towards butanol (48%) and higher alcohols, (81% and 75%) in comparison with the catalyst based on pristine alumina (28.9% and 40.5%). While the selectivity for butanol and higher alcohols is governed by the basicity of the catalysts, both metal function and basicity are required to drive ethanol conversion. Moderation of acidity helps in minimizing the formation of ethylene and other gaseous products. Analysis of used catalyst indicates that the structural and active phase characteristics are retained during use.

Keywords: Acidity, Basicity, Butanol, C$_4$+ alcohols, Ethanol conversion, Heterogeneous catalysts, High Selectivity, Metal function, Nickel-alumina, Oxide promoters

n-Butanol is considered as the next generation biofuel$^{1a,b}$ with several advantages over ethanol, such as, higher energy density, lower volatility and solubility in water and non-corrosive nature$^{2a,b,c}$. Besides, butanol blends well with gasoline and with higher air to fuel ratio, renders more efficient combustion. Currently, butanol is produced from propylene by the Oxo process, which is based on the use of the raw material derived from non-renewable resources, and involves application of high pressure, energy inputs and cost of production and hence lacks sustainability. Though an alternative bio-based fermentation process (ABE process) is in practice, a number of factors, like, low yield of butanol, higher cost of substrates and product recovery and solvent toxicity to the Clostridium stains, restrict its application on a larger scale$^3$. In this context, conversion of ethanol to butanol and higher alcohols, using the classical Guerbet condensation reaction$^4$ has emerged as an attractive proposition. Especially with the availability of bio-ethanol in plenty, from various bio-mass resources$^{5,6}$, such as, bagasse, rice, wheat straw, stems and leaves of corn, wastepaper and waste wood, processes for its conversion to butanol and other higher alcohols are being explored with keen interest, resulting in the revival of Guerbet alcohol chemistry and catalysts therein. Excellent reviews$^{7,8}$, covering various stages of development in the heterogeneous as well as homogeneous catalytic processes for the conversion of ethanol to butanol and higher alcohols, based on the chemistry of Guerbet process, have been published. While the debate on multi-step Guerbet route Vs direct self-condensation of ethanol to butanol continues$^9$, detailed reviews, on various catalysts systems, thermodynamic aspects and plausible reaction pathways for the formation of major as well as minor products, have also been reported$^{10a,b,c}$. Several types of heterogeneous catalysts, based on MgO, Mg–Al–O mixed oxides, Cu/CeO$_2$, basic zeolites, hydroxyapatite, solid acid supported Cu, alumina and carbon supported metal catalysts have been explored$^{10d}$ Different types of supported metal catalysts$^{12,25}$ that display significant activity for ethanol conversion towards butanol and higher alcohols formation have been investigated.

The key steps in Guerbet process include:

a) dehydrogenation of ethanol to acetaldehyde (ACL),

b) hydration of ACL to acetic acid (AAA),

c) hydration of AAA to ethanol (EAA),

d) dehydration of AAA to acetaldehyde (AAH),

e) dehydration of AAH to ethylene (AHE),

f) dehydration of EAA to ethylene (EAH).

In this work, we have investigated a new series of nickel-based catalysts, modified with promoters, La$_2$O$_3$, CeO$_2$, ZrO$_2$, MgO and TiO$_2$, for the conversion of ethanol to butanol and higher alcohols, at 200°C-220°C, in batch mode, under autogenous pressure.
b) conversion of ACL to crotonaldehyde (CRL) by aldol condensation followed by dehydration c) further hydrogenation of CRL to give butanol. While the initial step involves metal or pair of acidic and basic sites for alcohol dehydrogenation, aldol condensation and dehydration of the enolate species require basic sites and acidic sites respectively. Hydrogenation of CRL via butyraldehyde to butanol proceeds on metal sites. Alumina supported nickel catalysts, that present the requisite active sites for the above surface transformations, have been explored by several research groups for the conversion of ethanol. Cimino et al. observed that alumina and hydroxyapatite are active for ethanol conversion at lower temperature compared to MgO. Jordison et al. could achieve 55% conversion and 71% selectivity for total higher alcohols at 230°C under autogenous pressure, on 8% Ni on Al₂O₃ support modified with 9% La₂O₃, after 10 hrs on stream period. While Chistyakov et al. observed 63.5% ethanol conversion on Ni-Al₂O₃ at 275°C and 150 bar pressure, Ghasiaskar and Xu could achieve 35% conversion and 62% butanol selectivity on Ni-alumina catalyst at 250°C and 176 bar pressure in continuous flow mode. Appuzo et al. have observed that on Ni or Ru supported on MgO modified alumina support, MgO is dispersed as solid solution in alumina, resulting in increase in basicity and stability and the effective dispersion of Ni/Ru, leading to butanol yields up to 6-8%, with 40-60% ethanol conversion in the temperature range 350-400°C in continuous flow mode. A recent publication describes the techno-economic analysis of the ethanol conversion process, based on Ni/La₂O₃-Al₂O₃ catalyst, for possible commercial exploitation.

Achieving higher selectivity/yield for butanol and higher carbon number alcohols at higher ethanol conversion under moderate reaction conditions, remains a challenge. The distinguishing feature of the present work is towards improving the conversion and selectivity through modifications in alumina support, brought about by the addition (5% w/w of alumina) of metal oxides, like, La₂O₃, CeO₂, ZrO₂, MgO and TiO₂. Besides tuning the acid-base characteristics of alumina, the modifiers could influence the metal (Ni) dispersion, its electronic state and metal-support interactions and hence activity and selectivity. Such changes brought about by added metal oxides have been studied in detail, using different characterization techniques, like, XRD, temperature programmed reduction (TPR), acidity-basicity by ammonia and CO₂ TPD respectively and XPS. Observed activity and selectivity patterns for ethanol conversion have been correlated with the characteristics of the catalysts with a view to understand the mode of action of the catalysts and design catalysts with improved performance.

**Experimental Section**

**Materials**

Pural SB grade pseudo boehmite from M/s SASOL Germany, was used as such. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (98.0%), Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) (98.5%), (Merck), Lanthanum nitrate hexahydrate (La(NO₃)₂·6H₂O) (99.0%), Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) (99.5%) (Sisco Research Laboratories) Cerium nitrate hexahydrate (Ce(NO₃)₂·6H₂O) (99.9%), (CDH) and TiO₂ anatase (HOMBIKAT UV100 TiO₂) were used as received, without any further purification. Absolute alcohol (99.9%) from Changshu Hongsheng Fine Chemical Co. Ltd., China, was used as such for carrying out reactions.

**Preparation of catalysts**

Pural SB grade pseudo boehmite was calcined at 450°C in air for 4 h, to get unmodified gamma alumina support. Known amount of unmodified alumina support was dispersed in 20 mL of DM water with continuous stirring. Required quantity of La(NO₃)₃·6H₂O (to obtain 5% w/w of La₂O₃) was dissolved in the slurry and dispersed again by stirring. The slurry was evaporated to dryness at 80°C in a rotary evaporator, followed by drying in the oven at 120°C for 12 h. Lanthana modified alumina was then obtained by calcination of the dried material at 600°C for 12 h in nitrogen atmosphere. Similarly, required quantities of oxide precursors, namely, Ce(NO₃)₃·6H₂O, Mg(NO₃)₂·6H₂O, Zr(OCl)₂·6H₂O and Hombikat UV grade titania (to obtain 5% w/w loading of CeO₂,MgO, ZrO₂ and TiO₂ respectively with respect to alumina), were added to the alumina-water slurry, dispersed well, dried and calcined as described earlier, to get modified alumina supports. 8% w/w of Ni as aqueous nickel nitrate hexahydrate solution, was impregnated on to the supports by wet impregnation, dried at 120°C for 12 h and reduced under hydrogen gas flow at 500°C for 12 h to obtain the final catalysts.

**Characterization of catalysts**

Powder XRD diffraction patterns for the catalysts were recorded using Rigaku Corporation, Japan, Model Miniflex-II X-ray diffractometer, with Cu-Kα.
The catalysts were calcined in air at 300°C prior to TPR experiments. 50 mg of calcined catalyst was pre-treated at 300°C in high purity Ar gas (25 cm³/min) for 1 h and then cooled to room temperature in Ar flow. The gas was changed to 10% H₂ in Ar (25 cm³/min) at room temperature. After the stabilization of the baseline, TPR patterns were recorded from room temperature to 800°C with a heating rate 10°C/min. For TPD of ammonia, 50 mg of the sample was pre-treated at 300°C in helium flow of 20 mL/min for 1 h and cooled to room temperature in helium flow. The sample was saturated with ammonia by passing 10% NH₃ in helium gas over the catalyst for 20 min. After flushing out weakly adsorbed ammonia with helium flow at 373K, the baseline was established. TPD of adsorbed ammonia was then recorded by heating the sample in helium flow up to 650°C with a heating rate of 10°C/min. For TPD of CO₂ similar procedure was adopted using CO₂ as a probe molecule instead of ammonia.

Transmission electron micrographs were recorded using JEOL, Japan, Model 3010 Microscope. Few milligrams of the reduced samples (1-2 mg) were dispersed in a few mL (1-2 mL) of ethanol by ultrasonication for 15 min and a drop of the dispersion was placed on a carbon coated copper grid and allowed to dry in air at room temperature.

X-ray photoelectron spectra of the reduced catalysts were recorded using Omicron Nanotechnology, Oxford Instruments, UK, instrument with Mg Kα 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 was processed with the Casa XPS software.

**Evaluation of catalysts for ethanol conversion**

Reaction was carried in batch mode, using a 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 N₂ to remove air, the reactor was filled with nitrogen up to 10 kg/cm² and sealed. The reaction was carried out under autogenous pressure at 200°C and 220°C for 8 h with an agitator speed of 350 rpm. During the reaction the reactor pressure increased gradually with time and stabilized at 45-50 kg/cm² after 4 h. After the completion of 8 h, the reactor was cooled to room temperature and a sample of gaseous products for GC analysis was collected in a sample bulb by controlled depressurization 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 Electronic Supplementary Information.

**Results and Discussions**

**Characterization of catalysts**

**X-ray diffraction**

X-ray diffractogram for the pristine alumina support as presented in Fig S1 shows all major d-lines characteristic of gamma alumina phase at 2θ = 18.8, 36.8°, 45.8° and 66.8°, which correspond to (013), (111), (400) and (440) planes respectively and match closely with the reported values (JCPDS 46-1131). XRD patterns for Ni supported on pristine and modified alumina supports in reduced state are presented in Fig. 1. Diffractogram for reduced Ni/Al₂O₃ (Fig.1a) displays all major d-lines due to gamma alumina phase and in addition, d-lines at 2θ = 51.3° and 76.1° due to (200) and (220) planes for Ni metal (JCPDS-04-0850). The major d-line due to Ni metal at 2θ= 44.4° (111) is masked by the (400) line due to alumina. Since the intensity of the d-line at 2θ= 76.1° is very weak, the d-line at 2θ =51.3° was used to calculate the crystallite size of nickel for all the catalysts (Table.1). Under the preparation conditions adopted, strong metal-support interaction between Ni and alumina leading to the formation of nickel aluminate is possible⁵⁷. However, the d-lines due to nickel aluminate (at 2θ= 19.1°, 31.4°, 37.0°, 45.0° and 65.5°-JCPDS 10-339) are not discernible from those of alumina support, since both phases are structurally...
(spinel) similar. 2θ value for (400) plane corresponding to alumina in Ni/Al₂O₃ phase does show a decrease with respect to that for pristine alumina (2θ= 45.4 Vs 45.8) due to the migration and dispersion of Ni into alumina lattice, possibly leading to the formation of surface/bulk nickel aluminate.

Introduction of Ni and lanthana (Fig.1b) into the alumina phase does not result in any major structural modifications, with very little changes in alumina d-line positions. While no d-lines due to lanthana is observed, indicating its dispersion in alumina lattice, the d-lines due to Ni crystallites at 2θ= 53.2° and 75.1°are observed. Ni/Al₂O₃ (Fig.1c) displays major d-lines due to CeO₂ (28.3° (111), 33.1°(211), 56.4°(311), 76.6°(420) (JCPDS 34-03940), besides those for alumina and Ni metal. Major d-lines due to ZrO₂ and MgO (Fig.1 d and Fig.1e) are not distinctly observed in the patterns for Ni/ZrO₂-Al₂O₃ and Ni/MgO-Al₂O₃ possibly indicating that these oxides are well-dispersed on alumina phase, similar to the observations on lanthana modified catalyst. Similarly, in the diffractogram for Ni/TiO₂-Al₂O₃ (Fig.1 f) only one major d-line due to TiO₂ (anatase) at 2θ= 25.2° is observed. Though formation of nickel aluminate phase is possible in all samples, as explained earlier, distinct d-lines are not observed. Crystallite sizes for Ni on pristine and modified alumina supports, calculated by

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al₂O₃</td>
<td>174</td>
<td>0.44</td>
<td>10.1</td>
<td>Ni (200)</td>
</tr>
<tr>
<td>8%Ni/Al₂O₃</td>
<td>136</td>
<td>0.35</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>8%Ni/5%La₂O₃-Al₂O₃</td>
<td>121</td>
<td>0.36</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>8%Ni/5%CeO₂-Al₂O₃</td>
<td>129</td>
<td>0.36</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>8%Ni/5%ZrO₂-Al₂O₃</td>
<td>128</td>
<td>0.33</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>8%Ni/5%MgO-Al₂O₃</td>
<td>118</td>
<td>0.34</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>8%Ni/5%TiO₂-Al₂O₃</td>
<td>114</td>
<td>0.34</td>
<td>9.3</td>
<td></td>
</tr>
</tbody>
</table>
applying the Debye Scherrer equation, are presented in Table 1.

**Textural properties**

Nitrogen adsorption-desorption isotherms at 77K and pore-size distribution curves according to BJH method for pristine alumina and nickel supported on modified alumina (in reduced state) were obtained and studied. Pristine alumina displays Type IV adsorption-desorption isotherms characteristic of meso porous nature and Type II hysteresis curve, according to de Boer classification, indicating slit shaped pores. Introduction of Ni in alumina brings about perceptible change in surface area and pore volume of pristine alumina (Table 1). Introduction of nickel and modifiers does not significantly alter the overall pore structure of alumina, but for a modest decrease in surface area, pore volume and mean pore radius.

**Transmission Electron Microscopy**

Transmission electron micrographs for the reduced catalysts presented in Fig. 2 show fairly good dispersion of nickel crystallites on the supports. All catalysts exhibit needle shaped morphology as reported in literature for alumina supported nickel catalysts 28,30 a,b,c.

**Temperature programmed reduction**

TPR patterns for bare alumina support, nickel supported on pristine and modified alumina supported catalysts in calcined state are presented in Fig. 3. In order to study the presence of various reducible species, TPR profiles have been deconvoluted.
Depending on the nickel precursor and loading, the method of incorporation and pre-treatment/reduction procedures adopted, several states of reducible nickel phases have been observed. Further changes in the nature of the supports, like modifications by added metal oxides, namely, La$_2$O$_3$, CeO$_2$, MgO, ZrO$_2$ and TiO$_2$ are reflected in terms changes in overall reducibility, nickel dispersion and degree of metal-support interactions in modified supports. In the present work, based on the data from literature, three major reduction zones could be identified, in all the six catalysts, with characteristic reduction temperature ranges. Reduction maxima observed in the temperature range 100-400°C (Zone-1) are due to free or weakly bound nickel oxide, those in the temperature range 400-600°C (Zone-2) due to dispersed nickel oxide that exists in the form of solid solution in alumina matrix and the reducible phases in the temperature range 600-800°C (Zone-3) due to surface and bulk nickel aluminate formed by strong interaction with support.

As shown in Fig. 3, amongst the catalysts, Ni supported on pristine alumina displays relatively minimum reducibility as indicated by hydrogen consumption. All Ni catalysts supported on modified alumina are characterized by higher reducibility, in the following order: Ni/ CeO$_2$-Al$_2$O$_3$ > Ni/ TiO$_2$-Al$_2$O$_3$ > Ni/ La$_2$O$_3$-Al$_2$O$_3$ > Ni/ ZrO$_2$-Al$_2$O$_3$ > Ni/ MgO-Al$_2$O$_3$. Presence of Ni in metallic state is essential for the dehydrogenation-hydrogenation steps during ethanol conversion process and this aspect would be discussed in the following section. A compilation of TPR maxima in the three reduction zones and the corresponding hydrogen consumption (as % of total consumption) are given in Table 2. While these three distinct reduction zones (zones 1-3) are observed in all the six catalysts (Table 2), the relative proportions of the reducible phases within the catalysts differ with respect to the nature of modified supports. In the case of nickel supported on pristine alumina, based on hydrogen consumption, it is observed that the proportions of free or weakly bound nickel oxide (zone-1) and nickel oxide involved in the formation of surface/bulk nickel aluminate (zone-3), are larger compared to those on modified supports (Table 2). Addition of lanthana (Fig.S3b) increases the proportion of dispersed NiO at the expense of free NiO and NiO involved in surface/bulk nickel aluminate formation and overall reducibility of Ni$^{2+}$ increases, which is in line with the literature reports. With respect to the maxima (479°C) observed for NiO in dispersed state in Ni-Al$_2$O$_3$, the corresponding maxima for all the modified alumina catalysts are shifted to lower temperatures (461-470°C) (Table 2) indicating ease of reduction and increase in overall reducibility, as revealed by increase in hydrogen consumption (42.2 to 86%) in Zone-2. Especially in the case of Ni/ CeO$_2$-Al$_2$O$_3$, the redox pair Ce$^{3+}$/Ce$^{4+}$ is expected to facilitate the reduction of Ni$^{2+}$ and accordingly maximum overall reducibility is observed in this case (Fig.2d). Thus, the modifiers improve Ni dispersion, reducibility and modulate the nickel-support (alumina/ modified alumina) interactions and hence the characteristics of active phases.

X-ray Photoelectron Spectroscopy

XPS binding energy data for all the catalysts in reduced state have been presented in Table 3. XPS profiles for Ni core electron states in pristine and modified alumina supports are given in Fig.4 and those for modifier oxides in Fig.S4. Deconvolution of Ni2p$_{3/2}$ line for Ni supported on pristine alumina reveals two maxima, at 853.3 eV and 856.8 eV (Fig. 4a). With respect to the reported binding energy (BE) value of 852.6 eV$^{34,35}$ for clean Ni metal, the binding energy value for Ni dispersed on Al$_2$O$_3$ is on the higher side (+0.7 eV), revealing that Ni is in an electron deficient state. The other component of the 2p$_{3/2}$ peak at 856.8 eV is attributed to Ni 2p$_{3/2}$ in nickel aluminate.$^{35}$ In the case of Ni/La$_2$O$_3$-Al$_2$O$_3$ (Fig.4b) the peak at 835.4 eV is attributed to La 3d$_{5/2}$ for lanthana which is followed by its satellite peak at 838.3 eV$^{26}$.

Table 2 — Temperature programmed reduction characteristics of Ni/M,O$_2$-Al$_2$O$_3$ (M=La, Ce, Zr, Mg & Ti) catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>TPR maxima (°C)</th>
<th>(Hydrogen consumption (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zone-I (100°C)</td>
<td>Zone-II (400°C)</td>
</tr>
<tr>
<td>8%Ni/Al$_2$O$_3$</td>
<td>157, 278, 479</td>
<td>460, 735</td>
</tr>
<tr>
<td>8%Ni/5%La$_2$O$_3$-Al$_2$O$_3$</td>
<td>219, 355</td>
<td>461</td>
</tr>
<tr>
<td>8%Ni/5%CeO$_2$-Al$_2$O$_3$</td>
<td>175, 302</td>
<td>470</td>
</tr>
<tr>
<td>8%Ni/5%ZrO$_2$-Al$_2$O$_3$</td>
<td>217, 359</td>
<td>462</td>
</tr>
<tr>
<td>8%Ni/5%MgO-Al$_2$O$_3$</td>
<td>237, 371</td>
<td>467</td>
</tr>
<tr>
<td>8%Ni/5%TiO$_2$-Al$_2$O$_3$</td>
<td>229, 356</td>
<td>469</td>
</tr>
</tbody>
</table>
The observed BE of 835.4 eV for La 3d$_{5/2}$ is higher than the reported values for La$_2$O$_3$ (833.2 eV) and LaAlO$_3$ (833.8 eV) and is very close to the values of BE 835.0 eV$^{37}$ and 835.8 eV$^{38}$ reported for La dispersed in alumina phase. XPS profile in the region 850-860 eV is resolved into four peaks. The first pair at 851.9 eV and 853.1 eV is due to La3d$_{5/2}$ for lanthana and Ni 2p$_{3/2}$ for Ni metal. In the second pair, the peak
at 855 eV is the satellite peak for La3d3/2 and the one at 856.8 eV is the line for Ni 2p3/2 in nickel aluminate. XPS lines due to Ce4d3/2 core level are reported at 900.8 eV, 907.2 eV and 916.7 eV and 3d5/2 core levels at 882.4 eV, 888.8 eV and 898.1 eV.39-42 Corresponding XPS lines for Ce3+ are expected at 903.7 eV, 884.7 eV, 899.2 eV and 880.1 eV.39,42,43 In the present work, only two prominent XPS lines at 886 eV and 889.6 eV are observed for Ce, which could be assigned to Ce3+(884.7 eV) and Ce4+(888.8 eV), possibly indicating the presence of both oxidation states. ZrO2, MgO and TiO2 modified catalysts (Figs. 4 c, d and e) also display peaks at 853.8 eV and 853.3 eV and 852.1 eV due to Ni 2p3/2 for Ni metal and at 856.9 eV and 856.6 eV and 858.1 eV due to Ni 2p3/2 in nickel aluminate respectively. In the case of other modifier oxides, XPS line at 182.9 eV and 185.4 observed for Zr3d5/2 Zr3d3/2 are close to the reported44 binding energy values of 182.75 eV and 185.14 eV respectively. Similarly, the observed core level binding energy values of 50.1 eV for Mg2p and 456.9 eV and 462.3 eV for Ti2p are close to the respective reported values.45 Al 2p lines for La & Ce modified alumina display shift towards lower BE values at 73.6 eV and 73.3 eV respectively with respect to the corresponding XPS line for unmodified alumina at 74.2 eV. Such shift in BE is attributed to a strong interaction between Ni and surface Al ions.46 While no significant change in Al2p BE values are observed in ZrO2 and MgO modified alumina, BE for TiO2 modified alumina shifts to higher side. Modifiers thus influence the electronic state of the alumina phase.

**Acidity and basicity measurements**

Distribution of acid sites, as revealed by temperature programmed desorption profiles for ammonia (Fig. S5) for all the catalysts in the reduced state, is given in Table 4.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Weak °C/mmolg</th>
<th>Medium °C/mmolg</th>
<th>Strong °C/mmolg</th>
<th>Total mmolg</th>
<th>Acid site Density µmol/m²</th>
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<tr>
<td>8%Ni/Al2O3</td>
<td>283</td>
<td>385</td>
<td>474</td>
<td>2.38</td>
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<tr>
<td></td>
<td>0.53</td>
<td>1.32</td>
<td>0.53</td>
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<tr>
<td>8%Ni/5%La2O3-Al2O3</td>
<td>279</td>
<td>399</td>
<td>483</td>
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<td></td>
<td>0.47</td>
<td>1.01</td>
<td>0.40</td>
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<tr>
<td>8%Ni/5%CeO2-Al2O3</td>
<td>267</td>
<td>370</td>
<td>461</td>
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<td>12.9</td>
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<td></td>
<td>0.53</td>
<td>0.93</td>
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<tr>
<td>8%Ni/5%ZrO2-Al2O3</td>
<td>221</td>
<td>352</td>
<td>451</td>
<td>1.52</td>
<td>11.9</td>
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<td></td>
<td>0.25</td>
<td>0.75</td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8%Ni/5%MgO-Al2O3</td>
<td>229</td>
<td>356</td>
<td>455</td>
<td>1.19</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.6</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8%Ni/5%TiO2-Al2O3</td>
<td>211</td>
<td>398</td>
<td>482</td>
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</tbody>
</table>

Weak (200-300°C), medium (300-400°C) and strong (400-500°C) acid sites are observed in all the catalysts. Ni supported on pristine alumina displays maximum total acidity and acid sites density. While addition of lanthana and ceria to Ni/Al2O3 brings about reduction in total acidity and acid site density, the reduction is substantial with the supports modified by other three additives, ZrO2, MgO and TiO2. Moderation of overall acidity of alumina by addition of La2O3, CeO2, ZrO2 and MgO has been reported by Sánchez-Sánchez et al.47 Attenuation of acidity and increase in basicity of lanthana and ceria modified alumina have been observed by Garbarino et al.48

Distribution of basic sites, compiled on a similar basis, for all the catalysts in reduced state, is presented in Table 5. Corresponding CO2 desorption profiles are presented in Fig.S6 Weak (100-200°C), medium (200-300°C) and strong (300-500°C) basic sites are observed in all the catalysts. All catalysts based on modified alumina support display higher basicity and basic site density when compared to the catalyst supported on pristine alumina.

The observed CO2 TPD maxima for ceria modified catalyst (with characteristic desorption maxima at 199, 355 & 485°C) indicate the presence of relatively stronger basic sites, though the total basicity is less. Vazquez et al.48 could distinguish the nature of basic sites in La2O3-Al2O3 and CeO2-Al2O3 using conversion of isopropanol as the probe reaction. While on La2O3-Al2O3 only propene is observed, on CeO2-Al2O3 propene and acetone are observed as products, indicating the presence of strong basic sites responsible for dehydrogenation.

Results observed the present work on Ni/CeO2-Al2O3 are in line with the observations reported by Vazquez et al.48
In general, all catalysts with modified alumina supports, display relatively higher population of medium strength acidic/basic sites, which could influence the reaction pathways in ethanol condensation process. These aspects are discussed in the following section.

Conversion of ethanol to higher carbon number alcohols

Though the reaction has been carried out at 200°C and 220°C, for a complete understanding and analyses of ethanol conversion, product distribution and selectivity, the data at 200°C are considered.

### Table 5 — Distribution of basic sites by CO\textsubscript{2} TPD for Ni/M\textsubscript{x}O\textsubscript{y}-Al\textsubscript{2}O\textsubscript{3} (M=La, Ce, Zr, Mg and Ti) catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Weak °C/mmol/g</th>
<th>Medium °C/mmol/g</th>
<th>Strong °C/mmol/g</th>
<th>Total mmol/g</th>
<th>Basic site Density μmol/m\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>8%Ni/Al\textsubscript{2}O\textsubscript{3}</td>
<td>130</td>
<td>0.025</td>
<td>251</td>
<td>313</td>
<td>0.102</td>
</tr>
<tr>
<td>8%Ni/5%La\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}</td>
<td>128</td>
<td>0.049</td>
<td>274</td>
<td>358</td>
<td>0.392</td>
</tr>
<tr>
<td>8%Ni/5%CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}</td>
<td>199</td>
<td>0.183</td>
<td>355</td>
<td>485</td>
<td>0.165</td>
</tr>
<tr>
<td>8%Ni/5%ZrO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}</td>
<td>141</td>
<td>0.019</td>
<td>288</td>
<td>407</td>
<td>0.302</td>
</tr>
<tr>
<td>8%Ni/5%MgO-Al\textsubscript{2}O\textsubscript{3}</td>
<td>143</td>
<td>0.035</td>
<td>275</td>
<td>386</td>
<td>0.397</td>
</tr>
<tr>
<td>8%Ni/5%TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}</td>
<td>128</td>
<td>0.019</td>
<td>269</td>
<td>337</td>
<td>0.089</td>
</tr>
</tbody>
</table>

Scheme 1 — Possible transformations of ethanol and acetaldehyde on Ni/M\textsubscript{x}O\textsubscript{y}-Al\textsubscript{2}O\textsubscript{3} (M=La, Ce, Zr, Mg and Ti) catalysts

al\textsuperscript{48}.

Complete distribution of products, after 8 hrs of reaction at 200°C on all catalysts, is presented in Table S2. Besides unconverted ethanol, butanol, hexanol, octanol and ethylene are observed as the major products along with more than 20 minor products. Presence of small amounts of aldehydes, namely, acetaldehyde, crotonaldehyde and butyraldehyde, in the product streams from all catalysts, indicate that the process proceeds through the classical Guerbet reaction pathway. Scheme 1 presents possible transformations of
ethanol and acetaldehyde, the primary product in the process. Pathways for the formation of the desired products (butanol, hexanol and octanol) and minor products from acetaldehyde are illustrated in Scheme 1. Since the catalysts contain acidic and basic sites of different nature, strength and population, (Tables 4 and 5), ethanol and acetaldehyde undergo a range of transformations, resulting in the formation a number of minor products, which are grouped into:

i) Ether, ethyl acetate and acetal,

ii) C$_3$-C$_4$ aldehydes (acetaldehyde, crotonaldehyde and butyraldehyde),

iii) C$_4$+esters, aldehydes and ketones

iv) C$_1$ –C$_5$ gaseous hydrocarbon products (including ethylene, CO and CO$_2$).

Trends in the formation of the products (mole%) on the six catalysts are presented in Fig. 5a-5e.

Correlations on the product formation with inherent acidity-basicity of the catalysts are presented in Fig.6a to 6c. Formation of di-ethyl ether and ethyl acetate in small amounts (Fig. 5a) is due to inherent acidity of the catalysts. It is likely that the presence of relatively higher acidity on Ni/Al$_2$O$_3$ and Ni/La$_2$O$_3$-Al$_2$O$_3$ catalysts (Table 4) promotes further dehydration of ether to ethylene and hence ether is not observed on these catalysts. Relatively higher amounts of C$_3$-C$_4$ aldehydes in Ni/Al$_2$O$_3$ and Ni/La$_2$O$_3$-Al$_2$O$_3$ catalysts (Fig. 5b) compared to other four catalysts indicate that aldol condensation of acetaldehyde is slower on these two catalysts and is facilitated on the later group of catalysts due to higher basicity (Table 4). Higher basicity entails faster aldehyde condensation/ consumption. Besides, hydrogenation of crotonaldehyde and butyraldehyde are also favoured on these four catalysts due to higher reducibility/metallic nickel (Fig.2). On similar grounds, higher amounts of C$_4$+esters and ketones are observed on lanthana, ceria, magnesia and zirconia modified catalysts(Fig.5c), due to relatively higher basicity and consequent facile aldol condensation. Young et al. have observed that aldol condensation on titania is inhibited in presence of ethanol due to competitive adsorption. Hence formation of C$_4$+esters and ketones via aldol condensation is less on titania modified catalyst. Ni/Al$_2$O$_3$ has the lowest basicity.

Ethylene in significant amounts is formed (Fig. 5d) due to acid catalyzed conversion of ethanol to di-ethyl ether, followed by dehydration (Scheme 1). Fig. 6a shows a direct relationship between the total acidity of the catalysts and mole % ethylene. Higher ethylene formation observed on Ni/TiO$_2$-Al$_2$O$_3$, in spite of having lowest total acidity, is due to the presence of

![Fig. 5 — Trends in the formation of minor products during ethanol conversion on Ni/M$_x$O$_y$-Al$_2$O$_3$ (M=La, Ce, Zr, Mg &Ti) catalysts a) Ether and ethyl acetate b) C$_3$-C$_4$Aldehydes c) C$_4$+Esters andketones d) Ethylene and e) C$_1$–C$_5$ gaseous hydrocarbons]
strong acid sites with a characteristic desorption maximum at 482°C (Table 4). Young et al. observed that titania is highly acidic and converts ethanol to diethyl ether. Similarly, Ni/La\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} with strong acid sites (desorption maximum at 483°C, Table 4) also displays higher ethylene formation compared to other catalysts, wherein lower acidity levels lead to a decrease in ethylene formation. Thus, besides total acidity, strength of the acid sites is observed to be a crucial parameter. Similar correlation is observed between C\textsubscript{1}-C\textsubscript{5} hydrocarbons formation and acidity as well (Fig. 5e).

**Conversion of ethanol**

Conversion of ethanol and selectivity for butanol and higher alcohols at 200°C and 220°C are presented graphically in Fig. 7. With respect ethanol conversion of 38.2% on Ni catalyst supported on pristine alumina, moderate increase in conversion at 200°C is observed on Ni/La\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} (42.3%) and Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (41.1%) catalysts. While Ni/MgO-Al\textsubscript{2}O\textsubscript{3} and Ni/TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} display slightly lower ethanol conversion (36.2%), no change in ethanol conversion Fig. 6 — Correlations between a) Total acid sites and ethylene selectivity b) Total basic sites and higher alcohol selectivity and c) Total basic sites and butanol selectivity
is observed on Ni/ZrO$_2$-$\text{Al}_2\text{O}_3$ vis-a-vis Ni/Al$_2$O$_3$. Both lanthana and ceria modified catalysts display higher reducibility, especially of dispersed NiO, resulting in metallic Ni, responsible for initial and final steps in the ethanol conversion process, namely dehydrogenation of ethanol and hydrogenation of crotonaldehyde/butyraldehyde. On the contrary, reducibility of MgO and ZrO$_2$ modified catalysts only slightly higher than that for the base catalyst, Ni/Al$_2$O$_3$. Though titania modified catalysts displays high reducibility, ethanol conversion is lower, since the second major step, aldol condensation of acetone, is retarded due to competitive adsorption of ethanol$^{48}$. Moderate improvement in ethanol conversion observed for lanthana and ceria modified catalysts could be ascribed to improvements in reducibility. Jordison et al.$^{15}$ also observed moderate improvement on ethanol conversion on lanthana (55%) and ceria (50%) modified Ni/Al$_2$O$_3$ catalysts compared to the unmodified catalyst (46%) but at higher temperature, 230°C and after 10 hrs of reaction. In comparison with ethanol conversion values reported earlier on alumina supported nickel catalysts (Table S1), higher conversions at lower pressure and temperature are realized in the present work.

XRD and XPS results reveal the presence of both Ni metal and nickel alminate phases in reduced catalysts. Since all the catalysts are reduced in hydrogen at 500°C, based on the TPR profiles Fig. 2 for calcined catalysts, it is inferred that the highly dispersed NiO is reduced to nickel metal, which act as active sites for the dehydrogenation of ethanol to acetaldehyde. Ni$^{2+}$ in nickel alminate act as Lewis acid sites. Presence of acetaldehyde in particular, in the product streams of all catalysts, indicates that the rate of initial/primary aldol condensation of acetaldehyde, which is considered as the rate determining step$^{15,49}$, needs to be further enhanced to improve conversion. As ethanol conversion increases, the concentration of secondary aldehydes build up, which compete with primary aldehydes for the basic sites required for aldol condensation. Hence, only a marginal increase in ethanol conversion is observed, though ethanol dehydrogenation step is accelerated by Ni metal. Increasing the loading of basic oxides like ceria may lead to further improvement of the acetaldehyde condensation rate and hence ethanol conversion. Improving hydrogenation function by addition of a second metal could help to increase rate of hydrogenation of secondary aldehydes (crotonaldehyde, butyraldehyde etc.), which in turn increase ethanol conversion.

These two aspects, namely, increasing the loading of ceria and exploring addition of second metal to Ni are currently under investigation. According to Cimino et al.$^{12}$ alumina is active for ethanol conversion at a lower temperature compared to magnesia. Young et al.$^{48}$ in their studies on ethanol conversion and aldol condensation on TiO$_2$, hydroxyapatite (HAP) and MgO have observed that the activity for aldol condensation follows the order TiO$_2$> HAP >>MgO. Besides, on titania, aldol condensation rate is inhibited in presence of ethanol due to competitive adsorption, while it is not so with MgO and HAP. Such inherent variations in the characteristics of the promoter oxides could affect overall conversion of ethanol on nickel catalysts with modified supports. At 220°C ethanol conversion increases to 61 to 65% with modified catalysts compared to 45.5% with unmodified one.

**Selectivity towards butanol and higher alcohols**

In contrast to the moderate improvement in ethanol conversion, substantial increase in selectivity for butanol (BLS) and higher alcohols (HAS) is observed (Fig 6b, 6c) with catalysts based on modified supports. Ceria and magnesia modified catalysts display HAS of 81% and 75% respectively and 48% for BLS. Lanthana and zirconia modified catalysts also exhibit significant increase in selectivity for HAS and BLS compared to Ni catalyst supported on pristine alumina. Observed increase in selectivity for HAS and BLS are related to the increase in the basicity of catalysts with modified supports (Table 5, Fig.6b and 6c). Increase in the basicity essentially increases the rate of aldol condensation of aldehydes, which leads to the formation of butanol and higher alcohols. Though total basicity of Ni/Ce$_2$O$_3$-Al$_2$O$_3$ catalyst is the lower, the presence of strong basic sites in comparison with other catalysts, with characteristic desorption maxima at relatively higher temperatures, 199, 355 and 485°C (Table 5), could be responsible for higher butanol and C$_{4+}$ alcohols selectivity. Jian et al.$^{50}$ have attributed high butanol selectivity (55%) and yield (21.6%) observed on Cu-Ce/AC catalysts to high basicity of CeO$_2$ which promotes aldol condensation. Similarly, MgO and ZrO$_2$ modified catalysts with CO$_2$-desorption maxima at higher temperatures, 386°C and 407°C respectively (Table 5), also display higher butanol and C$_{4+}$ alcohols selectivity. Both strength and the population of basic sites are needed to achieve selectivity for higher alcohols.
Though substantial increase in ethanol conversion is observed at 220°C, the selectivity for butanol decreases from 45-48% at 200°C (with ceria, zirconia and magnesia modified catalysts) to 36-40% at higher temperature, possibly due to the conversion to higher alcohols and gaseous products. XRD, TEM and XPS data for a typical used catalyst show that the structural integrity and active phase characteristics are retained.

Role of acidic and basic sites in the ethanol conversion process has been studied by several researchers on different active phase/support systems and have been largely qualitative. A systematic study undertaken in the present work on the influence of support characteristics reveals simultaneous changes in the characteristics of the catalysts, like, reducibility of Ni²⁺, Ni metal dispersion, metal-support interaction and its electronic state besides acidity and basicity and clearly brings out property-performance correlations. While the selectivity for butanol and higher alcohols is governed by the basicity, both metal function and basicity are required to drive ethanol conversion. Moderation of acidity, on the other hand, helps in the minimization of ethylene and other gaseous products.

Recent studies by Benito et al. on Cu-hydrotalcite derived catalysts reveal slightly higher butanol selectivity (52.1%) but at lower conversion (32.1%), higher temperature (230°C) and after 12 h of reaction. Wang et al. have reported 19.1% yield of butanol at 50.1% ethanol conversion after 8 h at 275°C and 2MPa pressure, but the catalyst undergoes phase transformation to Ca(OH)₂ during reaction. Studies have been extended to bi-metallic catalysts based on Au and three component Cu-Ni-Mn catalysts as well, at higher temperatures and pressures. Though these studies are in the right direction, ethanol conversion and butanol/higher alcohols selectivity are not attractive. Balancing the dehydrogenation-hydrogenation functions and moderation of acidity-basicity (nature, strength and population of sites) to prevent the formation of numerous side products are the key aspects that need further investigation.

Conclusion
A new series of nickel (8% w/w of alumina) supported on alumina catalysts with the general formula Ni/MₓOₙ₋ₓ-Al₂O₃ (M=La, Ce, Zr, Mg and Ti, with 5% w/w MₓOₙ) has been evaluated for the conversion of ethanol to butanol and higher alcohols in batch mode. Presence of small amounts acetaldehyde, butanal and crotonaldehyde in the product pattern indicates that the process follows the Guerbet reaction pathway. Introduction of promoter oxides influences nickel metal dispersion, reducibility, metal support interactions and hence the electronic character of the active phase consisting of nickel metal and nickel aluminate. Besides, acid-base characteristics, ie., nature, strength and population of sites, also vary with respect to the promoter oxides. While ethanol conversion is governed by the metal function and basicity, selectivity for butanol and higher alcohols is influenced by the basicity of the catalysts. Moderation of acidity by the promoters retards the formation of ethylene and other C₁-C₅ hydrocarbon products. Increasing basicity of the catalysts with higher loading of ceria, improving metal function by addition of second metal with Ni and optimization of acidity-basicity to minimize side products formation are the useful strategies for achieving higher ethanol conversion activity and selectivity for butanol and higher alcohols.

Conflicts of interest
There is no conflict of interests among the authors.

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