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Tunable catalytic properties of bi-functional mixed oxides in ethanol conversion to high value compounds

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ABSTRACT

A highly versatile ethanol conversion process to selectively generate high value compounds is presented here. By changing the reaction temperature, ethanol can be selectively converted to >C_2 alcohols/oxygenates or phenolic compounds over hydrotalcite derived bi-functional $MgO–Al_2O_3$ catalyst via complex cascade mechanism. Reaction temperature plays a role in whether aldol condensation or the acetone formation is the path taken in changing the product composition. This article contains the catalytic activity comparison between the mono-functional and physical mixture counterpart to the hydrotalcite derived mixed oxides and the detailed discussion on the reaction mechanisms.

1. Introduction

The projected crude oil depletion along with increased greenhouse gas emissions has created great interest in developing technologies to produce fuels from renewable resources. In addition to fuels, a large fraction of chemicals are also produced from crude oil resources. Thus, developing biomass-based renewable resources to supplement or replace the crude-oil-based fuels and chemicals is very important for the sustainable future of humankind. It has been proven that ethanol can be produced from renewable resources via biochemical and thermochemical routes in very efficient manner [1–3]. So developing technologies that utilize ethanol as a building block to produce high value compounds can advance us toward freedom from fossil based resources. There are numerous literature articles on converting ethanol to higher alcohols and other valuable compounds [4–10]. Here we show that ethanol can be selectively converted to >C_2 alcohols/oxygenates or to phenolic compounds on $MgO–Al_2O_3$ catalyst derived from hydrotalcite (HT) by changing the reaction temperature alone. Alcohols with higher carbon number (C_2+) offer advantages as petrol substitutes because of their higher energy density and lower hygroscopicity [11] and higher alcohols can be used as intermediates to generate jet-fuel and diesel-range hydrocarbons [4]. Phenolic compounds are the key participant in the production of many different commodities, e.g., insulating material, paint and nylon fibers. Currently most phenolic compounds are generated from the crude-oil derivative benzene [12].

Conversion of ethanol to 1-butanol over mixed oxides is a well-known process [5] and the conversion of ethanol to acetone [13] and isophorone [14] compounds are reported sporadically but to our awareness we have not seen any publication on generating ethanol to 1-butanol and phenolic compounds in single catalytic step over the same catalyst. In this paper, the influence of reaction temperature on the structured bi-functional mixed oxide catalyst to convert ethanol to high value compounds was discussed.

2. Experimental

2.1. Materials

The catalyst of interest in this work, HT [$Mg_6Al_2(CO_3)(OH)_{16}·4H_2O$, purchased from Sigma–Aldrich, part# 652288] is made up of anionic clays in which divalent cations [Mg^{2+}] within brucite-like layers are replaced by trivalent cations [Al^{3+}] [15]. Calcination at high temperature decomposes the HT via dehydration, dehydroxylation, and decarbonization to $MgO–Al_2O_3$ having strong Lewis basic sites associated with the $M^{n+}O^{2-}$ acid-base pair sites [16–18]. This gives the combination

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of acid-base (bi-functional) properties required for the complex sequence of reaction mechanisms to convert the ethanol to high molecular weight oxygenates [19–21]. Reactions over HT derived $MgO–Al_2O_3$ catalyst have been shown to generate 1-butanol selectively via Guerbet reaction, and this catalyst is also used in many other research areas such as transesterification and alcohol dehydrogenation [22,23]. To show the uniqueness of the HT derived $MgO–Al_2O_3$, magnesium oxide (MgO), aluminium oxide (Al_2O_3) and the physical mixture of MgO and Al_2O_3 with 3–1 ratio were also tested at similar operating conditions and the results were presented here. The MgO and Al_2O_3 materials were purchased from Sigma–Aldrich. The ethanol (200 proof) used in the experiments was purchased from Decon Labs, Inc.

2.2. Catalyst testing

The catalyst testing experiments were conducted on a down flow gas-phase reactor arrangement. The catalyst of interest was placed in the middle of the reactor tube (isothermal zone) and heated using a tube furnace. Ethanol and carrier gas nitrogen (N_2) was fed from the top of the reactor. The liquid product samples were collected in the bottom of the reactor in a cold trap (ice bath) arrangement. Later the collected liquid products were analysed in the gas chromatography-flame ionisation detector and by gas chromatography/mass spectrometry. The non-condensable gases from the cold trap passed through the flow meter and were analysed in the gas chromatography-thermal conductivity detector. Before use, the catalyst was pressed and sieved to 60–100 mesh and calcined at 500 °C in air atmosphere. 2 g of catalyst loading was used in the experiments with 0.002 ml/min of ethanol feed rate. The gas samples were collected every one hour interval and the liquid samples were collected every 24 h.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns of all the catalyst tested were recorded on a Phillips X-Pert (50 kV and 40 mA) diffractometer using Cu Kα radiation (λ¼ 1.5437 Å). Each sample was scanned in the range between 20° and 80°. Ammonia (NH_3) and carbon dioxide (CO_2) Temperature Programmed Desorption (TPD) analyses were performed on the catalysts tested for the acid and base measurements. For the NH_3–TPD measurement, sample material was saturated with NH_3 at room temperature in a flow of 15.7% NH_3 in helium (He) and for the CO_2–TPD measurement, sample material was saturated with CO_2 at room temperature in a flow of 5% CO_2 in He. After saturation, the weakly bound NH_3/CO_2 was desorbed prior to the measurement at 50 °C for 3 h at a He flow rate of 25 ml min^{-1}. The desorption curve was then attained at a heating ramp of 10 °C min^{-1} from 50 °C to 800 °C at a He flow rate of 25 ml min^{-1}. The off-gas was analyzed on a Micromeretics Autochem II equipped with a PFEIFFER mass spectrometer.

3. Results and discussion

The experiments were conducted between 350 °C and 450 °C at atmospheric pressure condition. The operating conditions, ethanol conversion and the carbon selectivity to the primary compounds [ethylene, diethyl ether (DEE), acetaldehyde, 1-butanol and phenolic compounds] are listed in Table 1. Except MgO catalyst, both the ethanol conversion and the ethylene selectivity tend to increase for all the catalyst tested with the increase in temperature. Over MgO at 350 °C the conversion of ethanol is only 20% and the major products in the liquid composition were acetaldehyde and 1-butanol. At 450 °C the ethanol conversion increased to around 80% and the liquid product contains aldehydes, ketones and alcohols up to carbon number C_{10}.

Table 1
Conversion of ethanol, and carbon selectivity to primary compounds at 350 °C and 450 °C over various catalysts.

Catalyst	Temp	Ethanol	Carbon selectivity (%)				
	(°C)	Conversion (%)	Ethylene	DEE	Acetaldehyde	1-Butanol	Phenols
MgO	350	20	7	1.5	39	18	0
MgO	450	84	9	1.5	14	11	0
Al_2O_3	350	85	70	<20	0.1	0	0
Al_2O_3	450	99	90	<1	0	0	0
$MgO–Al_2O_3$[a]	350	88	41	34	2	0.5	0
$MgO–Al_2O_3$[a]	450	98	58	1.7	0	0	0
$MgO–Al_2O_3$[b]	350	62	17	4	5	42	<1
$MgO–Al_2O_3$[b]	450	98	47	0	0	<1	35

[a] $MgO–Al_2O_3$ physical mix 3–1 ratio.
[b] $MgO–Al_2O_3$ derived from HT with 3–1 ratio.

Over Al_2O_3 at 350 °C the conversion of ethanol is around 85% and the conversion of ethanol reached approximately 100% at 450 °C. Ethylene was identified as the primary compound at both temperatures. At lower temperatures high level of DEE also generated via inter molecular dehydration of ethanol. The spent catalyst collected after the 450 °C experiment was very dark in color which shows the high levels of coking at the elevated temperature. At 350 °C over physical mixture of $MgO–Al_2O_3$ the ethanol conversion was around 88% and it showed activity for both intra molecular dehydration to ethylene and inter molecular dehydration to DEE and at 450 °C only ethylene was identified as the primary compound. For both temperatures almost negligible levels of products derived via coupling chemistry were identified on the physical mix catalyst. At 350 °C over $MgO–Al_2O_3$ derived from HT with 3–1 ratio generated products with high selectivity towards butanol with other minor by-products and at 450 °C the selective for phenolic compounds was around 35% and high levels of ethylene was also detected. Only the major compounds identified were listed in the Table 1. Particularly for the MgO and physically mixed $MgO–Al_2O_3$ at 450 °C experiments acetone, higher alkenes, unsaturated aldehydes and some levels of higher alcohols due to cross condensation were identified in the product stream.

Figs. 1 and 2 depict the liquid product chromatograms of the ethanol conversion over $MgO–Al_2O_3$ derived from HT at 350 °C and 450 °C. The compounds identified from the liquid products produced from 350 °C experiments consisted primarily of C_2+ alcohols up to C_8. Small fractions of aldehyde and ether compounds up to C_{10} were also identified at this temperature range. The compounds identified from the liquid products produced from 450 °C experiments consisted primarily of phenolic compounds (phenol, methyl phenol and dimethyl phenol). Small fractions of C_3+ ketones were also identified at this temperature. The concentration of the ketone compounds increased with temperature between 350 °C and 450 °C.

Fig. 3 shows the XRD pattern of the MgO, Al_2O_3 and HT catalysts that are calcined at 500 °C for 4 h. The acquired XRD pattern for the MgO, Al_2O_3 materials resembles the literature information [24]. The HT derived material with 3–1 ratio between MgO and Al_2O_3 shows the predominance of MgO due to its highest presence. Fig. 4 shows the CO_2 TPD profiles and the amount CO_2 desorbed from the MgO, Al_2O_3, physical mixture of $MgO–Al_2O_3$ with 3–1 ratio and HT derived $MgO–Al_2O_3$ with 3–1 ratio. All the samples analysed shows more than one kind of basic site. Al_2O_3 exhibits only weak and medium strength basic sites [20,25], whereas weak, medium and strong basic sites were observed in the case of MgO [20]. The physical mix shows the peaks from the combination of both MgO and Al_2O_3. The HT derived mixed oxide shows a small peak corresponds to the weak base site followed by a broad peak observed corresponding to the combined medium and strong basic sites. The amount of basic sites was in the similar range between the MgO,

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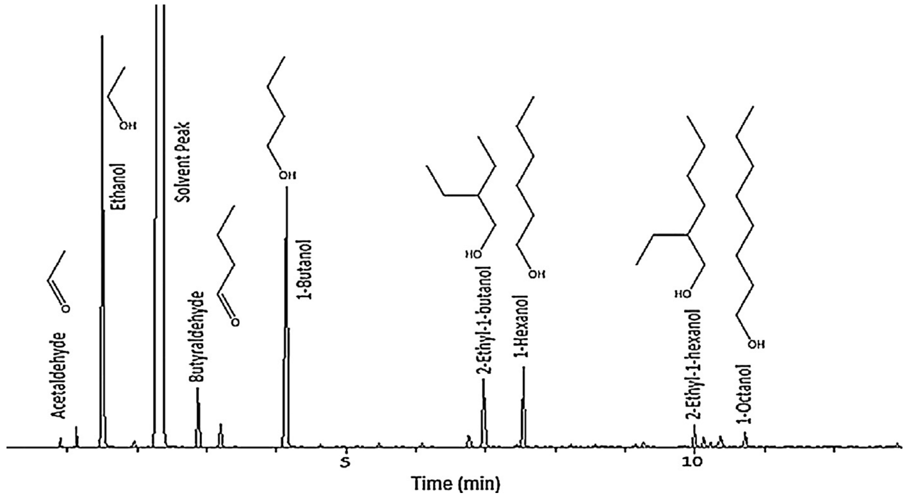

Fig. 1. Liquid product chromatogram of ethanol conversion over MgO-Al_2O_3 derived from HT at 350 °C.

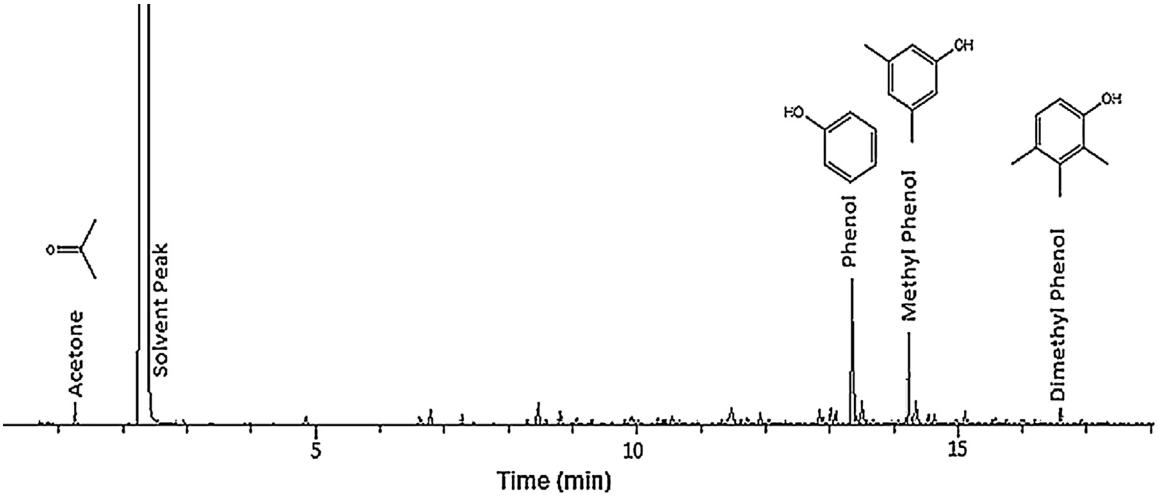

Fig. 2. Liquid product chromatogram of ethanol conversion over MgO-Al_2O_3 derived from HT at 450 °C.

Al_2O_3 and physical mix (ranges between 140 and 200 μmol g^{-1}) but the strengths varied in wide range between weak, medium and strong basic sites. The total basic sites measured for the HT derived material was more than two folds higher than the other catalysts tested and around 90% of the total sites located on the medium and the high strength basic site region.

Fig. 5 shows the NH_3 TPD profiles of the MgO, Al_2O_3, physical mix of MgO–Al_2O_3 with 3–1 ratio and HT derived MgO–Al_2O_3 with 3–1 ratio. The MgO sample does not show any acid sites. Physical mixture shows the acidity with respect to the amount of Al_2O_3. HT derived material contains more acidic sites than the pure alumina. But compared with the total basic sites the measured acidic sites were several folds lower and this result is in agreement with the literature information [20,24]. For all the materials tested the total measured acid sites from the NH_3 TPD were below 5 μmol g^{-1}.

In cascade catalysis various chemical steps combine in one step without separating the intermediates and this has been successfully employed in the enzymatic catalysis using two essential tools: site-isolation and substrate selectivity [26]. In the heterogeneous catalysis the concerted multi-functional pathway requires the active sites co-exist in molecular distances so the proximity between the active sites with different functionality and the chemical nature to complete the complex network of reaction mechanism very efficiently [27]. The ordered structure of the HT derived mixed oxide provide the required proximity between the basic and acidic active sites that are required for the cascade chemistry such as ethanol conversion to 1-butanol or phenolic compounds.

In the following section the unique change in reaction mechanism with the temperature change on the ethanol conversion over MgO–Al_2O_3 derived from HT will be discussed. Based on the experimental results and the literature information, the reaction scheme of the ethanol at 350 °C is shown in Scheme 1. At low temperatures, ethanol generates ethylene via intramolecular dehydration, and diethyl ether and C_4+ ethers (cross-dehydration between ethanol and higher alcohol products) via intermolecular dehydration. Butanol is primarily generated via a sequence of complex reaction mechanisms. First ethanol dehydrogenates to generate acetaldehyde, then acetaldehyde goes through aldolation to form hydroxybutanal, followed by a condensation reaction to give an alpha, beta unsaturated aldehyde compound (crotonaldehyde), which then goes through a sequence of hydrogenation reactions to form butanal and finally butanol. Butanol can also be generated via direct condensation of ethanol, but the liquid product composition identification proves that the indirect mechanism via aldehyde is the major pathway for the higher alcohol generation [5,18–20,27,28]. Basic sites play the internal hydride transfer role to generate the higher alcohol compounds [29,30]. Some literature information also points out that Meerwein–Ponndorf–Verley

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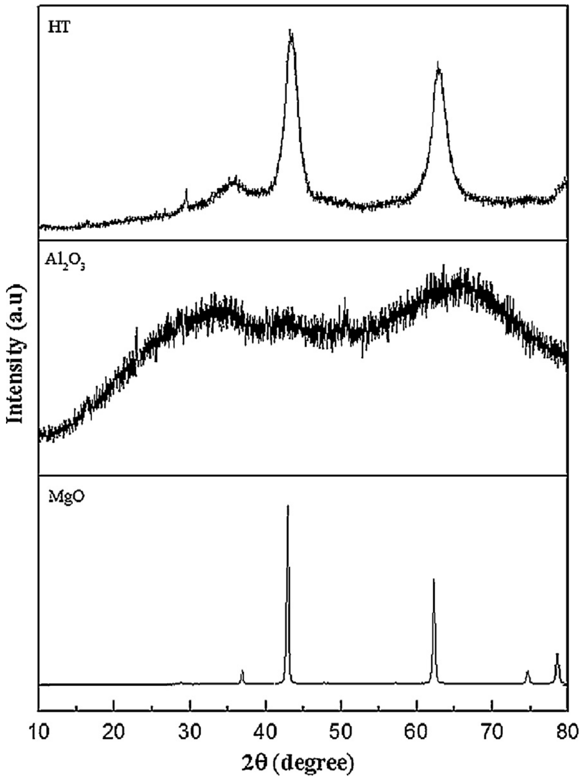


Fig. 3. XRD profile of the MgO, Al_2O_3 and HT derived MgO-Al_2O_3 with 3 to 1 ratio.

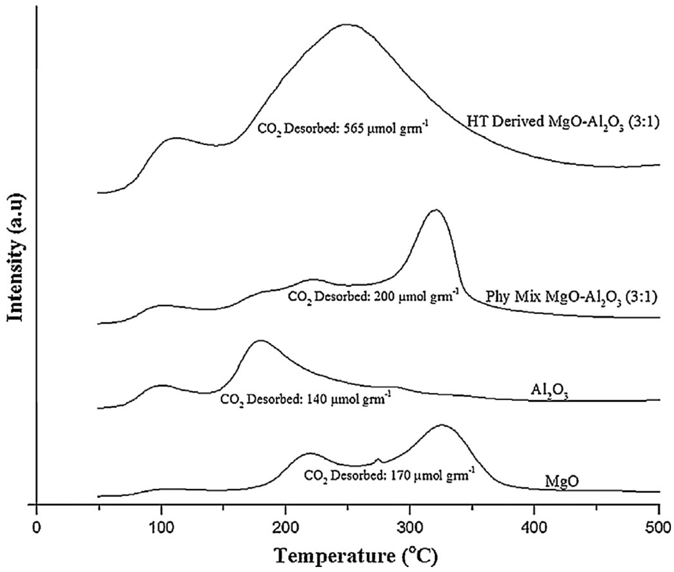
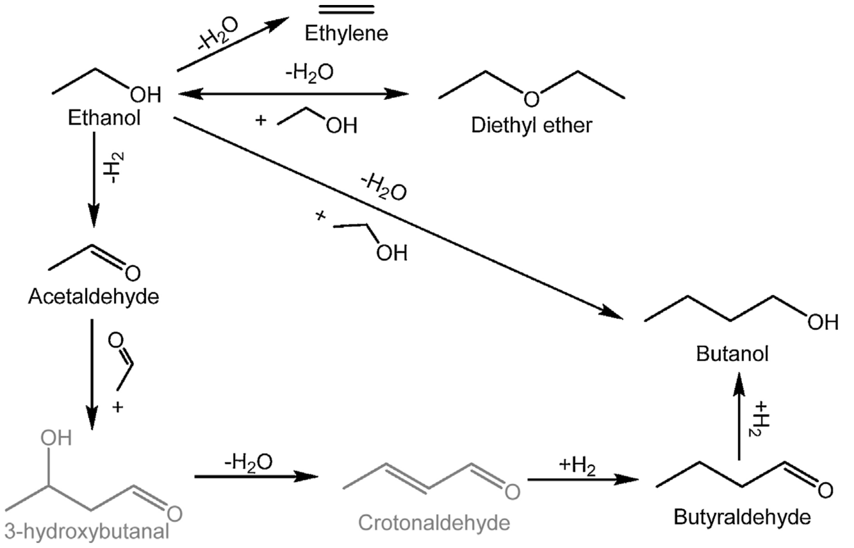


Fig. 4. CO_2 TPD profiles and the amount CO_2 desorbed from the MgO, Al_2O_3, physical mix of MgO-Al_2O_3 with 3 to 1 ratio and HT derived MgO-Al_2O_3 with 3 to 1 ratio.

reaction (MPV), in which the hydrogen from the feed ethanol is directly transferred to the unsaturated aldol product to form butanol and acetaldehyde, is responsible for the final hydrogenation step [5,31,32]. The product distribution also contains significant amounts of higher alcohols and aldehydes generated from the cross-condensation of the product butanol and ethanol to form C_4+ compounds. In addition to the alcohols and the aldehydes, ethers with carbon number between C_4 and C_{10} were identified at minor levels in the liquid product composition.

At 450 °C and higher temperatures, ethanol primarily converted to phenol and alkylated phenols. Ethylene generation is higher in gaseous composition compared to the low temperature experiments. Based on the experimental findings and the literature information, the reaction pathway of the ethanol to generate phenolic compounds at 450 °C and higher temperature is shown in Scheme 2. Based on the product liquid composition, it can be concluded that acetone is an intermediate compound for the phenolic compound formation [33,34]. The formation of acetone from ethanol can occur via several mechanisms. For example, ethanol dehydrogenate to form acetaldehyde followed by the aldolation to form hydroxybutanal, then intermolecular hydride transfer to form hydroxybutanone, which then decomposes to give acetone, carbon monoxide and hydrogen [19,21]. In the gas-phase product composition, no carbon monoxide was detected; only small levels of carbon dioxide was detected. Due to the presence of water and the carbon monoxide together potentially go through water-gas shift reaction to form carbon dioxide but the nature of the HT derived catalyst and temperature regime at which the experiment was conducted does not promote the water-gas shift reaction so



Scheme 1. Proposed reaction mechanism for the conversion of ethanol at low temperature (350 °C) over MgO-Al_2O_3 derived from HT. Compounds shown in grey colour are intermediates that are not identified in the product slate.

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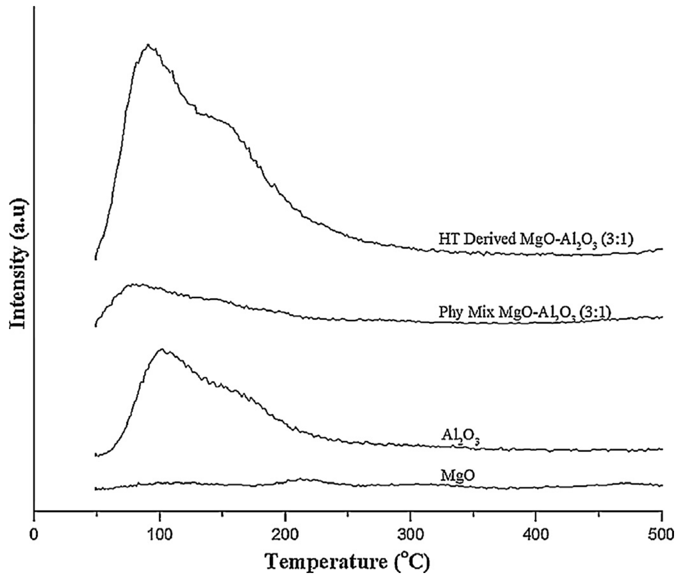
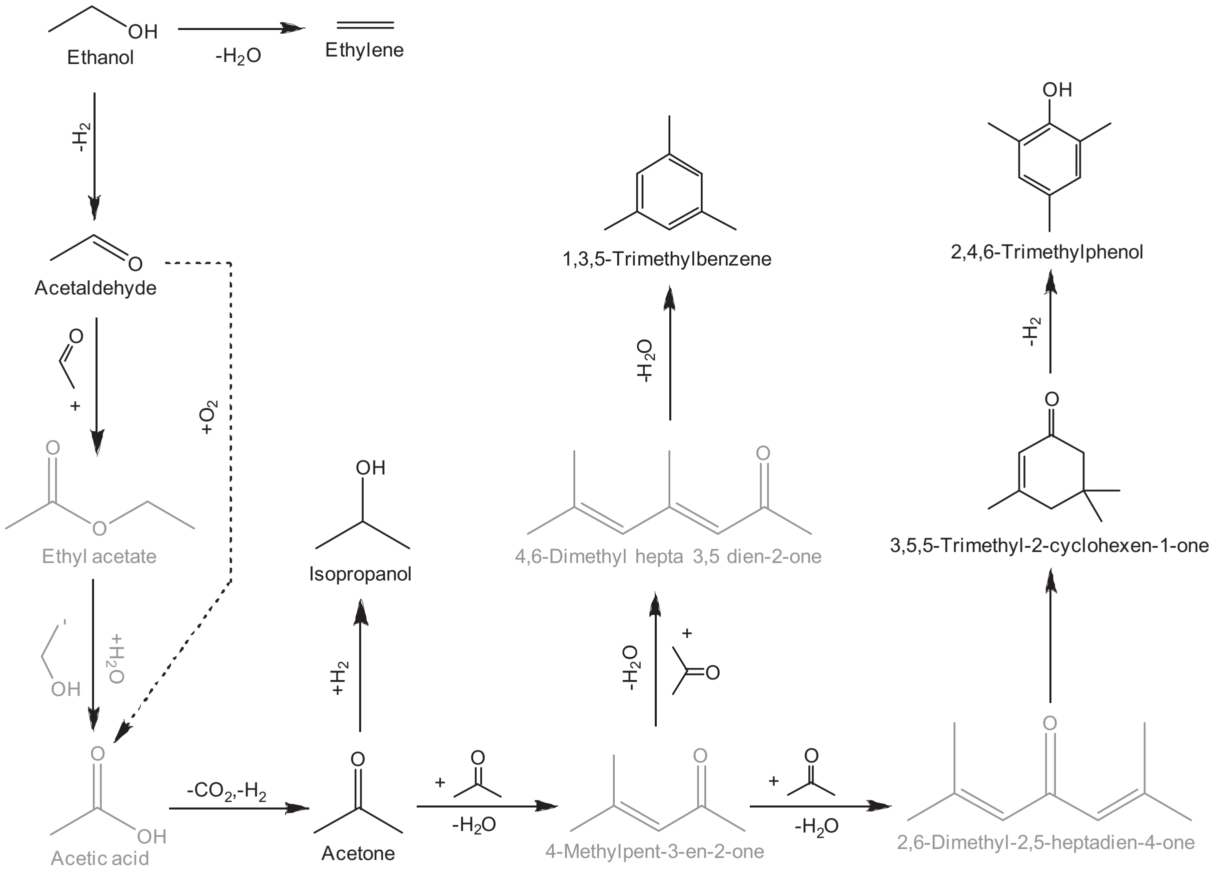


Fig. 5. NH_3 TPD profiles of the MgO, Al_2O_3, physical mix of MgO-Al_2O_3 with 3 to 1 ratio and HT derived MgO-Al_2O_3 with 3 to 1 ratio.

it is difficult to believe this pathway is responsible for the acetone formation.

The other pathways, such as Tishchenko reaction, dimerisation of acetaldehyde to form esters then hydrolysis to form acetic acid and ethanol followed by acetic acid ketonisation to form acetone [35,36], and/or the oxidation of aldehyde to form acetic acid and ketonization to form acetone from acetic acid, can also potentially play a role in generating acetone [37,38]. Very small levels of acetic acid presence in the product stream from the ethanol conversion experiments and the close to 100% conversion levels of acetic acid to ketone compounds when the acetic acid was co-fed with ethanol supports later stated pathway that forms acetic acid as an intermediate is the potential reaction mechanism for the acetone formation. Ethanol conversion and product selectivities to various compounds were the same when acetic acid was co-fed with ethanol. More in situ experiments are necessary to positively confirm exact pathway that leads to the formation of acetone from ethanol. Once the acetone is formed, it goes through sequence of condensation reactions to form mesityl oxide followed by phorones [14]. As per literature information, phorones undergo 1, 6-internal Michael cyclisation to give isophorone. Then the aromatization of isophorone occurs via dienone to form trimethyl phenol and hydrogen. Finally the methyl phenols and phenol are formed by the dealkylation of the dimethyl phenol [39,40].

The combination of the acid-base properties and the active site location of the MgO–Al_2O_3 derived from HT plays a key role in the complex reaction mechanism involved in converting the ethanol to higher alcohol/oxygenate or the phenolic compounds in a one-step process. Modifications of Mg and Al allow changing the acid-base properties of the catalysts and subsequently improving the selectivity and the yield of the target compounds. At higher temperatures, selectivity to ethylene increases due to the increased dehydration activity. Irrespective of the temperature, the butene selectivity did not change. This shows that the dehydration activity is very low for the higher alcohols that are generated from the reaction. In addition, conversion of ethanol to acetaldehyde is



Scheme 2. Proposed reaction mechanism for the conversion of ethanol at high temperature (450 °C) over MgO-Al_2O_3 derived from HT. Compounds shown in grey colour are intermediates that are not identified in the product slate.

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considered to be the rate-determining step in generating the higher oxygenates [32,41]. Based on this phenomenon, ethanol can be dehydrogenated to acetaldehyde over a catalyst such as copper and then exposed to the HT derived catalyst at a desired temperature to improve the overall ethanol conversion and carbon selectivity toward the desired product class.

4. Conclusion

In conclusion, at temperatures around 350 °C ethanol can be converted over bi-functional $MgO–Al_2O_3$ derived from HT catalyst to C_2+ oxygenates containing alcohols and aldehydes, which can easily be mild-hydrogenated (aldehydes to alcohols) to generate a mixture of higher alcohols ($C_4–C_{10}$). These higher alcohols can be used in the gasoline blend stock, as a building block for the hydrocarbon fuels and as a building block for chemical commodities. At temperatures higher than 450 °C, the product composition shifts to a mixture of phenolic compounds. These phenolic compounds can be used in the production of many different commodities. More research toward understanding the chemistry and identifying the catalyst role will play a major role in developing this process to commercial scale.

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