



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

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

Karthikeyan K. Ramasamy^{a,*}, Michel Gray^a, Heather Job^a, Colin Smith^a, Yong Wang^{a,b,*}^a Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA^b The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164-2710, USA

ARTICLE INFO

Article history:

Received 3 August 2015

Received in revised form 9 November 2015

Accepted 18 November 2015

Available online xxx

Keywords:

Ethanol

Butanol

Hydrotalcite

Mixed oxides

Guerbet

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.

© 2016 Published by Elsevier B.V.

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 [$Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$, 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 Mn^+O^{2-} acid-base pair sites [16–18]. This gives the combination

* Corresponding authors at: Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA.

E-mail addresses: karthi@pnnl.gov (K.K. Ramasamy), yong.wang@pnnl.gov (Y. Wang).

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–Al₂O₃ 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–Al₂O₃, magnesium oxide (MgO), aluminium oxide (Al₂O₃) and the physical mixture of MgO and Al₂O₃ with 3–1 ratio were also tested at similar operating conditions and the results were presented here. The MgO and Al₂O₃ 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 (N₂) 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 K α radiation (λ 1.5437 Å). Each sample was scanned in the range between 20° and 80°. Ammonia (NH₃) and carbon dioxide (CO₂) Temperature Programmed Desorption (TPD) analyses were performed on the catalysts tested for the acid and base measurements. For the NH₃–TPD measurement, sample material was saturated with NH₃ at room temperature in a flow of 15.7% NH₃ in helium (He) and for the CO₂–TPD measurement, sample material was saturated with CO₂ at room temperature in a flow of 5% CO₂ in He. After saturation, the weakly bound NH₃/CO₂ 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 Micromeritics 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 C₁₀.

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 ₂ O ₃	350	85	70	<20	0.1	0	0
Al ₂ O ₃	450	99	90	<1	0	0	0
MgO–Al ₂ O ₃ ^a	350	88	41	34	2	0.5	0
MgO–Al ₂ O ₃ ^a	450	98	58	1.7	0	0	0
MgO–Al ₂ O ₃ ^b	350	62	17	4	5	42	<1
MgO–Al ₂ O ₃ ^b	450	98	47	0	0	<1	35

^a MgO–Al₂O₃ physical mix 3–1 ratio.

^b MgO–Al₂O₃ derived from HT with 3–1 ratio.

Over Al₂O₃ 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–Al₂O₃ 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–Al₂O₃ 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–Al₂O₃ 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–Al₂O₃ derived from HT at 350 °C and 450 °C. The compounds identified from the liquid products produced from 350 °C experiments consisted primarily of C₂+ alcohols up to C₈. Small fractions of aldehyde and ether compounds up to C₁₀ 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 C₃+ 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, Al₂O₃ and HT catalysts that are calcined at 500 °C for 4 h. The acquired XRD pattern for the MgO, Al₂O₃ materials resembles the literature information [24]. The HT derived material with 3–1 ratio between MgO and Al₂O₃ shows the predominance of MgO due to its highest presence. Fig. 4 shows the CO₂ TPD profiles and the amount CO₂ desorbed from the MgO, Al₂O₃, physical mixture of MgO–Al₂O₃ with 3–1 ratio and HT derived MgO–Al₂O₃ with 3–1 ratio. All the samples analysed shows more than one kind of basic site. Al₂O₃ 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 Al₂O₃. 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,

Download English Version:

<https://daneshyari.com/en/article/6505095>

Download Persian Version:

<https://daneshyari.com/article/6505095>

[Daneshyari.com](https://daneshyari.com)