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Biogasoline and High Alcohols Production by One Step Ethanol Conversion on Densified MgO Catalyst with Enhanced Concentration of Surface Active Sites

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Ethanol conversion was carried out on two MgO catalysts that differ in concentration of surface basic sites by a factor of 4. The sites density was increased by chemical densification of MgO-aerogel that created high-angle grain boundaries defect areas between its nanocrystals. This process using the novel catalytic material converted ethanol in one step to biofuel containing C_5+ paraffins, olefins, aromatics and oxygenates with about 50% yield. This improved performance was attributed to enhanced trapping of hydrogen entities formed at the surface after dissociative adsorption of alcohols molecules at the defect sites produced by densification.

1. Introduction

The condensation of ethanol to higher alcohols according to Guebert reaction was studied on many solid catalysts. The best performance was recorded on basic catalytic materials MgO (Ndou et.al., 2003) hydrotalcite (Carlini et.al., 2004) and hydroxyapatite (Tsuchida et.al., 2008a; 2008b). Tsuchida et.al. (2008a) demonstrated that hydroxyapatite $Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}{\cdot}nH_2O$ with optimal Ca/P ratio of 1.64 converts ethanol to a C_5+ hydrocarbons mixture containing paraffins, olefins, aromatics and oxygenates with gasoline properties with 62.5 % yield in a one step process at 500°C with 15.8 % EtOH-He mixture at EtOH WHSV of 1 h^{-1}. A mechanism for the synthesis of biogasoline from ethanol was proposed, consisting of the successive propagation of synthesis of Guebert alcohols followed by dehydration/dehydrogenation of generated alcohols. It is well established that Guebert condensation occurs on solid bases surfaces usually containing pairs of base-acid sites and includes aldol condensation of adsorbed aldehyde produced by dehydrogenation of alcohol, with another alcohol followed by hydrogenation of aldol (Tsuchida et.al. 2008b). The hydrogen entities trapped by surface basic-acidic sites in the first step of aldehyde formation (Fig 1) are used at the aldol hydrogenation step yielding a higher alcohol. It was proposed that hydrogenation of the aldol intermediate

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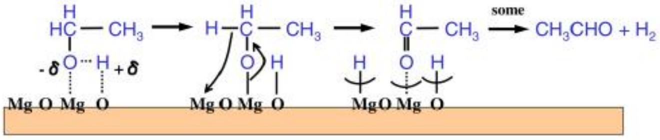


Figure 1: Dehydrogenation mechanism from ethanol on MgO catalyst.

on MgO catalysts surface is a limiting step of the process. The hydrogen entities trapped after acetaldehyde formation on the catalysts surface as hydride by Mg acidic Lewis site and proton at neighbor basic oxygen ion at short distance migrate and release from the surface as H_2 molecules. The hydroxyapatite with higher distance between acid and base sites stabilizes better the hydrogen entities at the catalysts surface enriching it with hydrogen that facilitates the propagation of Guebert alcohols synthesis.

Recently Vidruk et. al. (2009) demonstrated that the surface basicity of MgO can be increased by as much as an order of magnitude by densification of nanocrystalline magnesium oxide increasing the surface interface between the primary nanoparticles. This produced and stabilized additional low coordinated ions on the surface of grain boundaries areas increasing the concentration of low-coordinated basic sites. It was proposed that ions disorder created at the grain boundaries areas of MgO provide ionic pairs at different Mg-O distances including that higher than 0.210 nm characteristic for non-defect periclas structure. This can stabilize the hydrogen entities formed on catalysts surface facilitating the formation of higher alcohols and biogasoline.

2. Experimental

MgO-I was prepared by wetting of MgO (Merck, 8 m^2/g) with distilled water at a ratio of 0.09 (g_{MgO}/g_{water}). The solid was separated by decantation and dried at 120 °C for 16 h. It yielded a material with surface area of 35 m^2/g and bruscite ($Mg(OH)_2$) structure according to XRD. After pretreatment/activation in He at 550-750°C for 2 h, the surface area of the MgO material with periclas structure of 40-153 m^2/g and crystal size 10-25 nm. The MgO-II catalyst was prepared by chemical densification of magnesia aerogel described elsewhere (Vidruk et. al., 2009). The The $Mg(OH)_2$ aerogel was twice impregnated with an excess of solution containing Mg-ethoxide dissolved in toluene - methanol. The final dehydration to get densified MgO was conducted in inert atmosphere (He) immediately before testing at temperatures 550-750 ^oC for 2 h. It yielded a material with surface area of 80-170 m^2/g. and crystal size 7-18 nm. The catalysts were characterized by N_2-adsorption (surface area), XRD (structure, crystal size), surface titration with phenolphthalein indicator (basicity).

Ethanol (Bio lab) gas phase condensation reactions were studied at atmospheric pressure and 350-500 °C. The experiments were carried out in a stainless steel 13 mm ID and 20 cm long vertical fixed bed reactor. The reactor was heated in a tubular furnace controlled by Eurotherm controller with a thermocouple placed at the centre of the catalyst bed. The catalysts (0.7-2.5 g) were used in the form of powder diluted with quartz particles. Liquid ethanol was fed using HPLC pump through a preheater (330 °C). It was diluted with a carrier gas (He flow rate: 12-14 cm^3/min) prior to entering the reactor. The reaction products were liquefied and collected in an ethanol – cooled receiver at (-15)-(-20) °C. The lower alcohol condensation reactions products including water were analyzed by GC. The biofuel product of ethanol condensation reactions was analyzed by Agilent 190915-433 gas chromatograph with a mass spectrometer (GCMS) in the range M/Z= 33-500, equipped with 5973 mass selective detector.

3. Results and discussion

The effect of increasing of surface sites density created at nanocrystals grain boundaries by MgO densification on ethanol condensation was studied by comparison of the performance of two catalysts in Guebert ethanol condensation at 450 ^{o}C and biofuel production at 500^{o}C. The testing results showed that catalytic activity is strongly affected by activation temperature. For both materials the best activity was measured after activation at 650^{o}C. The catalysts characteristics measured after activation at this temperature are listed in Table 1. Densification of MgO –arerogel increased the surface basicity by a factor of 4 and the surface sites density by a factor of 2. This was reflected by a significant increase of higher C_4 and C_6 alcohols selectivity and yield measured at WHSV required for 20 % ethanol conversion (Table 2). This can be a result of higher production of acetaldehyde intermediate and/or stabilizing more hydrogen entities on the surface of densified MgO-II catalyst thus improving the hydrogenation of surface aldol intermediate. Two fixed-bed reactors in series were used to test the effect of preliminary dehydrogenation of EtOH to acetaldehyde with Cu-Cr and Cu-Zn catalysts. Dehydrogenation was efficient at low temperature (250 ºC). Increasing the yield of acetaldehyde over a wide range up to about 60 % and appearance of molecular H_2 in gas phase did not affect much the condensation performance of both MgO catalysts over a wide range of temperatures. This observation is consistent with the mechanism that the limiting step of ethanol condensation reactions with MgO catalyst is the aldol hydrogenation requiring stabilized atomic hydrogen species. This was tested by comparing the thermal dehydroxylation of the two catalysts at activation step using DTG analysis. The surface dehydroxylation occurring at 550-750 ^{o}C requires proton abstraction from surface hydroxyls similar to that occurred by removal of atomic hydrogen species during ethanol condensation on MgO. It was found that densification

Table 1 Properties of MgO catalysts

	Surface area, m^2/g	MgO Crystal size, nm	Pore volume, cm^3/g	Basicity	
				(mmol/g)*10^2	(mmol/m^2)*10^3
MgO-I	65	16	0.4	143	22
MgO-II	130	11	1.2	585	45

Table 2. Performance of MgO catalysts in EtOH condensation to higher alcohols measured at 20% EtOH conversion

Catalyst	Reaction rate [mol EtOH/(gcat*h)] * 10^3	n-Butanol selectivity [%]	n-Hexanol selectivity [%]
MgO-I	36	15	1
MgO-II	110	21	3

shifts the DTG peak maximum to higher temperatures evident for formation of more stable surface hydrogen species.

At higher temperatures, the MgO-I did not display significant dehydration/dehydrogenation activity yielding only oxygenates dissolved in water (one liquid fraction, Figure 3) and gas. The densified MgO-II aerogel at T=500 ºC and WHSV=2.5 h^{-1} yielded light gases and liquid product consisting of two fractions (Figure1) - dense water solution and low-density (0.8 cm^3/g) biogasoline phase. The gas phase (25% yield on carbon basis) consisted of C_1-C_5 paraffins, olefins and oxygenates. The low density organic phase (biofuel) obtained with ~50 % yield contained oxygenates (alcohols, aldehydes, ketones) dissolved in hydrocarbon fraction which

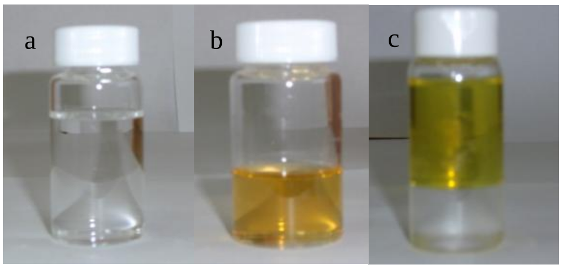


Figure 2: Ethanol(a) adn its condensation products obtained with MgO-I(b) and MgO-II(c).

Table 3 The main biofuel components comprising the chart obtained by GCMS.

Retention time[min]	Component name	Retention time[min]	Component name
1.95	2-Octanol	7.86	Propylbenzene
2.09	2-Hepten	7.95	2-Ethyl-Hexanal
2.17	Cyclohepten	8.17	1-ethyl,3-methyl Benzene
2.32	2-Methyl,1-Butanol	8.64	4-Octanone
2.51	4-Methyl,1,4 Hexadiene	8.79	1-ethyl,2-methyl Benzene
2.61	2-Ethyl-Butanal	9.14	3-Octanone
2.69	Toluene	9.27	1,2,3-trimethyl-Benzene
2.94	3-Hexanone	9.59	2-Ethyl-Hexenal
3.11	3-Hexanol	9.81	5-Decene
3.31	2-Octene	10.26	1,2,4-trimethyl-Benzene
3.58	2-Ethyl,2-Butenal	10.43	Cyclopropyl-Benzene
3.77	1,4 Dimethyl-1-cyclohexene	10.67	2-Methyl,1-Hexanol
4.14	2-Ethyl-Butanol	10.8	Benzyl alcohol
4.56	3-Hexen-1-ol	11.27	1,3 diethyl Benzene
4.69	Ethylbenzene	11.47	Butyl-Benzene
5.01	Formic acid. hexyl ester	11.64	2-methyl- Phenol
5.71	Xylene	12.77	2-Nonanone
5.95	Nonene	14.33	2-ethyl Phenol
6.03	2-Heptanol	15.64	2-ethyl,5-methyl-Phenol
6.96	3-Methyl,4-Heptanone	19.2	Thymol

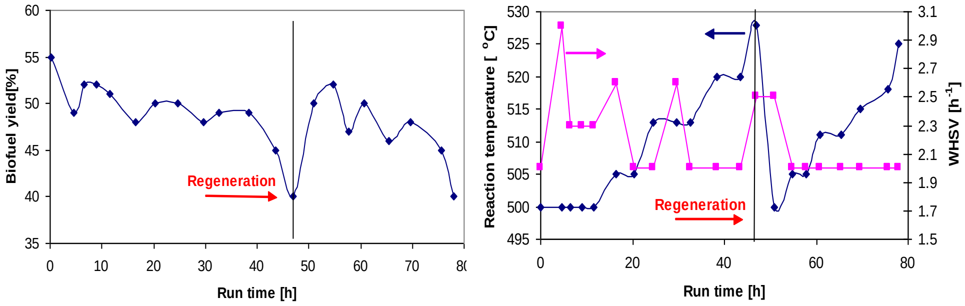
consisted of paraffins, olefins and light aromatics (GC-MS), 7 wt% water (detected by its selective removal with 3A molecular sieve) and 5 % of unreacted ethanol. The high density aqueous phase (25 % yield) – consisted of lower oxygenates (30 wt%) dissolved in water. The ethanol conversion measured at these conditions was 90 %. The GC-MS chart recorded with the low-density biofuel phase comprised a series of peaks at different retention times corresponding to more than 100 diverse compounds. The most abundant C_6-C_{10} paraffins, olefins, aromatic hydrocarbons and oxygenates are listed in Table 3. The density and distillations patterns of obtained biofuel are shown in Table 4. Compared to the biofuel obtained by Tsuchida et.al. (2008a) it displayed lower boiling temperatures at <50 % of distillation and higher boiling points at >50 % distillation. This is evident for different molecular compositions of biofuels produced with MgO and hydroxyapatite catalysts. The density and distillation characteristics of obtained biogasoline are close to the requirements of gasoline standard.

The continuous one-step run of biofuel production from ethanol conducted with MgO-II catalyst at starting temperature of 500 ^{o}C and starting WHSV of 2.5 h^{-1} showed that the catalysts activity slowly but visibly decreased with increasing of run time. It was possible to keep the biofuels yield at the level of 50 % for a period of 50 h (Figure 5a) increasing the temperature and/or decreasing the WHSV as shown in Figure 5b. The reason for deactivation was deposits of heavy hydrocarbons blocking the catalyst pores and access to the active sites at the catalysts surface. The catalyst activity indicated by ethanol conversion and biofuel yield recovered to its initial value after oxidative regeneration. The regeneration was conducted inside the reactor in 10/90 cm^3/min

Table 4 Biofuel property in comparison to gasoline standard.

Fuel characteristic		Biofuel produced over MgO-II	Israel gasoline standard (2007)	Biofuel produced over hydroxyapatite (Tsuchida T., 2008a)
Fuel property	Units			
Density	kg/m^3	830	720-775	-
Initial boiling point	°C	56		71
10 vol%	°C	70		80
20 vol%	°C	75	Max 70	81
30 vol%	°C	78		84
40 vol%	°C	82		87
50 vol%	°C	84	Max 100	91
60 vol%	°C	93		98
70 vol%	°C	116		112
80 vol%	°C	132	Max150	125
90 vol%	°C	167		148
95 vol%	°C	205		171
Final boiling point	°C	244	Max 210	224
Residue	vol%	0.5	Max 2.0	0.5

air/nitrogen flow by increasing the temperature from 350 to 650 °C when the CO_2 evolution diminished reaching finally a negligible value at 650 ^{o}C. The analysis and calculation of the amount of CO_2 evolved during the catalyst regeneration showed that 1.2 g of carbon was deposited per g of MgO (II) catalyst during the first run. This means that for continuous production of biofuel from ethanol with densified MgO catalyst there is a need to depress the coke deposition, i.e. by insertion of transition metals and conducting the process under hydrogen pressure.



(a) (b)

Figure 5. Effect of run time on biofuel production from ethanol with MgO-II catalyst.

4. Conclusion

Densification of nanostructured MgO increases the catalytic activity of the material in Guebert alcohol synthesis from ethanol. It provides successive propagation of this process at 500 ^{o}C followed by dehydration/dehydrogenation of higher condensation products yielding biofuel with gasoline characteristics.

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