The Isomerization of Fermentation Butanol on Alumina-$Li_3Cr_2(PO_4)_3$ Catalyst

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The isomerization of fermentation butanol on alumina-$Li_3Cr_2(PO_4)_3$ catalyst and the influence of treatments of catalyst in argon, hydrogen and oxygen plasmas on its catalytic activity was studied. Plasma chemical treatment was found to be a method for increasing catalyst activity and changing its selectivity by dehydrogenation stop and dehydration activation. The highest activity in the dehydration of butanol was observed after treating the catalyst in hydrogen and oxygen under glow discharge conditions.

Keywords: butanol, isomerization, dehydration, plasma treatment

Alcohol-based fuels have been used as replacements for gasoline in combustion engines and for fuel cells. The four alcohols that are typically used as fuels are : methanol, ethanol, propanol and butanol. Ethanol is the most widely used fuel due to its lower toxicity properties and wide abundance. Alcohols are of oxygenate family. The oxygen of the hydroxyl group contributes to combustion. In theory, alcohol fuels in engines and fuel cells are oxidized to form carbon dioxide and water. In reality, incomplete oxidation is an issue and causes many toxic by-products including carbon monoxide, aldehydes, carboxylates, and even ketones.

The generic reaction for complete alcohol oxidation in either a combustion engines or a fuel cell is :

$$C_x H_{2x+2} O + (3x/2) O_2 \rightarrow x CO_2 + (x+1) H_2O$$

It is important to note this reaction occurs in a single chamber in a combustion engine to convert chemical energy to mechanical energy and heat, while in a fuel cell, this reaction occurs in two separate chambers (an anode chamber where the alcohol is oxidized to carbon dioxide and a cathode chamber where oxygen is reduced to water).

Butanol is a four-carbon alcohol, a clear neutral liquid with a strong characteristic odor. It is miscible with most solvents (alcohols, ether, aldehydes, ketones, aliphatic and aromatic hydrocarbons), is sparingly soluble in water and is a highly refractive compound.

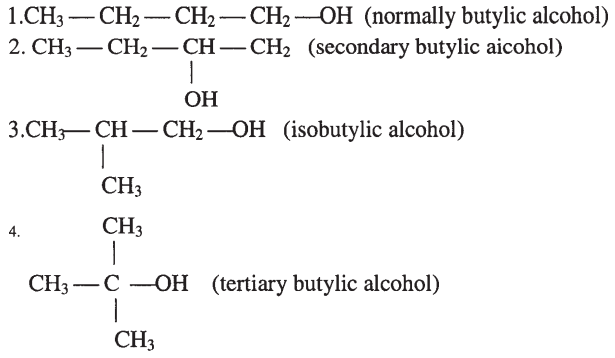
Butanol is one of the biofuels that has the potential to substitute for gasoline and can be produced from domestically abundant biomass sources including corn.

Butanol is a chemical that has excellent fuel characteristics. It contains approximately 22% oxygen, which when used as a fuel extender will results in more complete fuel combustion. Use of butanol as fuel will contribute to clean air by reducing smog-creating compounds, harmful emissions (carbon monoxide) and unburned hydrocarbons in the tail pipe exhaust.

Butanol has research and motor octane numbers of 113 and 94, compared to 111 and 92 for ethanol. The motor octane number of n-butanol is 94. For mixture of isomers of butanol the motor octane number increase to 113.

Butanol is produced chemically by either the oxo process starting from propylene or the aldol process starting from acetaldehyde.Butanol is also produced by fermentation of corn and corn-milling byproducts.

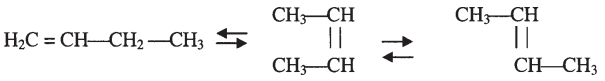
Butanol is presented at four isomers [1] :



Three stages are necessary to obtained of latest three isomers:

- dehydration of normally butilyc alcohol, with butenes obtained
- isomerization of butenes
- hydration of isobutenes

By catalytic dehydration of n-butylic alcohol are obtained a mixture of butenes. The simultaneous formation of the three isomeric butenes is due to the existence of the following equilibrium relationship [2] :



If the catalyst does not award selectivity of process, two parallel reactions occur; alcohol dehydration with the formation of butenes and dehydrogenation with the formation of methyl ethyl ketone. This second process is uncalled for.

The modification of the surface of catalysts and their regeration under the action of a plasma chemical treatments causes the appearance of new surface structures, which increase activity, selectivity, and operation stability [3]. It has been found that Spillover effect specific for metals deposited on acid supports accentuates catalytic activity for hydrogenation [4]. As in the case of hydrogenation process, the dehydration process occurs with synergistic effects which can be explained by the emergence of a "remote control mechanism" acting by migration of spillover oxygen species [5].

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Solid electrolytes of a general formula $Li_3M_2(PO_4)_3$ (M^{3+} = Sc, Cr, Fe, In) is very active in process of isomerization of butenes [6].

Hydration of isobutenes could occur on the tungsten oxide catalyst at 200-300°C and P= 10-35 Mpa. Above 300°C , could be yield polymerization of butenes [5].

The water is added to butenes by Markovnikov mechanism [6].

The purpose of this work was to study the isomerization of fermentation butanol on alumina- $Li_3Cr_2(PO_4)_3$ catalyst and the influence of treatments of catalyst in argon, hydrogen and oxygen plasmas on its catalytic activity.

Experimental part

The $Li_3Cr_2(PO_4)_3$ was prepared by solid-state synthesis and mixed by mechanical method with 70% γ-Al_2O_3. The formation paste was homogenized and dried al 90-100°C in an air oven, broken into pieces, and sieved to give 10-15 mesh granules. The obtained material was shaped in tablets (ϕ = 4mm) and calcined at 450°C for 4 h.The specific surface area of catalyst samples determined by BET method was 163 m^2/g.

The composition of the surface layer of the samples was characterized by X-ray photoelectron spectroscopy.The photoelectron spectra were recorded on a PHi QUANTERA SXM 2010 spectrometer high sensitivity large and micro-area spectroscopy, superior inorganic and organic depth profiling, and the fully automated analysis of insulating or conductive samples.

The acidity of the surface was determined spectrophotometrically from pyridine adsorption.The samples (10 mg) were preliminarily heated in a desicator at 70 °C for 50 min.

A solution of pyridine in octane (5 mL, initial concentration 0.25 µmol/L was then added. Pyridine adsorption was determined after holding adsorption systems for 24 h at 23°C or heating them for 30 min at 70°C. The UV spectra were recorded at room temperature on a JASCO V-570 UV-Vis-NIR spectrophotometer with double beam system with single monochromator 190-2500nm, halogen lamp (330-2500nm),baseline flatness ± 0.002abs (200-2500nmm), detector PbS photocell and detector change-over: selectable anywhere between 750nm and 900nm (grating will be changed at the same wavelength).

Plasma chemical treatment was performed in a glow discharge burning zone in various gas media (argon, hydrogen and oxygen) using a vacuum flow electric discharge unit. Alternating current (50 Hz frequency) was used. The work conditions were those indicated in table 1.

Sample	Gas	P (torr)	I (mA)	U (V)	t (°C)
2	Ar	1.0	180	2000	100
3	H_2	1.0	180	2000	20
4	O_2	1.0	180	2000	220

Catalytic experiments were performed at 100-300°C on a flow reactor.The analysis was carred out with an in line Hewlet Packard Gas Chromatograph (carrier gas helium, flame ionoation detector, volume flow rate 1,3 L/h).

Alumina- $Li_3Cr_2(PO_4)_3$ catalyst in butanol isomerization was studied for four surface states : initial (sample 1) and after plasma chemical treatment in oxygen (sample 2), hydrogen (sample 3), argon (sample 4).

Results and discussions

The surface area of alumina - $Li_3Cr_2(PO_4)_3$ which was 163 m^2/g before plasma treatment and 170, 168 and 165 m^2/g for samples 2,3 and 4 respectively.

In table 2 are presented the results obtained in studying the surface of catalyst samples by XPS.

The Auger parameters, P/Cr and O/Cr surface atomic rations of samples differ insignificantly. The binding energies of chromium, phosphorus and oxygen do not change after plasma chemical treatments.

The results of testing surface acidity in experiments with pyridine adsorption are shown in figure 1 in the form of diagram. Acording to the histograms shown, the numbers of pyridine adsorption centers at 23°C (the number of electron acceptor centers, a_{23}^{o}) were equal for the samples subject to plasma chemical treatment in O_2 and H_2 . After treatment in argon, this number increased approximately twofold. The adsorption of pyridine considerably increased as the temperature grew (the number of electron acceptor centers at 65°C, a_{65}^{o}). The activated character of adsorption can be explained by the diffusion of pyridine molecules into phosphate lattice micropores.

The fraction of activated adsorption:

$$\gamma = \frac{a_{65}^{o} - a_{23}^{o}}{a_{23}^{o}} \times 100\% \quad (1)$$

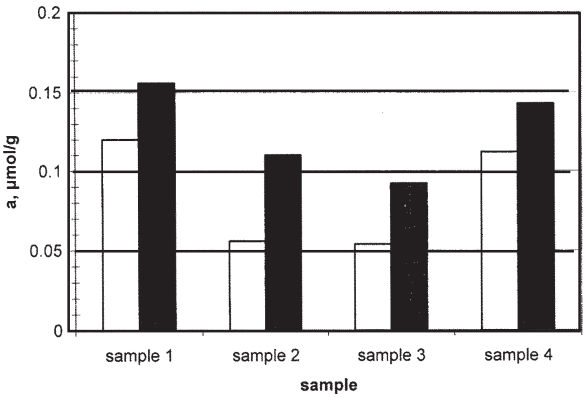

Fig. 1.Influence of plasma chemical treatment on pyridine adsorption of alumina-Li3Cr2(PO4)3 samples at (□) 23 and (■)) 65°C

Table 1
CONDITIONS OF PLASMA CHEMICAL TREATMENT: P IS THE PRESSURE OF THE PLASMA-FORMING GAS, I IS THE FILAMENT CURRENT AND U IS THE VOLTAGE ON ELECTRODES

Sample	Atomic ratio		Auger parameter	Binding energy(ev)		
	P/Cr	O/Cr		P 2p	Cr 2p	O 1s
1	5.81	16.3	2065.8	134.2	728.5	533.3
2	5.96	16.5	2065.6	134.5	728.9	533.7
3	5.94	16.9	2065.5	134.5	728.8	533.5
4	5.97	16.4	2065.5	134.5	728.6	533.5

Table 2
X-RAY PHOTOELECTRON SPECTRUM DATA ON ALUMINA- $Li_3Cr_2(PO_4)_3$

depends on the characteristics of plasma chemical treatment. It decreases in the series of plasma-forming gases : sample 2 (120%) → sample 3 (80%) → sample 4 (27%).

Data on the influence of plasma chemical treatments on the characteristics of the catalytic activity of alumina-$Li_3Cr_2(PO_4)_3$ are presented in table 3. We constructed Arrhenius dependences lnW- 1/T and determined experimental activation energies over the temperature range where conversion did not exceed 50% (table 3).

Two parallel reactions occur on samples: 1 and 4, over the temperature range studied ; alcohol dehydration with the formation of butenes (fig.2) and dehydrogenation with the formation of methyl ethyl ketone (fig.3).

Table 3

CHARACTERISTIC OF THE CATALYTIC ACTIVITY OF SAMPLES (W_1 AND W_2 ARE THE PERCENTAGES OF ALCOHOL CONVERSION INTO BUTENES AND METHYL ETHYL KETONE, RESPECTIVELY ; S IS THE SELECTIVITY OF DEHYDRATIOM(%); E_1 AND E_2 ARE THE ACTIVATION ENERGIES OF BUTANOL DEHYDRATION AND DEHYDROGENATION, RESPECTIVELY , kJ/mol)

Characteristic	Sample 1	Sample 2	Sample 3	Sample 4
W_1 (300°C) %	20	35	43	12
W_2 (300°C) %	9	0	0	10
S (300°C) %	60	100	100	55
W_1 (350°C) %	41	68	80	33
W_2 (350°C) %	14	0	0	18
S (350°C) %	67	100	100	58
W_1 (400°C) %	59	87	91	56
W_2 (400°C) %	24	0	0	27
S (400°C) %	73	100	100	71
E_1 (kJ/mol)	85	70	65	86
E_2 (kJ/mol)	51	—	—	53

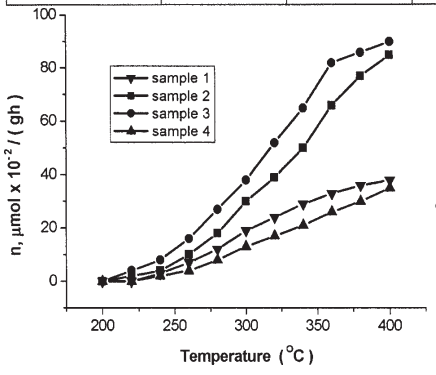

Fig.2. Temperature dependence of the yields of butenes on alumina-$Li_3Cr_2(PO_4)_3$: (1) before and (2-4) after plasma chemical treatment in (2) oxygen, (3) hydrogen and (4) argon

The surface of the catalyst had the lowest activity after argon plasma treatment (sample 4). At low temperatures, the percentages of alcohol conversion in dehydration with butenes formation and dehydrogenation with methyl ethyl ketone formation were almost equal and at 400°C , the yild of butenes (W_1) was twofold than that of methyl ethyl ketone (W_2). The activation energies of butenes and ketone formation were 86 and 53 kJ/mol, respectively. A decrease in the catalytic activity of the surface of the catalyst after plasma chemical treatment in Ar compared with the initial catalyst state correlates with decrease in the fraction of

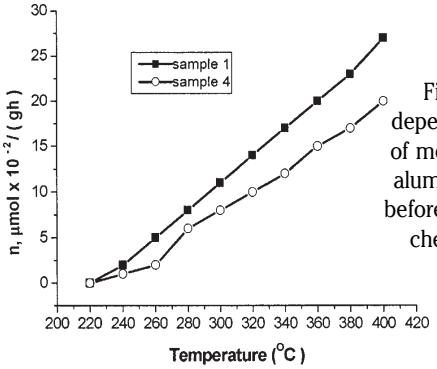

Fig. 3.Temperature dependence of the yields of methyl ethyl ketone on alumina - $Li_3Cr_2(PO_4)_3$: (1) before and (4) after plasma chemical treatment in argon

activated pyridine adsorption, that is, a decrease in the number of difficulty accessible acid centers.

After plasma chemical treatment in oxygen of catalyst (sample 2), reaction products contained butenes only. Dehydrogenation centres were absent and methyl ethyl ketone does not form. The temperature dependence of the yild of butenes is shown in figure 2. The activation energy was E_1 = 70 kJ/mol (table 3) , which was lower than the activation energy on the initial sample (E_1 = 85 kJ/mol).This sample exhibited 100% selectivity with respect to butenes form.

After plasma chemical treatment in hydrogen of catalyst (sample 3), dehydration only also occurs. This sample gave the largest alcohol conversion and highest yield of butenes (table 3 , fig.2.). The yield of butenes was close to 90% at 400°C. Dehydrogenation centres were absent and methyl ethyl ketone does not form. The activation energy of dehydration decrease at 65 kJ/mol, this sample also exhibited 100% selectivity with respect to butenes form.

By hydration of reaction mixed products (after isomerization on the sample 2 and 3) on tungsten catalyst at 250°C, 10-15 percentes of n-butanol were detected.

Conclusions

The results obtained show that glow-discharge hydrogen and oxygen plasma treatment likely changes the nature of catalytic centers of butene formation and decreases the number of such centers.

Surface state of catalyst after plasma chemical treatment in Ar is unstable and number of dehydrogenation centers not differ of their initial state.

Changes in reaction activation energies for the samples treated in a glow-discharge plasma in hydrogen and oxygen are evidence of changes in the state of the surface of the catalyst.

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