Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Mendeleev Commun., 2012, **22**, 150–151
Mendeleev Communications

Catalytic activity of thermally treated $Li_3Fe_2(PO_4)_3$ in the conversion of butan-1-ol

Anna I. Pylinina* and Irina I. Mikhalenko

Peoples' Friendship University of Russia, 117198 Moscow, Russian Federation.
Fax: +7 495 952 0745; e-mail: pylinina@list.ru; imikhalenko@mail.ru

DOI: 10.1016/j.mencom.2012.05.013

The effect of the thermal treatment of the LISICON catalyst in hydrogen and atmospheric oxygen on the activity and selectivity in butan-1-ol conversion was studied.

Solid-state ion conducting materials, also known as superionic or fast ion conductors, have been intensively developed. These materials can be used in solid-state electrochemical devices such as sensors,[1,2] membranes,[3] and catalysts.[4–6]

Solid electrolytes with the general formula $Li_3M_2(PO_4)_3$ (M = Sc, Cr, Fe or In), which are referred to as LISICONs, were discovered in 1983.[7,8] The conductivity of these materials caused by the transfer of lithium ions reaches $\sim10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 300 °C. Lithium phosphates can be prepared by solid state and hydrothermal syntheses, crystallization from melts and sol-gel method.

Changes in the activity and selectivity of butanol decomposition on lithium–iron phosphates (LISICON and NASICON) and the surface acidity after plasma-chemical treatment in glow discharges of oxygen, hydrogen and argon were reported.[9,10] The plasma treatment increased the catalytic activity and selectivity, and the highest activity in the dehydration of butanol was observed with H_2 as a plasma-forming gas.

The aim of this work was to study the effects of thermal treatment in hydrogen and atmospheric oxygen on the activity and selectivity of the LISICON catalyst in butan-1-ol conversion.

The $Li_3Fe_2(PO_4)_3$ catalyst was prepared by a solid state synthesis.[11] The product was white powder with a BET specific surface area of 12 $m^2\ g^{-1}$, as determined by nitrogen desorption on a Gazochrom-1 gas analyzer. The specific surface areas of the catalyst thermally treated in oxygen and hydrogen at 400 °C and a flow rate 1.5 $dm^3\ h^{-1}$ for 40 min were 14 and 13 $m^2\ g^{-1}$, respectively.

The surface layer composition of $Li_3Fe_2(PO_4)_3$ was characterized by X-ray photoelectron spectroscopy (XPS) (Table 1). An XSAM-800 spectrometer with $AlK\alpha_{1,2}$ radiation (1486.6 eV) was used. The C 1*s* line (*E* = 285 eV) was used as an internal reference.

The conversion of butan-1-ol was performed in a U-shaped continuous-flow microreactor at atmospheric pressure and 200–400 °C with the use of 30 mg of the catalyst. Butan-1-ol diluted with He was fed to the reactor at a partial pressure of 760 Pa; the total flow rate was 1.1 $dm^{-3}\ h^{-1}$. The reaction mixture was analyzed on an LKhM chromatograph equipped with a 3 m stainless-steel column containing Porapak Q and a flame-ionization detector at 150 °C using helium as a carrier gas.

The XPS data (Table 1) show that the surface layer of LISICON does not correspond to the stoichiometric composition. The P/Fe and O/Fe atomic ratios are higher by a factor of 2, which is indicative of an excess phosphate concentration on the surface of $Li_3Fe_2(PO_4)_3$. The value of E_b (Fe 2*p*) = 713±0.2 eV corresponds to the Fe^{3+} form.

Table 1 XPS data for $Li_3Fe_2(PO_4)_3$.

$Li_3Fe_2(PO_4)_3$	Atomic ratio		Binding energy/eV		
	P/Fe	O/Fe	P 2*p*	Fe 2*p*	O 1*s*
According to stoichiometry	1.5	6			
Real surface	3.3	11.1	133.9	712.8	531.7

Alcohol dehydration with the formation of butene and dehydrogenation with the formation of an aldehyde simultaneously occurred over the test temperature range. The aldehyde yield was many times higher than that of butene regardless of temperature in the range of 250–370 °C. This behaviour is difficult to explain. The chemisorbed species OH_S and H_2O_S deactivate the active surface. With increasing temperature, the surface coverage of dehydrogenating inhomogeneous sites with butanol decreases, but the heat of alcohol adsorption Q_A increases so that the apparent activation energy E_a becomes formally equal to zero according to the $E_a = E_a^0 - \alpha Q_A$ Brönsted–Polanyi–Semenov relationship with heat effect fraction α.

Note that LISICON catalyst pretreatments had no significant influence on dehydrogenating activity.

The dehydration reaction on $Li_3Fe_2(PO_4)_3$ began at 250 °C, and the yield of butane was 12% at 370 °C [Figure 1(*a*), curve *1*] at a maximum total alcohol conversion of about 70%.

The activity of a working catalyst in dehydration differed from that on a fresh surface: a maximum yield of butene was 4% and the activation energy increased by a factor of 1.8 (Table 2). Thus, the initial state of dehydration centres is unstable.

The catalytic behaviour of the Li–Fe phosphate (LISICON) can be compared with that of Na–Zr phosphates (NASICON

Table 2 Product yields ($N/10^8$ mol h^{-1} m^{-2}), selectivity at (*1*) 300 and (*2*) 360 °C, activation energies E_a and logarithm of prefactors $\ln N_0$ in butanol dehydration reaction over $Li_3Fe_2(PO_4)_3$ catalyst: sample 1 – without treatment, samples 2, 3 – treatment in O_2 and H_2, respectively.

Sample	N^{Butene}		$N^{Butanal}$		S^{Butene} (%)		E_a^{but}/ kJ mol^{-1}	$\ln N_0^{but}$	α^{but}
	1	*2*	*1*	*2*	*1*	*2*			
Initial activity									
1	3.5	9.5	65	65	5	13	70	–2.8	
2	6.2	12	65	70	8	15	42	–8	5.5×10^{-3}
3	2	8.2	60	60	3	10	74	–2.2	1.8
Repeated experiments									
1	0	3	73	73	0	4	121	+6.2	
2	6	11	65	65	8.5	13	51	–6	5.0×10^{-6}
3	3	8	60	60	4.8	12	69	–3.3	7.5×10^{-5}

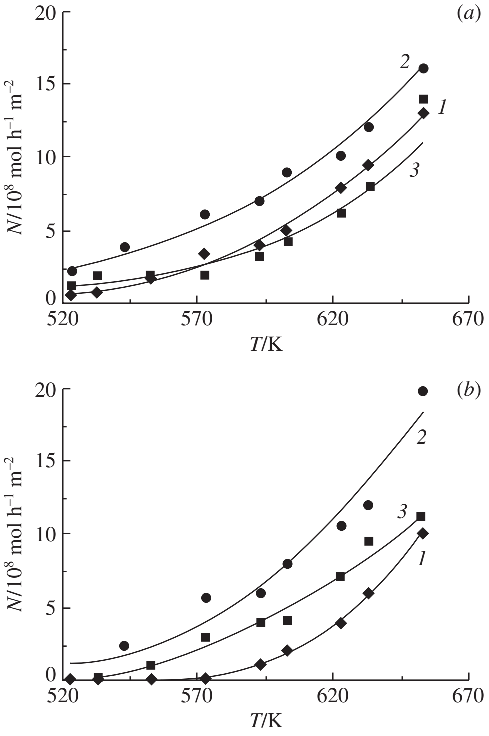

Figure 1 Temperature dependences of butene yield on LISICON catalyst (*1*) before and after thermal treatments in (*2*) O_2 and (*3*) H_2: (*a*) initial surface, (*b*) repeated experiments.

catalysts), which were previously tested in the same reaction.[5] The dehydration activity of $NaZr_2(PO_4)_3$ is superior to that of $Li_3Fe_2(PO_4)_3$ but no dehydrogenation activity was observed under these experimental conditions. This feature probably results from differences between the LISICON and NASICON acid–base properties.[5,9] The dehydrogenation activity can be attributed to the reduction ability of the Fe (rather than Zr) ions located in the channels of the Li(Na)SICON structure. The extent of this reduction obviously depends on the nature of ion and on the structural features of these phosphates.

After thermal treatment in atmospheric oxygen, we obtained the highest alcohol conversion and the highest butene yield. The total butanol conversion was close to 90% at 370 °C. At $T < 350$ °C, the yield of butene on sample 2 was twice as high as that on sample 1 (Figure 1). The activation energy of olefin formation was $E_a^{but} = 42$ kJ mol^{-1}, which was lower by a factor of 1.7 than that in case of sample 1. Note that the catalyst activity after O_2 pretreatment was reproducible in repeated experiments.

After thermal treatment in hydrogen, the surface of this catalyst had the lowest activity: the total butanol conversion was 75% at 370 °C. The activation energy of butene formation over samples 1 and 3 was the same for 'fresh' surfaces (70 and 74 kJ mol^{-1}, respectively), so the state of the dehydrating catalytic sites remains unchanged after H_2 pretreatment. Note that this state was more stable because of the same LISICON activity after catalytic experiments, as well as in the case of O_2 treatment.

We analyzed the effect of treatment on the total number of dehydrating surface centres *N* using the ratio $\alpha = N_{2\,\mathrm{or}\,3}/N_1$ (Table 2). On a 'fresh' LISICON surface, the number of dehydration centres increased by a factor of ~2 only after H_2 treatment and drastically decreased after O_2 treatment (by a factor of 180 – 1/5.5×10^{-3}). Note that for 'working' surface we obtained the diminishing of N_0 for both treatments, so the activating effect is related to a decrease in E_a.

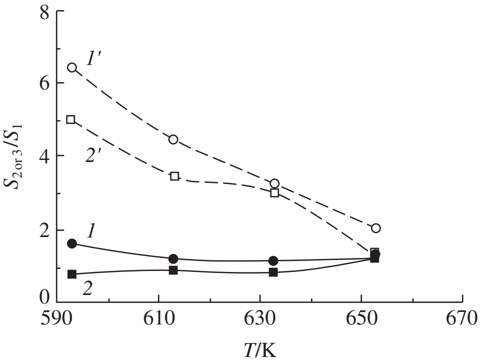

Figure 2 Effect of temperature on the selectivity ratio of butene formation after treatments in O_2 (*1*, *1'*) and H_2 (*2*, *2'*) to ones before treatment (*1'*, *2'* – repeated experiments).

The selectivity ratio $S^{but}_{2\,\mathrm{or}\,3}/S^{but}_1$ for initial activity remained unchanged with temperature and close to 1 (Figure 2). However, in repeated experiments, the ratio increased by a factor of 5–7 with decreasing temperature.

Thus, we found that thermal treatment exerted a smaller effect on complex phosphate catalysts than plasma chemical activation,[9,10] but this procedure prevents the deactivation of LISICON catalysts. Thermal treatment in O_2 increased the yield of butene and caused the formation of active catalytic centres with a lower binding energy between butanol and lithium–iron phosphate.

References

1 N. Yamazoe and N. Miura, *Sens. Actuators B*, 1994, **20**, 95.
2 D.-D. Lee and D.-S. Lee, *IEEE Sens. J.*, 2001, **1**, 214.
3 G. F. Tereshchenko, N. V. Orekhova, M. M. Ermilova, A. A. Malygin and A. I. Orlova, *Catal. Today*, 2006, **118**, 85.
4 S. N. Ienealem, S. G. Gul'yanova, T. K. Chekhlova, M. M. Ermilova, A. I. Orlova, V. I. Pet'kov and A. G. Timakin, *Zh. Fiz. Khim.*, 2000, **74**, 2273 (*Russ. J. Phys. Chem. A*, 2000, **74**, 2082).
5 A. I. Pylinina, E. P. Dobrova, I. I. Mikhalenko and T. V. Yagodovskaya, *Zh. Fiz. Khim.*, 2005, **79**, 650 (*Russ. J. Phys. Chem. A*, 2005, **79**, 552).
6 A. I. Pylinina, I. I. Mikhalenko, M. M. Ermilova, N. V. Orekhova and V. I. Pet'kov, *Zh. Fiz. Khim.*, 2010, **84**, 465 (*Russ. J. Phys. Chem. A*, 2010, **84**, 400).
7 E. A. Genkina, L. N. Dem'yanets and A. K. Ivanov-Shits, *Pis'ma Zh. Eksp. Teor. Fiz.*, 1983, **38**, 257 (*JETP Lett.*, 1983, **38**, 305).
8 F. D'Yvoire, M. Paintard-Screpel, E. Bretey and M.De la Rochere, *Solid State Ionics*, 1983, **9–10**, 851.
9 A. I. Pylinina, I. I. Mikhalenko, A. K. Ivanov-Shits, T. V. Yagodovskaya and V. V. Lunin, *Zh. Fiz. Khim.*, 2006, **80**, 1011 (*Russ. J. Phys. Chem. A*, 2006, **80**, 882).
10 A. I. Pylinina, I. I. Mikhalenko, T. V. Yagodovskaya and V. D. Yagodovskii, *Zh. Fiz. Khim.*, 2010, **84**, 2372 (*Russ. J. Phys. Chem. A*, 2010, **84**, 2172).
11 A. K. Ivanov-Shits and I. V. Murin, *Ionika tverdogo tela* (*Solid State Ionics*), St. Petersburg University, St. Petersburg, 2000, vol. 1 (in Russian).

Received: 23rd November 2011; Com. 11/3838