

Ethanol Total Oxidation Over Calcined Layered Double Hydroxides Modified with Organic Components

KUI – 9/2013
Received August 14, 2012
Accepted November 13, 2012

J. Ludvíková,^a K. Jirátová,^{a*} J. Klempa,^a H. Raabová,^b
Z. Zapivovarski Votipka,^b and F. Kovanda^b

^a Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, v.v.i., Rozvojová 135, 165 02 Prague 6 – Suchbát, Czech Republic

^b Department of Solid State Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague, Czech Republic

Coprecipitation of Co, Mn, and Al nitrates by a solution of Na₂CO₃ and NaOH in the presence of Pluronic® P123 has led to layered double hydroxide (LDH) precursors with hydrocalcite-like structure. Their calcination gave spinel-type mixed oxides; the presence of organic template increased both BET and mesopore surface areas of the calcined products. TPR profiles of the samples modified with Pluronic® P123 exhibited a shift of reduction maxima to lower temperatures, similarly as increasing sodium content in the catalysts. However, though the physical-chemical properties of Co-Mn-Al mixed oxides and their catalytic activity in ethanol oxidation were slightly improved, the changes evolved by the presence of Pluronic® P123 during precipitation of LDH precursors were rather small.

Key words: Layered double hydroxides, Pluronic® P123, mixed oxides, volatile organic compounds oxidation

Introduction

Interests in the surfactant templated synthesis of mesoporous silica and other metal oxides with narrow pore size distribution have been greatly intensified ever since the discovery of MCM-41 family of periodic mesoporous materials in 1992.¹ Mesoporous materials like MCM-41 or SBA-15 synthesized in the presence of organic components¹ possess high surface area and large pore sizes, which permit the anchoring of metals with tiny particle size and, therefore, performing catalytic reactions that were recently either not possible or possible but with substantially higher concentration of catalytically active components. The MCM-41 or SBA-15 mesoporous catalysts containing Co were tested in the total oxidation of toluene and showed reasonable catalytic activity.²

A simple procedure for the synthesis of ordered large-pore (up to 14 nm) mesoporous metal oxides, including TiO₂, ZrO₂, Nb₂O₅, Ta₂O₅, Al₂O₃, SnO₂, WO₃, HfO₂, and mixed oxides SiAlO_y, Al₂TiO_y, ZrTiO_y, SiTiO_y, and ZrW₂O_y was developed.^{3,4} Amphiphilic poly(alkylene oxide) block copolymers were used as structure-directing agents in non-aqueous solutions for organizing network-forming metal species. Inorganic salts instead of alkoxides or organic metal complexes were used as precursors. The formed thermally stable mesoporous oxides had robust inorganic frameworks and thick channel walls, within which a high

density of nanocrystallites could be nucleated and grown. These novel mesoporous metal oxides are likely formed through a mechanism that combines block copolymer self-assembly with alkylene oxide complexation of the inorganic metal species.

In the present work, we have tried to find out whether the organic template (polyethyleneglycole-type tribloc copolymer Pluronic® P123) added during coprecipitation of the Co-Mn-Al layered double hydroxide (LDH) precursors has an effect on the porous structure and catalytic properties of the resulting LDH-related mixed oxides. The effect of sodium present in various amounts in the Co-Mn-Al mixed oxide catalysts on the catalyst properties was examined as well, as its changeable amount in the mixed oxides could mask the effect of Pluronic® P123. The synthesized materials were characterized by various techniques and the found physical-chemical properties were correlated with the activity in total oxidation of ethanol and discussed in detail.

Experimental

Catalysts preparation

The Co-Mn-Al LDH precursors containing various amounts of sodium cations were prepared by coprecipitation.^{5,6} According to the number of washing steps, the catalysts contained various amounts of sodium. Six samples of the mixed oxide catalysts with different Na content were pre-

* Corresponding author: Ing. Květa Jirátová, CSc.
e-mail: jiratova@icpf.cas.cz

pared; they were labelled as Co4MnAl with content of Na given in wt. %, e.g., Co4MnAl/Na-0.17.

The Co-Mn-Al LDH precursors modified with Pluronic® P123 were synthesized in the presence of the organic template dissolved in the aqueous solution of nitrates; the coprecipitation reaction or homogeneous precipitation in the presence of hydrolysing urea was applied. Five samples of the mixed oxide catalysts prepared from the LDH precursors modified with Pluronic® P123 were obtained:

I) The LDH precursor was prepared by coprecipitation. An aqueous solution (300 ml) of Co, Mn, and Al nitrates with Co:Mn:Al molar ratio of 4:1:1 and total metal ion concentration 0.6 mol l^{-1} , in which was dissolved 6.0 g of Pluronic® P123, was added with flow rate of 5.0 ml min^{-1} into 1000 ml batch reactor containing 200 ml of distilled water. The coprecipitation reaction was carried out under vigorous stirring at $30 \text{ }^\circ\text{C}$ and $\text{pH} = 10.0 \pm 0.1$ (the alkaline solution of $0.5 \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$ and $3 \text{ mol l}^{-1} \text{ NaOH}$ was simultaneously added). After 2 h aging at $30 \text{ }^\circ\text{C}$ under stirring, the suspension was divided into two parts. The first one was filtered and the product was thoroughly washed with distilled water and dried at $60 \text{ }^\circ\text{C}$. Mixed oxide obtained after calcination at $500 \text{ }^\circ\text{C}$ was denoted as PI-I/ Na_2CO_3 /30°C-w. The other part of the suspension was placed into Teflon-lined stainless steel autoclave and aged under hydrothermal conditions at $120 \text{ }^\circ\text{C}$ for 12 h. The product was then filtered off, washed thoroughly with distilled water and dried at $60 \text{ }^\circ\text{C}$. The calcined sample was denoted as PI-I/ Na_2CO_3 /120°C-w.

II) The LDH precursor was prepared by homogeneous precipitation in the presence of hydrolysing urea. An aqueous solution (700 ml) with Co:Mn:Al molar ratio of 4:1:1, total metal ion concentration 0.6 mol l^{-1} and urea concentration 1.8 mol l^{-1} was prepared by dissolution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (81.49 g), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (17.57 g), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (26.26 g), urea (75.67 g), and Pluronic® P123 (14.0 g) in distilled water. The solution was placed into 1000 ml batch reactor and stirred vigorously at $80 \text{ }^\circ\text{C}$ for 40 h. The obtained product was filtered off and the filtration cake was only slightly washed with a small amount of distilled water. A part of the filtration cake was then dried at $60 \text{ }^\circ\text{C}$ and calcined at $500 \text{ }^\circ\text{C}$; the obtained sample was denoted as PI-II/urea/80°C-nw. The remaining product was thoroughly washed; the calcined sample was denoted as PI-II/urea/80°C-w.

III) The LDH precursor was prepared by homogeneous precipitation in the presence of hydrolysing urea in the same way as described above but the reaction was carried out under hydrothermal conditions at $145 \text{ }^\circ\text{C}$ for 22 h. An aqueous solution (800 ml) with Co:Mn:Al molar ratio of 4:1:1, total metal ion concentration of 0.24 mol l^{-1} and urea concentration 1.2 mol l^{-1} contained 16.0 g of Pluronic® P123; hydrogen peroxide in excess of 100 % related to Mn content was added to the solution to boost the oxidation of Mn^{2+} cations. The obtained product was thoroughly washed with distilled water and dried at $60 \text{ }^\circ\text{C}$. The mixed oxide obtained after calcination was denoted as PI-III/urea/145°C-w.

Characterization of the samples

The elemental analysis of the prepared products was performed by atomic absorption spectroscopy (AAS). A sample

(0.2 g) was dissolved in 1.5 ml of hot hydrochloric acid (35 wt. %) and the obtained solution was diluted with distilled water to 25 ml. The concentrations of Co, Mn, Al, and Na were determined using a Spectr AA880 instrument (Varian).

Powder X-ray diffraction patterns were recorded using a Seifert XRD 3000P instrument with Co K radiation ($\lambda = 0.179 \text{ nm}$, graphite monochromator, goniometer with Bragg–Brentano geometry) in 2θ range $10 - 80^\circ$, step size 0.05° . Qualitative analysis was performed with the High-Score package (PANalytical, The Netherlands, version 1.0d).

Surface area and mesoporous structure of the catalysts was determined by physisorption of nitrogen using Micromeritics ASAP 2020 instrument after catalysts drying at $105 \text{ }^\circ\text{C}$ for 24 h under vacuum of 1 Pa. The adsorption-desorption isotherms of nitrogen at $-196 \text{ }^\circ\text{C}$ were treated by the standard Brunauer–Emmett–Teller (BET) procedure to calculate the specific surface area s_{BET} . The specific surface area of mesopores s_{meso} and the specific volume of micropores v_{micro} were determined by t-plot method. Pore-size distribution (pore radius $1 - 100 \text{ nm}$) was calculated from the desorption branch of the adsorption-desorption isotherm by the advanced Barrett–Joyner–Halenda (BJH) method. The Lecloux–Pirard standard isotherm^{7,8} was employed for the t-plot as well as the pore-size distribution evaluation.

Temperature-programmed reduction (TPR) measurements of the calcined samples (0.025 g) were performed with a H_2/N_2 mixture (10 mol % H_2), flow rate 50 ml min^{-1} and linear temperature increase $25 \text{ }^\circ\text{C min}^{-1}$ up to $1000 \text{ }^\circ\text{C}$. Changes in H_2 concentration were detected with a mass spectrometer Omnistar 300 (Pfeiffer Vakuum). Reduction of the grained CuO (particle size $0.16 - 0.315 \text{ mm}$) was performed to calculate absolute values of the hydrogen consumed during reduction.

Temperature-programmed desorption (TPD) of NH_3 was carried out to examine acid properties of the catalysts surface, respectively. The measurements were accomplished with 0.050 g of a sample in the temperature range $25 - 1000 \text{ }^\circ\text{C}$, with helium as a carrier gas and NH_3 as adsorbing gases. Prior to the measurements, the samples were heated in the flow of helium at $500 \text{ }^\circ\text{C}$. After cooling the samples in helium to $30 \text{ }^\circ\text{C}$, the heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ was applied. During the experiments the following mass contributions m/z were collected: 16- NH_3 . The spectrometer was calibrated by dosing an amount (840 μl) of NH_3 into the carrier gas (He) in every experiment. The TPR and TPD experiments were evaluated using OriginPro 7.5 software with an accuracy of $\pm 5 \%$.

Catalyst activity and selectivity measurements

The catalytic reaction was carried out in a fixed-bed glass reactor (5 mm inside diameter) in the temperature range from 100 to $400 \text{ }^\circ\text{C}$. The temperature of the furnace was linearly increased by the rate of $3.5 \text{ }^\circ\text{C min}^{-1}$. The catalyst (0.10 g of the sieved grains with the particle size of $0.16 - 0.315 \text{ mm}$) was examined at $80 \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1}$ space velocity (GHSV). The inlet concentration of ethanol in the air was 1 g m^{-3} (ethanol was chosen as a model compound). Reaction products were analysed using a gas chromatograph Hewlett-Packard 6890 equipped with a FID detector and a capillary column (HP-5 19091 J-413, $30 \text{ m} \times 0.32 \text{ mm}$

× 0.25 μm with 5 % phenyl methyl siloxane). The accuracy of the conversion and selectivity determination was ± 2 %. Temperatures t_{50} and t_{90} (the temperatures at which 50 and 90 % conversion of the examined VOC were observed) were chosen as a measure of the catalyst activity. To analyse the activity of the catalysts more precisely, the values of specific activities a were calculated from the equation

$$a = \frac{p q_v x \alpha}{m [w(\text{Co} + \text{Mn})] R T}$$

where p means atmospheric pressure, q_v total flow rate, x initial molar fraction of ethanol in the reaction mixture, α degree of ethanol conversion at temperatures 200 – 400 °C, m catalyst mass, w mass fraction in the calcined catalyst, R molar gas constant, and T temperature. Selectivity in ethanol conversion was evaluated as the maxima GC peak area of byproducts observed during oxidation of ethanol.

Results and discussion

Precipitates arising by reaction of nitrates with a base containing Na ions always contain various amounts of Na coming from the precipitating agent. In dependence on the precipitates washing intensity, the concentration of Na can vary in a wide range. Changeable amount of sodium in the mixed oxides could cover the effect of Pluronic® P123 added to the initial solutions of nitrates, and for that reason, we first examined the effect of sodium on the properties of Co-Mn-Al oxides and then the effect of Pluronic.

Properties of the Co-Mn-Al LDH precursors and related mixed oxides with various Na content

The Co-Mn-Al LDH precursors with different extent of washing were prepared. Sodium content in the calcined samples varied from 0.17 to 3.7 wt. % (Table 1). The contents of Co, Mn and Al fluctuated around 58, 10 and 5.5 wt. %, respectively. The Co:Mn:Al molar ratio in the pre-

pared samples corresponded approximately to the value adjusted in the nitrate solution used for the synthesis of precursors but the analysis of solid samples showed slightly lower contents of Mn and Al compared to expected Co:Mn:Al molar ratio of 4:1:1 (Table 1).

Well-crystallized hydrotalcite-like phase was found in the powder XRD patterns of the coprecipitated LDH precursors. In some samples, trace amounts of MnCO_3 (rhodochrosite) admixture were detected. Diffraction lines corresponding to sodium nitrate were found in the powder XRD patterns of the precursors, in which higher concentrations of sodium were determined (not shown here). Spinel-type mixed oxides were formed after calcination of the LDH precursors at 500 °C; no other phase was found in the calcined samples even when they contained higher amounts of sodium (more than 3 wt. % Na).

Increasing amount of Na in the samples affected porous structure of the calcined products (Table 2). BET surface area and also surface area of mesopores of the Co4MnAl/Na-3.59 sample containing 3.59 wt. % of Na decreased nearly to a half compared to the Co4MnAl/Na-0.17 catalyst with low concentration of Na (from 93 to 46 and from 59 to 29 m² g⁻¹, respectively). In accordance with this finding, the volume of micropores decreased and average radius of mesopores, calculated as $r_{\text{meso}} = 2v_{\text{meso}}/s_{\text{BET}}$, gradually increased to nearly twofold value (from 5.3 to 9.0 nm). Mesopores volume was practically not influenced by increasing amount of Na in the samples; it indicates that sodium cations in the solid cause redistribution of particle sizes during calcination, most likely by way of very small particles melting, diminishing their numbers with the result of the decrease in micropore volume and the increase in average pore size.

However, not only porous structure is influenced by presence of sodium in the mixed oxide catalysts. Formerly it was found that potassium as an admixture in the Co-Mn-Al mixed oxides changes their surface properties and reduci-

Table 1 – Mass loss of the catalyst precursors during 4 h calcination at 500 °C and results of chemical analysis of the calcined samples

Tablica 1 – Gubitak mase uzoraka tijekom kalcinacije 4 h na 500 °C i rezultati kemijske analize kalciniranih uzoraka

Sample Uzorak	Mass loss / % Gubitak mase / %	wt. % of Na mas. % Na	wt. % of Co mas. % Co	wt. % of Mn mas. % Mn	wt. % of Al mas. % Al	Molar ratio Molarni omjer Co : Mn : Al
Co4MnAl/Na-0.17	29.77	0.17	60.50	9.95	5.98	4 : 0.70 : 0.86
Co4MnAl/Na-0.21	29.00	0.21	56.31	11.51	5.65	4 : 0.88 : 0.88
Co4MnAl/Na-0.39	29.91	0.39	55.07	11.47	5.65	4 : 0.89 : 0.90
Co4MnAl/Na-2.97	31.27	2.97	59.93	9.59	5.56	4 : 0.68 : 0.81
Co4MnAl/Na-3.59	47.12	3.59	60.59	9.21	5.33	4 : 0.66 : 0.78
Co4MnAl/Na-3.71	31.29	3.71	58.74	9.31	5.50	4 : 0.67 : 0.81
PI-I/Na ₂ CO ₃ /30°C-w	25.82	0.06	54.9	11.4	5.65	4 : 0.89 : 0.90
PI-I/Na ₂ CO ₃ /120°C-w	28.62	0.03	56.3	11.4	5.58	4 : 0.87 : 0.87
PI-II/urea/80°C-w	30.68	0	63.6	0.27	10.2	4 : 0.02 : 1.40
PI-II/urea/80°C- nw	30.69	0	62.1	0.40	9.77	4 : 0.03 : 1.37
PI-III/urea/145°C-w	38.65	0	60.6	12.2	6.00	4 : 0.86 : 0.86

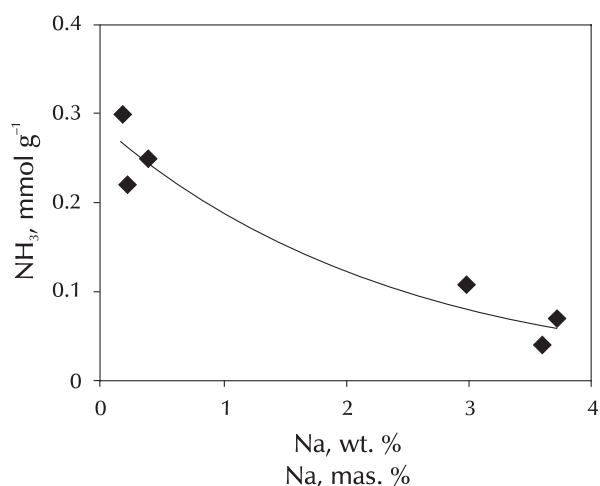


Fig. 1 – Dependence of acidity, given as mmol NH₃ g⁻¹ desorbed in the range 25 – 500 °C, on the Na content in the Co-Mn-Al mixed oxide catalysts

Slika 1 – Ovisnost kiselosti, dane kao mmol NH₃ g⁻¹ desorbirano od 25 do 500 °C, o sadržaju natrija u katalizatoru od trostrukog Co-Mn-Al-oksida

bility;⁵ sodium can act similarly. It was confirmed by TPD measurements that the acidity, calculated as ammonia to Co-Mn-Al mixed oxide mass ratio, of the calcined samples was decreasing with increasing Na content (Fig. 1): from 0.30 mmol NH₃ g⁻¹ found for the Co₄MnAl/Na-0.17 sample with the lowest Na content to 0.07 mmol NH₃ g⁻¹ found for the Co₄MnAl/Na-3.71 sample (Table 2).

Temperature-programmed reduction of the mixed oxides can be efficiently used for checking the conditions of catalysts precursor preparation as it reflects the changes in composition, size of oxide particles, crystallinity, etc. The TPR profiles of the Co-Mn-Al catalysts containing various amounts of Na are demonstrated in Fig. 2. All TPR patterns exhibited two broad peaks with t_{\max} of around 380 and 700 °C. Based on the published data,⁵ the low-temperature

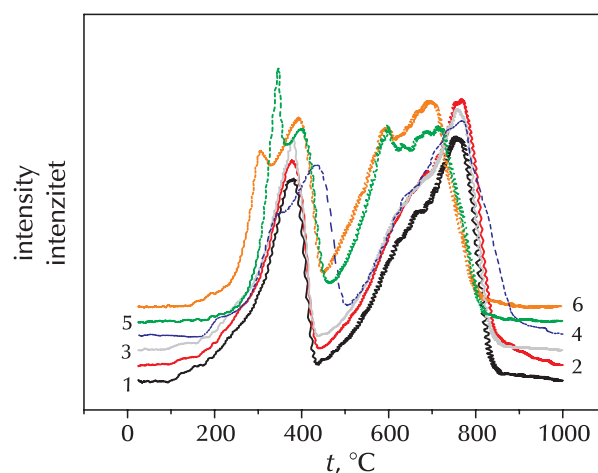


Fig. 2 – H₂-TPR profiles of the Co-Mn-Al mixed oxides containing various amounts of sodium.

1 – Co₄MnAl/Na-0.17; 2 – Co₄MnAl/Na-0.21; 3 – Co₄MnAl/Na-0.35; 4 – Co₄MnAl/Na-2.97; 5 – Co₄MnAl/Na-3.59; 6 – Co₄MnAl/Na-3.71.

Slika 2 – Rezultati H₂-TPR-a trostrukog Co-Mn-Al-oksida s različitim sadržajem natrija.

1 – Co₄MnAl/Na-0.17; 2 – Co₄MnAl/Na-0.21; 3 – Co₄MnAl/Na-0.35; 4 – Co₄MnAl/Na-2.97; 5 – Co₄MnAl/Na-3.59; 6 – Co₄MnAl/Na-3.71.

reduction peak detected at 200 – 400 °C can be ascribed to reduction of Co^{III} to Co^{II} and to reduction of Mn^{IV} to Mn^{III} oxides. Presence of kinetic effects during TPR measurements makes assignment of the TPR peaks to individual chemical compounds extremely difficult. The high-temperature reduction peak at 400 – 700 °C was attributed to the reduction of Co^{II} to Co⁰, Mn^{III} to Mn^{II} oxides and Co aluminate.^{6,9}

Increasing Na amount in the Co-Mn-Al mixed oxide catalysts caused a slight shift of both main peaks to lower temperatures. With increasing sodium content, a new, easily reducible peak (t_{\max} of about 306 °C), particularly distinct in

Table 2 – Physical-chemical properties of the Co-Mn-Al mixed oxides containing various amounts of Na. Moulding pressure 4 MPa, calcination 4 h at 500 °C.

Tablica 2 – Fizikalno-kemijska svojstva trostrukih Co-Mn-Al-oksida s različitim sadržajem natrija. Uzorci su komprimirani pod tlakom 4 MPa i kalcinirani 4 h na 500 °C.

Sample Uzorak	wt. % of Na mas. % Na	S_{BET} m ² g ⁻¹	V_{meso} cm ³ g ⁻¹	V_{micro} mm ³ g ⁻¹	S_{meso} m ² g ⁻¹	r_{meso} nm	H ₂ -TPR ^a mmol g ⁻¹	H ₂ -TPR ^b mmol g ⁻¹	t_{\max}^c °C	NH ₃ -TPD ^a mmol g ⁻¹
Co ₄ MnAl/Na-0.17	0.17	93	0.34	21.9	59	5.3	4.01	13.20	378	0.30
Co ₄ MnAl/Na-0.21	0.21	82	0.33	16.3	53	5.8	4.23	13.62	377	0.22
Co ₄ MnAl/Na-0.39	0.39	85	0.33	19.5	53	6.1	3.98	11.80	377	0.25
Co ₄ MnAl/Na-2.97	2.97	55	0.31	11.8	32	8.8	4.96	13.54	348; 433	0.11
Co ₄ MnAl/Na-3.59	3.59	46	0.37	8.9	29	12.7	4.68	12.76	347; 397	0.04
Co ₄ MnAl/Na-3.71	3.71	66	0.37	15.1	38	9.0	4.78	12.92	306; 393	0.07

^a 25 – 500 °C

^b 25 – 1000 °C

^c Low-temperature peak (see Fig. 2)

Niskotemperaturni signal (vidi sliku 2)

Table 3 – Catalytic activity and selectivity of the calcined Co-Mn-Al LDHs containing various amounts of sodium in ethanol oxidation

Tablica 3 – Katalitička aktivnost i selektivnost u oksidaciji etanola kalciniranih LDH s različitim sadržajem natrija

Sample Uzorak	$t_{50}(\text{EtOH})$ °C	$t_{90}(\text{EtOH})$ °C	$t_{50\text{VOC}}$ °C	$t_{90\text{VOC}}$ °C	$\frac{a(\text{EtOH})}{\text{mmol g}^{-1}\text{s}^{-1}}$	$\frac{a(\text{CO}_2)}{\text{mmol g}^{-1}\text{s}^{-1}}$	GC peak area of max. conc. / pA s GC-signal maks. konc. / pA s	
							CH ₃ CHO	CO
Co4MnAl/Na-0.17	124	175	169	210	0.90	0.78	74	74
Co4MnAl/Na-0.21	105	180	164	216	0.98	0.80	63	73
Co4MnAl/Na-0.39	133	174	178	207	0.94	0.84	76	91
Co4MnAl/Na-2.97	110	150	140	184	0.95	0.85	48	9
Co4MnAl/Na-3.59	104	157	142	194	0.96	0.84	58	21
Co4MnAl/Na-3.71	100	180	147	195	1.00	0.86	59	0

the samples containing high amount of sodium (3.59 and 3.71 wt. % Na), appeared in the low-temperature reduction peak. This new reduction peak can be ascribed to the reduction of free Co^{III} oxide. The relative ratio of the low-temperature TPR peak to the sum of both TPR peaks is slightly increasing with increasing Na content. Quantitative data concerning TPR are summarized in Table 2. The ratio of hydrogen amount consumed in the low temperature region to total hydrogen consumption is about 0.30 for the Co4MnAl/Na-0.17 catalyst, while it reaches the value of 0.37 for the Co4MnAl/Na-3.71 catalyst with the highest sodium content. Similar easier reduction was found with the spinel-like oxide NiCo₂O₄¹⁰ and attributed to enhanced oxidation of Co²⁺ to Co³⁺ to form Co₃O₄.^{11,12} Reducibility, i.e. the amount of hydrogen consumed during TPR measurements in the range 25 – 500 °C, was not influenced by Na content in the samples as substantially as the acidity. The amount of H₂ consumed in the range 25 – 500 °C

slightly increased with increasing amount of Na (the increase of only 30 % was found).

Similarly as potassium¹² sodium also improved catalytic properties of Co-Mn-Al mixed oxides in the ethanol total oxidation. Temperature $t_{50\text{VOC}}$ that is necessary for achieving 50 % conversion of all organic compounds in the reaction mixture to CO₂ decreased with increasing Na concentration in the samples. Thus, increasing amount of Na in the catalyst leads to higher activity in total oxidation of ethanol (Table 3). Sodium, like other alkali metals, decreases strength bond of the electrons, activates oxygen and thus the catalyst can react more easily with an organic compound. The $t_{50\text{VOC}}$ value for the catalyst without Na was obtained by extrapolation of the dependence of the $t_{50\text{VOC}}$ values observed for the catalysts with various concentration of Na to zero Na value and was determined as 175 °C.

Catalytic activity can be evaluated with higher accuracy by calculating specific catalytic activities that take into account slightly different concentrations of active components in the examined catalysts. The a values for ethanol oxidation and CO₂ formation are shown in Table 3. It can be seen that specific activities $a(\text{EtOH})$ and $a(\text{CO}_2)$ slightly increased with increasing Na concentration in the catalysts. Specific activity of the catalysts in CO₂ formation copies the dependence of ethanol oxidation, but the values are lower as the main reaction byproduct, acetaldehyde, is oxidized with more difficulty than ethanol (Fig. 3).

Selectivity of the Co-Mn-Al catalysts with increased concentration of Na also differs from that of catalysts without Na (Table 3). Maximum concentration of acetaldehyde (main byproduct of the oxidation reaction) slightly decreased with increasing concentration of Na in the catalysts. Remarkable difference in the catalysts selectivity can be seen in the formation of the other important byproduct, carbon monoxide. Its maximum concentration, expressed as FID detector response, in the reaction mixture decreased from around 80 pA s for the catalysts with low Na concentration to zero for the catalysts with Na concentration higher than 3.5 wt. %. The finding documents that the presence of Na in the Co-Mn-Al mixed oxide catalyst increases the ability of the catalyst to oxidize ethanol.

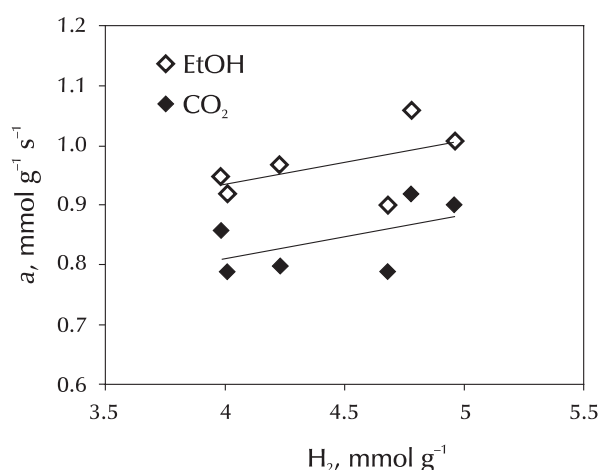


Fig. 3 – Dependence of specific activity of ethanol oxidation and CO₂ formation over Co-Mn-Al mixed oxide catalysts containing various amounts of Na on hydrogen consumption obtained during TPR measurements in the range of 25 – 500 °C

Slika 3 – Ovisnost specifične aktivnosti trostrukih Co-Mn-Al-oksida s različitim sadržajem natrija u oksidaciji etanola i nastajanju CO₂ o potrošnji vodika tijekom TPR-a u temperaturnom rasponu 25 – 500 °C

Properties of the Co-Mn-Al LDH precursors precipitated in the presence of organic template and related mixed oxides

Results of chemical analysis of the catalysts prepared using Pluronic® P123 during precipitation of the precursors are summarized in Table 1. The cation composition of the samples prepared by homogeneous precipitation in the presence of hydrolysing urea was noticeably different from that of coprecipitated ones. Relatively low pH (7.1) was measured in the final suspension after 40 h reaction at 80 °C which caused low Mn content in the obtained products since Mn cations are precipitated at higher pH values (about 8.5). Co cations in the solution were not fully precipitated as well (pH of about 8 is required for complete Co precipitation); complexation of Co cations with dissolved ammonia originating during urea hydrolysis may also occur. From the results described above it is obvious that sodium remaining in the precipitate affects properties of the calcined samples. Therefore, to analyse the effect of organic modifier (Pluronic® P123) addition only, it is necessary to avoid the contribution of Na to catalytic activity. Therefore, the samples modified with Pluronic® P123, having low or negligible concentration of Na, were compared with the samples having comparable sodium concentration (Co₄MnAl/Na-0.17 and Co₄MnAl/Na-0.21 samples).

Powder XRD measurements showed formation of products with hydrotalcite-like structure during coprecipitation in the presence of organic template (Pluronic® P123). Hydrothermal treatment of the coprecipitated sample resulted in improving crystallinity of the product; higher and sharper diffraction lines were observed in the corresponding powder XRD patterns (Fig. 4). Compared to the LDH precursors precipitated from the nitrate solutions without organic template, the presence of Pluronic® P123 did not change the powder XRD patterns of the obtained products. The precursors prepared by urea method at 80 °C also exhibited the hydrotalcite-like structure. The homogeneous precipitation at 145 °C under hydrothermal conditions led to formation of a mixture of Co, Mn, and Al carbonates; no LDH was detected in this sample (Fig. 4). Spinel-type mixed oxides were formed during calcination of all precursors prepared in the presence of Pluronic® P123 (Fig. 5); no effect of organic template on phase composition of the calcined products was observed.

The main aim of the contribution was to find out whether organic template, like Pluronic® P123, used during precipitation of the Co-Mn-Al LDH precursors, could influence the porous structure and other properties of the dried precipitates and calcined products. The results describing the most important characteristic values of the precipitates are shown in Table 4. The data demonstrate that the use of organic template during coprecipitation of the LDH precursor can slightly increase the surface area of the calcination product (the PI-I/Na₂CO₃/30°C-w sample). Aging of the LDH precursor at high temperature (120 °C) under hydrothermal conditions is not beneficial for the formation of high surface area in the related mixed oxide as it can even decrease its s_{BET} . The sample prepared by homogeneous precipitation of Co, Mn, and Al nitrates with urea at 80 °C followed by washing, led to a sample with lower surface area than that of the non-washed sample after calcination

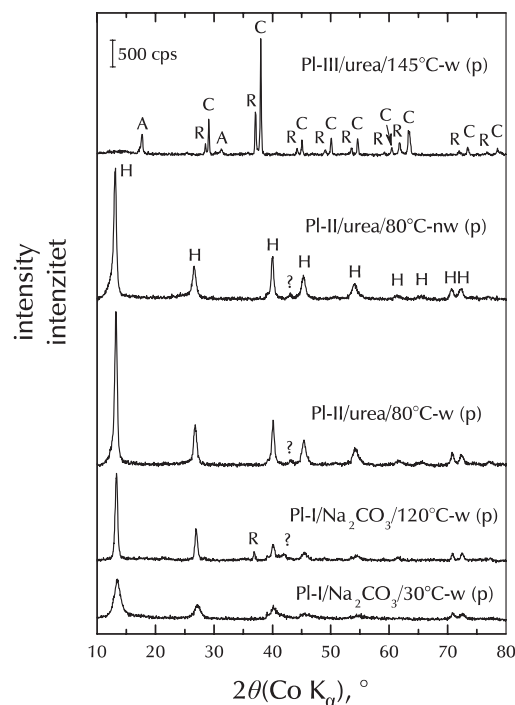


Fig. 4 – Powder X ray diffraction patterns of the precursors prepared by precipitation reaction in the presence of Pluronic® P123. H – hydrotalcite-like LDH; A – $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3\text{H}_2\text{O}$ (aluminium ammonium carbonate hydroxide hydrate); C – CoCO_3 (sphaerocobaltite); R – MnCO_3 (rhodochrosite); ? – unidentified.

Slika 4 – Difraktogram praha prekursora pripravljenog precipitacijom u prisutnosti polimera Pluronic® P123. H – LDH struktura hidrotalcita; A – $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3\text{H}_2\text{O}$ (aluminijev amonijev hidroksid karbonat hidrat); C – CoCO_3 (sferokobaltit); R – MnCO_3 (rodokrozit); ? – nepoznato.

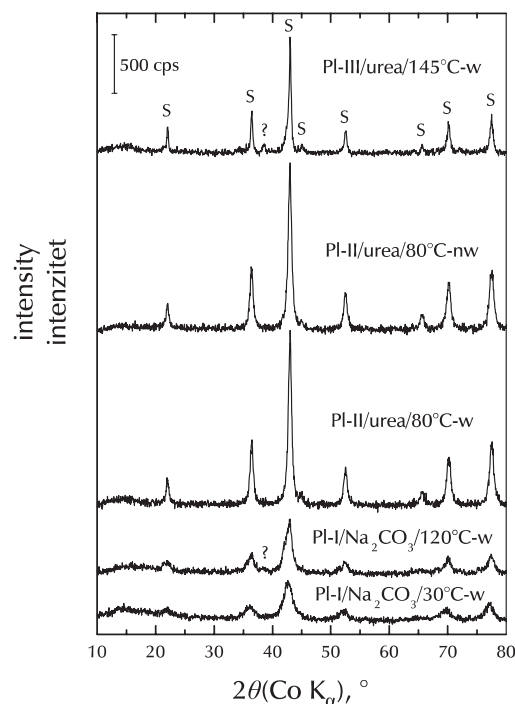


Fig. 5 – Powder XRD profiles of the Co-Mn-Al mixed oxide catalysts obtained from precursors prepared in the presence of Pluronic® P123. S – spinel; ? – unidentified.

Slika 5 – Difraktogram praha trostrukog Co-Mn-Al-oksida pripravljenog uz Pluronic® P123. S – spinel; ? – nepoznato.

Table 4 – Physical-chemical properties of the Co-Mn-Al mixed oxides obtained from precursors prepared in the presence of Pluronic® P123 (precursors were pelletized at 4 MPa and calcined at 500 °C for 4 h in air)

Tablica 4 – Fizikalno-kemijska svojstva trostrukih Co-Mn-Al-oksida pripravljenih uz Pluronic® P123 (prekursori su komprimirani pod tlakom 4 MPa i kalcinirani na zraku 4 h na 500 °C)

Sample Uzorak	wt. % of Na mas. % Na	Mass loss / % Gubitak mase / %	$\frac{m(\text{Pluronic P123})}{m(\text{Co}(\text{NO}_3)_2)}$ g g^{-1}	S_{BET} $\text{m}^2 \text{g}^{-1}$	V_{meso} $\text{cm}^3 \text{g}^{-1}$	V_{micro} $\text{mm}^3 \text{g}^{-1}$	r_{meso} nm	$\text{H}_2\text{-TPR}^a$ mmol g^{-1}	$\text{NH}_3\text{-TPD}^a$ mmol g^{-1}
Co4MnAl/Na-0.17	0.17	29.77	0	93	0.34	21.9	5.3	4.01	0.42
Co4MnAl/Na-0.21	0.21	29.00	0	82	0.33	16.3	5.8	4.23	0.22
PI-I/Na ₂ CO ₃ /30°C-w	0.06	28.62	0.10	120	0.50	19.3	7.0	3.65	0.32
PI-I/Na ₂ CO ₃ /120°C-w	0.03	25.82	0.10	76	0.39	18.5	8.2	3.85	–
PI-II/urea/80°C-w	0	30.68	0.17	55	0.22	12.4	6.1	2.78	0.27
PI-II/urea/80°C-nw	0	30.69	0.17	129	0.48	27.7	5.2	3.15	0.36
PI-III/urea/145°C-w	0	38.65	0.43	46	0.24	10.5	9.2	11.84	0.35

^a 25 – 500 °C

Table 5 – Porous structure of the Co-Mn-Al mixed oxides obtained from precursors prepared in the presence of Pluronic 123 and pelletized at various moulding pressures

Tablica 5 – Poroznost trostrukih Co-Mn-Al-oksida pripravljenih uz Pluronic® P123 i komprimiranih pod različitim tlakovima

Sample Uzorak	Moulding pressure / MPa Tlak tiješnjenja / MPa	S_{BET} $\text{m}^2 \text{g}^{-1}$	V_{meso} $\text{cm}^3 \text{g}^{-1}$	V_{micro} $\text{mm}^3 \text{g}^{-1}$	r_{meso} nm
PI-I/Na ₂ CO ₃ /30°C-w	2	113	0.35	25.9	4.9
PI-I/Na ₂ CO ₃ /30°C-w	3	125	0.64	28.2	8.4
PI-I/Na ₂ CO ₃ /30°C-w	4	120	0.50	19.3	7.0
PI-I/Na ₂ CO ₃ /120°C-w	2	70	0.38	15.4	8.2
PI-I/Na ₂ CO ₃ /120°C-w	3	78	0.43	17.8	8.5
PI-I/Na ₂ CO ₃ /120°C-w	4	76	0.39	18.5	8.2

(the PI-II/urea/80°C-nw sample). Performing homogeneous precipitation with urea under hydrothermal conditions at 145 °C, followed by washing and calcination, led to the PI-III/urea/145°C-w sample with the lowest surface area. It is necessary to note that the corresponding precursor had different phase composition (Fig. 4). Positive effect of Pluronic® P123 added during the synthesis of precursors can also be seen in the increase of both the volume of mesopores and the mean radius of pores when the obtained precursor was not washed before calcination. Under such conditions, bulky molecules of Pluronic® P123 were evidently not removed from the precipitate and their presence in the solids before calcination led to a slight improvement of porous structure of the catalysts.

Dried precipitates are usually formed into pellets or extrudates, in order to apply them in an industrial catalyst reactor. Common moulding pressure used during extrusion of catalyst precursor pastes varies in the range from 2 to 4 MPa. In this regard, it was interesting to test whether porous structure of the samples prepared in the presence of Pluronic® P123 was not substantially changed with increasing moulding pressure. Table 5 shows that surface area of the PI-I/Na₂CO₃/30°C-w sample moulded at higher pressures (3 and 4 MPa) slightly increased (about 10 %),

similarly as the surface area of the other sample (PI-I/Na₂CO₃/120°C-w) treated under hydrothermal conditions. Higher changes in volume of mesopores and micropores and mean radius of mesopores were identified with the sample prepared at low reaction temperature. The product before hydrothermal treatment exhibited lower crystallinity; therefore, pore volume of micropores during moulding diminishes and, consequently, mesopores radii increase. Porous structure of the sample prepared under hydrothermal conditions did not alter so much because its structure was sufficiently hardened during the preparation step.

As mentioned previously, the catalysts prepared by coprecipitation of Co, Mn, and Al nitrates with a solution of Na₂CO₃ and NaOH (without Pluronic® P123) exhibited two reduction peaks during TPR measurements, low- and high-temperature ones, corresponding to reduction of Co, Mn oxides and Al-containing spinels, respectively. Similarly, all catalysts prepared in the presence of Pluronic® P123, except the PI-III/urea/145°C-w sample, were reduced to two steps represented by the low- and high-temperature peaks (Fig. 6). Position of the peak maxima, however, slightly differed from those measured with the samples prepared without organic template (the Co4MnAl/Na-0.17 and Co4MnAl/Na-0.21 catalysts showed

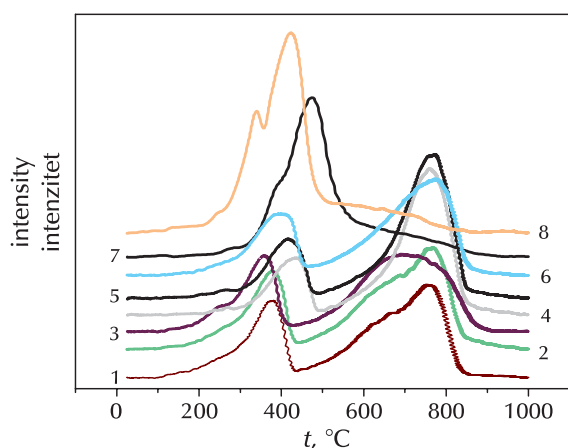


Fig. 6 – H_2 -TPR profiles of the Co-Mn-Al mixed oxides obtained from precursors prepared in the presence of Pluronic® P123. TPR profiles of Co4MnAl/0.17 and Co4MnAl/0.21 samples are included for comparison.

1 – Co4MnAl/Na-0.17; 2 – Co4MnAl/Na-0.21; 3 – PI-I/Na₂CO₃/30°C-w; 4 – PI-I/Na₂CO₃/120°C-w; 5 – PI-II/urea/80°C-w; 6 – PI-II/urea/80°C-nw; 7 – PI-III/urea/145°C-w / after testing; 8 – PI-III/urea/145°C-w / fresh.

Slika 6 – Rezultati H_2 -TPR-a trostrukog Co-Mn-Al-oksida pripravljenog uz Pluronic® P123. Za usporedbu su priloženi rezultati mjerenja uzoraka Co4MnAl/0.17 i Co4MnAl/0.21.

1 – Co4MnAl/Na-0.17; 2 – Co4MnAl/Na-0.21; 3 – PI-I/Na₂CO₃/30°C-w; 4 – PI-I/Na₂CO₃/120°C-w; 5 – PI-II/urea/80°C-w; 6 – PI-II/urea/80°C-nw; 7 – PI-III/urea/145°C-w / nakon testiranja; 8 – PI-III/urea/145°C-w / svježe.

nearly identical peaks). Peak maxima of the PI-I/Na₂CO₃/30°C-w catalyst coprecipitated in the presence of Pluronic® P123 and the analogous (hydrothermally treated) PI-I/Na₂CO₃/120°C-w sample somewhat varied: t_{max} of the sample coprecipitated at 30 °C were shifted to lower temperatures, whereas that of the sample treated at 120 °C

were shifted to higher temperatures. The finding indicates occurrence of bigger particles in the PI-I/Na₂CO₃/120 °C-w mixed oxides.

The TPR profiles of the catalysts obtained from the precursors prepared by homogeneous precipitation at 80 °C revealed again two reduction peaks, the low-temperature one being smaller than the high-temperature peak. Very likely, particles of the Co oxides (these samples contained only a slight amount of Mn) were bigger and uniform in size and the amount of Al-containing spinels could be increased as well. There was no observable effect of precursor washing.

The Co-Mn-Al mixed oxide obtained from the precursor prepared by urea method under hydrothermal conditions at 145 °C revealed significantly different reduction pattern: the catalyst was reduced only in one, three times larger, main peak at 421 °C with a shoulder at $t_{max} = 340$ °C; the high-temperature peak appearing around 760 °C was completely missing. Such course of the TPR pattern indicates that in this sample a mixture of oxides rather than mixed oxide is present. The powder XRD pattern of the corresponding precursor exhibited distinct carbonate phases (Fig. 4), which were probably transformed into mixture of oxides during calcination. Diffraction lines characteristic for a spinel-type oxide were found in the powder XRD pattern of the PI-III/urea/145°C-w sample (Fig. 5). It is worth noting that diffraction patterns of some Co, Mn, and Al oxides are very similar (e.g. Co₃O₄, Mn₃O₄, and CoAl₂O₄). Such mixture of oxides was, however, rather unstable, as the TPR pattern of the sample after catalyst testing showed substantial shift of the temperature maxima to higher temperatures and considerable decrease of the amount of reducible components.

Activity of the catalysts modified with Pluronic® P123 was also studied in the total oxidation of ethanol (Table 6).

Table 6 – Catalytic activity and selectivity of the Co-Mn-Al mixed oxides obtained from precursors prepared in the presence of Pluronic® P123 in the ethanol oxidation

Tablica 6 – Katalitička aktivnost i selektivnost u oksidaciji etanola Co-Mn-Al-oksida pripravljenih uz Pluronic® P123

Sample Uzorak	wt. % of Na mas. % Na	t_{50} (EtOH) °C	t_{90} (EtOH) °C	t_{50VOC} °C	t_{90VOC} °C	$\frac{a(EtOH)}{mmol\ g^{-1}s^{-1}}$	$\frac{a(CO_2)}{mmol\ g^{-1}s^{-1}}$	GC peak area of max. conc. / pA s	
								GC-signal maks. konc. / pA s	
								CH ₃ CHO	CO
Co4MnAl/Na-0.17	0.17	124	175	169	210	0.92	0.79	74	74
Co4MnAl/Na-0.21	0.21	105	180	164	216	0.98	0.80	73	63
PI-I/Na ₂ CO ₃ /30°C-w	0.06	120	213	202	239	0.90	0.77	51	63
PI-I/Na ₂ CO ₃ /120°C-w ^{a)}	0.03	108	180	163	214	0.93	0.80	85	80
PI-I/Na ₂ CO ₃ /120°C-w ^{b)}	0.03	110	141	152	200	0.93	0.78	120	78
PI-I/Na ₂ CO ₃ /120°C-w ^{c)}	0.03	141	138	150	199	0.92	0.79	0	68
PI-II/urea/80°C-w	0	210	269	251	296	0.82	0.75	0	42
PI-II/urea/80°C-nw	0	235	278	265	308	0.77	0.72	0	44
PI-III/urea/145°C-w	0	143	216	203	230	0.84	0.71	0	54

Pelletizing pressure: a) 2 MPa, b) 3 MPa, c) 4 MPa

Tlak tiješjenja: a) 2 MPa, b) 3 MPa, c) 4 MPa

Compared to mixed oxide catalysts obtained from coprecipitated precursors with low Na content (the Co4MnAl/Na-0.17 and Co4MnAl/Na-0.21 samples), the catalysts prepared from the precursors modified with Pluronic® P123 exhibited higher temperatures necessary for achieving 50 and 90 % conversion of ethanol. The PI-III/urea/145°C-w catalyst, obtained from the precursor prepared by homogeneous precipitation at 145 °C in the presence of Pluronic® P123, exhibited low surface area and mesopore volume but the highest pore size and amount of easily reducible components. However, its catalytic activity in total ethanol oxidation was low most probably because of low surface area. Specific activity related to the amount of active metals (Co and Mn) was practically identical for all examined catalysts. The catalysts obtained from precursors prepared by homogeneous precipitation with urea showed slightly lower catalytic activity. The reason for this result is probably either low concentration of Mn in the precipitates or low surface area. Selectivity of the catalysts prepared with Pluronic® P123 differed from those of the non-modified ones: concentration of both acetaldehyde and CO were the lowest with the catalysts prepared by homogeneous precipitation. The highest concentration of CO observed with the catalyst (PI-I/Na₂CO₃/120°C-w) pelletized at 3 MPa (Table 4) is remarkable. Explanation of this finding is, however, difficult, as the physical properties of the catalyst do not differ significantly from those of other catalysts.

Conclusions

Coprecipitation of Co, Mn, and Al nitrates by a solution of Na₂CO₃ and NaOH in the presence of Pluronic® P123 led to LDH precursors with hydrotalcite-like structure; their calcination at 500 °C gave spinel-type mixed oxides. The presence of organic template during coprecipitation increased to some extent both BET and mesopore surface areas of the calcined products. Moulding of these catalyst precursors under increased pressure did not cause collapse of their porous structure – mesopore volume and size of mesopores even increased slightly.

TPR profiles of the samples modified with Pluronic® P123 exhibited a shift of reduction maxima to lower temperatures. The PI-III/urea/145°C-w catalyst, examined after catalytic reaction, revealed a shift of reduction maxima to higher temperatures and considerable decrease in the amount of reducible components. Contrary to other samples, this catalyst showed no significant reduction at high temperatures (700 – 800 °C); it can be explained by different phase composition of the precursor, which contained no LDH phase but a mixture of Co, Mn, and Al carbonates. Increasing sodium content in the catalysts caused somewhat easier reduction of the oxides composing the catalysts.

Catalytic activity of the catalysts obtained by calcination of the coprecipitated precursors modified with Pluronic® P123 in the total oxidation of ethanol was slightly better than that of the non-modified ones. In spite of the observed improvement of physical-chemical properties and catalytic activity in ethanol oxidation, it is necessary to state that the changes evolved by the presence of Pluronic® P123 during precipitation of LDH precursors were rather small.

ACKNOWLEDGEMENT

The authors thank the Czech Science Foundation for the financial support (project P106/10/1762).

List of symbols and abbreviations

Popis simbola i kratica

a	– specific activity, mmol g ⁻¹ s ⁻¹ – specifična aktivnost, mmol g ⁻¹ s ⁻¹
GHSV	– gas hourly space velocity, m ³ kg ⁻¹ h ⁻¹ – prostorna brzina strujanja plina, m ³ kg ⁻¹ h ⁻¹
m	– mass, kg, g – masa, kg, g
m/z	– (relative molecular) mass-to-charge number ratio, 1 – omjer (relativne molekularne) mase i nabojnog broja, 1
p	– pressure, Pa – tlak, Pa
q_V	– flow rate, m ³ s ⁻¹ – obujamni protok, m ³ s ⁻¹
R	– universal gas constant, $R = 8,314 \text{ J K}^{-1} \text{ mol}^{-1}$ – opća plinska konstanta, $R = 8,314 \text{ J K}^{-1} \text{ mol}^{-1}$
r_{meso}	– radius of mesopore, nm – polumjer mezospore, nm
S_{BET}	– specific surface area, m ² g ⁻¹ – specifična površina, m ² g ⁻¹
S_{meso}	– specific surface area of mesopores, m ² g ⁻¹ – specifična površina mezopora, m ² g ⁻¹
t	– temperature, °C – temperatura, °C
T	– thermodynamic temperature, K – termodinamička temperatura, K
t_{50}, t_{90}	– temperatures of 50 % and 90 % conversion, °C – temperatura konverzije 50 % i 90 %, °C
t_{max}	– temperature of max. reduction, °C – temperatura najveće redukcije, °C
V_{meso}	– specific volume of mesopores, cm ³ g ⁻¹ – specifični volumen mezopora, cm ³ g ⁻¹
V_{micro}	– specific volume of micropores, mm ³ g ⁻¹ – specifični volumen mikropora, mm ³ g ⁻¹
w	– mass fraction, 1 – maseni udjel, 1
x	– mole fraction, 1 – molni udjel, 1
α	– degree of conversion, 1 – stupanj konverzije, 1
θ	– Bragg angle, ° – Braggov kut, °
λ	– wave length, nm – valna duljina, nm
AAS	– atomic absorption spectroscopy – atomska apsorpcijska spektroskopija
BET	– Brunauer–Emmett–Teller
BJH	– Barret–Joyner–Hallenda
cps	– counts per second – impulsi u sekundi
FID	– flame ionization detector – plameno-ionizacijski detektor

- GC – gas chromatography
– plinska kromatografija
- LDH – layered double hydroxide
– slojeviti dvostruki hidroksid
- TPD – temperature-programmed desorption
– temperaturno programirana desorpcija
- TPR – temperature-programmed reduction
– temperaturno programirana redukcija
- VOC – volatile organic compound
– hlapivi organski spoj
- XRD – X-ray diffraction
– rendgenska difrakcija

References

Literatura

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **359** (1992) 710–712.
2. A. Szegedi, M. Popova, C. Minchev, *J. Mater. Sci.* **44** (2009) 6710–6716.
3. P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Nature* **396** (1998) 512.
4. P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* **11** (1999) 2813–2826.
5. K. Jiráťová, J. Mikulová, J. Klempa, T. Grygar, Z. Bastl, F. Kovanda, *Appl. Catal.* **A 361** (2009) 106.
6. L. Obalová, K. Pacultová, J. Balabánová, K. Jiráťová, Z. Bastl, M. Valášková, Z. Lacný, F. Kovanda, *Catal. Today* **119** (2007) 233.
7. K. S. W. Sing, R. T. Williams, *Adsorpt. Sci. Technol.* **22** (2004) 773–782.
8. A. Lecloux, J. P. Pirard, *J. Colloid Interf. Sci.* **70** (1979) 265–281.
9. M. Haneda, Y. Kintaichi, N. Bion, H. Hamada, *Appl. Catal.* **B 46** (2003) 473.
10. M. Chen, X. M. Zheng, *J. Mol. Catal.* **A 221** (2004) 77.
11. Y. Li, D. Nakashima, Y. Ychihashi, S. Nishiyama, S. Tsuruya, *Ind. Eng. Chem. Res.* **43** (2004) 6021.
12. D. Nakashima, Y. Ychihashi, S. Nishiyama, S. Tsuruya, *J. Mol. Catal.* **259** (2006) 108.

SAŽETAK

Potpuna oksidacija etanola na kalciniranim slojevitim dvostrukim hidroksidima modificiranim organskim polimerom

J. Ludvíková,^a K. Jiráťová,^{a*} J. Klempa,^a H. Raabová,^b Z. Zapivovarski Votipka^b i F. Kovanda^b

Koprecipitacijom nitrata kobalta, mangana i aluminijske izazvanom otopinama Na₂CO₃ i NaOH u prisutnosti polimera Pluronic® P123 nastaju slojeviti dvostruki hidroksidi (LDH) strukture hidrotalcita koji kalciniranjem prelaze u trostruke okside tipa spinela. Organski predložak povećava specifičnu površinu i površinu mezopora kalciniranog produkta. Uz polimer su maksimumi redukcije pomaknuti prema nižim temperaturama, a jednako utječe povećanje količine natrija u katalizatoru.

Međutim, iako su fizikalno-kemijska svojstva trostrukih Co-Mn-Al-oksida i njihova katalitička aktivnost u oksidaciji etanola bila poboljšana, promjene uslijed prisutnosti polimera tijekom taloženja LDH-prekursora su prilično male.

^a Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, v.v.i., Rozvojová 135, 165 02 Prague 6 – Suchbátka, Češka Republika

^b Department of Solid State Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague, Češka Republika

Prispjelo 14. kolovoza 2012.

Prihvaćeno 13. studenog 2012.