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Supported mixed oxide catalysts for the total oxidation of volatile organic compounds

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ABSTRACT

Supported mixed oxide catalysts of various cation composition were obtained by heating (500 °C) of layered double hydroxide (LDH) precursors deposited on Al_2O_3/Al support (anodized aluminum foil) or grained alumina calcined at various temperatures during hydrothermal reaction in aqueous solutions of Co, Cu, Ni, and Mn nitrates. The M^{II}–(Mn)–Al LDHs (M^{II} = Co, Ni–Co, Ni–Cu, and Co–Cu) with only low Mn content were obtained. NiO-like and spinel-like mixed oxides but no distinct Cu-containing phases were detected in the supported catalysts. A low-temperature peak ascribed to reduction of an amorphous copper oxide was detected in TPR patterns of the supported mixed oxides containing Cu. TPR results indicated reduction of Ni- and Co-containing species at temperatures higher than 400 °C; it can be explained by formation of spinel-like phases and high structural ordering of the calcination products. Heating of grained alumina support at high temperatures (>550 °C) resulted in substantial decrease in surface area and, consequently, the amount of deposited active species. Among the examined catalysts, the Ni–Cu–(Mn)–Al mixed oxide showed the highest catalytic activity. Slight acetaldehyde formation during ethanol deep oxidation over the supported mixed oxides was observed.

1. Introduction

Volatile organic compounds (VOCs) in industrial gases are dangerous pollutants and represent a serious environmental problem. Concentration of VOCs in air can be reduced applying the catalytic total oxidation to carbon dioxide and water as the final products. Catalysts containing noble metals or transition metal oxides are currently used; the latter are cheaper and less sensitive to deactivation [1]. Efficient mixed oxide catalysts can be easily prepared by a controlled thermal decomposition of layered double hydroxide (LDH) precursors. Layered double hydroxides, known also as hydrotalcite-like compounds or anionic clays represent a class of synthetic layered materials with general chemical composition of $M^{II}_{1-x}M^{III}_{x}(OH)_2A^{n-}_{x/n}\cdot yH_2O$ where M^{II} and M^{III} are divalent and trivalent metal cations and A^{n-} is an n-valent anion. Heating of LDHs gives finely dispersed mixed oxides of M^{II} and M^{III} with large surface area and good thermal stability. Various LDH-related mixed oxides were studied as catalysts for total oxidation of VOCs, with most using toluene or ethanol as representative compounds [2–8]. The coprecipitated LDH precursors are usually obtained as a fine powder, which has to be formed into pellets and calcined. In such catalysts, a considerable part of the grain volume is often not fully utilized because of internal and external diffusion in case the reaction is very fast. Therefore, deposition of thin active layer on a supporting material is advantageous.

The formation of LDH phases was observed during impregnation of γ-alumina with aqueous solutions containing divalent metal cations at ambient temperature and near neutral pH [9]. A controlled growth of LDH crystals has been applied for obtaining oriented LDH films on porous anodic alumina [10] and the mixed oxides prepared by thermal decomposition of deposited LDHs maintained the original morphology of the precursor film [11]. In our recent work [12] we have studied the formation of LDH phase on porous anodic alumina in diluted aqueous solutions of Co and Mn nitrates under hydrothermal conditions. The surface hydration of aluminum oxide and subsequent formation of boehmite-like phase took place before LDH crystallization. The present work focused on preparation of LDH-related mixed oxide catalysts deposited on Al_2O_3/Al support (anodized aluminum foil) and grained alumina calcined at various temperatures. The deposition of LDH precursors was carried out in aqueous solutions containing various transition metal nitrates (Co, Cu, Ni, Mn) under hydrothermal conditions. The physical chemical properties of the deposited mixed oxides and their catalytic activity in ethanol total oxidation were studied.

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2. Materials and methods

2.1. Preparation of samples

The Al_2O_3/Al support was obtained by anodic oxidation of the aluminum foil (purity >99.9%, thickness 0.1 mm) in 2.8 M H_2SO_4 for 60 min at room temperature and current density of 30 mA cm^{-2}. The anodized foil was thoroughly washed and then dried at 60 °C. A set of grained alumina supports differing in surface area was also prepared. The sample of commercial alumina (Cherox 33-00, Czech Republic) was sieved to obtain grains with particle size of 0.160–0.315 mm. This sample (calcined originally at 550 °C) was additionally heated in a laboratory microwave oven at various temperatures ranging from 750 to 1050 °C. The non-calcined aluminum hydroxide used for alumina preparation was added to the set of the supports (grained sample with particle size of 0.160–0.315 mm dried at 130 °C).

The method reported by Chen et al. [10] was adopted for LDH deposition. The Al_2O_3/Al support (4 cm × 12 cm) was vertically placed into aqueous solutions (75 ml) containing various divalent metal nitrates (total metal ion concentration of 0.1 mol l^{-1}) and ammonium nitrate (0.6 mol l^{-1}); pH = 6.8 was adjusted by adding diluted aqueous ammonia solution. The deposition was carried out under hydrothermal conditions in 100 ml Teflon lined stainless steel bombs at 140 °C for 65 h. The composition and molar ratios of metal cations in used solutions were adjusted as follows: Co–Mn (2:1), Ni–Co–Mn, Ni–Cu–Mn, and Co–Cu–Mn (all 1:1:1). Then the precursors of supported catalysts were taken out, rinsed with distilled water and dried at 60 °C. The supported mixed oxide catalysts were obtained by calcination of washed and dried samples at 500 °C for 4 h in air.

The mixed oxide catalysts deposited on alumina grains were prepared by analogous way. The grained support (4 g) was placed into aqueous solution (600 ml) of Ni, Cu, and Mn nitrates (Ni:Cu:Mn molar ratio of 1:1:1, pH = 6.8) and stirred in 1000 ml stainless steel autoclave for 70 h at 140 °C. Then the grained samples were filtered off, washed thoroughly with distilled water, dried at 60 °C in air and calcined at 500 °C for 4 h in air.

2.2. Characterization of the samples

The content of transition metals (Co, Cu, Mn, and Ni) in the deposited products was determined by AAS method using a Spectr AA880 instrument (Varian) after dissolving the samples (0.10–0.15 g of the supports after deposition) in hydrochloric acid.

Powder X-ray diffraction (XRD) patterns were recorded using a Seifert XRD 3000P instrument with Co Kα radiation ($\lambda = 0.179$ nm, graphite monochromator, goniometer with the Bragg–Brentano geometry) in 2θ range 10–80°, step size 0.05°. The qualitative analysis was performed with a HighScore software package (PANalaytical, The Netherlands, version 1.0d).

Scanning electron micrographs (SEM) of the samples were taken with a Hitachi S-4700 scanning electron microscope. No conductive layer was applied for observing the samples in order to maintain all surface details at high resolution. A low accelerating voltage of about 2 kV was applied to avoid the surface charging.

Surface area of the calcined samples was determined by adsorption/desorption of nitrogen at −196 °C using Micromeritics ASAP 2010 instrument. The BET method was applied for data evaluation.

Temperature programmed reduction (TPR) measurements of the calcined samples (0.2 g) were performed with a H_2/N_2 mixture (10 mol% H_2), flow rate 50 ml min^{-1} and linear temperature increase 20 °C min^{-1} up to 1000 °C. A change in H_2 concentration was detected with a mass spectrometer Omnistar 300 (Pfeiffer Vakuum). Reduction of the grained CuO (0.160–0.315 mm) was repeatedly performed to calculate absolute values of the hydrogen consumed during reduction of the calcined samples.

2.3. Catalytic measurements

The catalytic measurements were carried out in a fixed-bed glass reactor (5 mm i.d.) under unsteady-state reaction temperature with heating rate of 2.0 °C min^{-1} in the range from 100 to 400 °C. The catalysts deposited on Al_2O_3/Al support were cut to small pieces (approximately 2 mm × 2 mm) and the weight of 0.4 g was placed into the reactor; the catalysts deposited on the grained aluminas were used as prepared. The catalysts were examined at 20 $m^3\,kg^{-1}\,h^{-1}$ space velocity; GHSV calculated for the conditions in the reactor by using the apparent density of the catalysts in the bed (approximately 0.40 g cm^{-3} for the catalysts deposited on Al_2O_3/Al support and 0.89 g cm^{-3} for the catalysts deposited on grained aluminas) was around 8000 h^{-1} and 18,000 h^{-1}, respectively. The inlet concentration of ethanol in the air was 1 g m^{-3}. Reaction products were analysed using a Hewlett-Packard 6890 gas chromatograph equipped with a FID detector and a capillary column (HP-5 19091 J-413, 30 m × 0.32 mm × 0.25 mm with 5% phenylmethyl silicone). Temperatures T_{50} and T_{90} (the temperatures, at which 50 and 90% conversion of ethanol were observed) were chosen as a measure of the catalysts activity. Selectivity in ethanol conversion was evaluated as the GC peak area of byproducts analysed at 95% conversion of ethanol. The accuracy of the conversion and selectivity determination was ±3%.

3. Results and discussion

3.1. Formation of LDH precursors and mixed oxides on supporting materials

Well-crystallized hydrotalcite-like phases were found in powder XRD patterns of the Al_2O_3/Al support after hydrothermal deposition, together with two sharp diffraction lines, corresponding to aluminum in the support (Fig. 1). Boehmite (AlOOH) was also formed during hydrothermal treatment of the Al_2O_3/Al support as a result of surface aluminum oxide hydration [12]. Chemical analysis of the dried samples indicated only low incorporation of Mn into the deposited solid (Table 1); preferred formation of M^{II}–Al LDHs was expected. Therefore, the samples deposited on Al_2O_3/Al support were denoted as M^{II}–(Mn)–Al (M^{II} = Co, Ni–Co, Ni–Cu, and Co–Cu). The difference in molar ratios of metal cations determined in the solutions and deposited LDHs can be explained by various values of pH, at which the metal cations in solutions used for hydrothermal deposition are precipitated; the following pH values have been reported for precipitation of divalent metal hydroxides in 0.01 M solutions: Cu 5, Ni 7, Co 7.5, and Mn 8.5 [13].

Relatively homogeneous layers consisting of thin curved LDH platelets with nearly perpendicular orientation to the Al_2O_3/Al support were observed in SEM images (Fig. 2a). The same morphology of the deposited products was also found in the calcined samples (Fig. 2b). Heating of LDHs deposited on Al_2O_3/Al support led to a formation of M^{II}–(Mn)–Al mixed oxides with only slight Mn content (Table 2). NiO-like and spinel-like mixed oxides were found in powder XRD patterns of the Ni- and Co-containing samples (Fig. 1). No distinct oxide phases containing Cu were detected in the Ni–Cu–(Mn)–Al and Co–Cu–(Mn)–Al samples despite the relatively high amount of Cu determined by chemical analysis.

Total amounts of hydrogen consumed during reduction (25–1000 °C) of the M^{II}–(Mn)–Al mixed oxides deposited on both Al_2O_3/Al and grained Al_2O_3 supports are summarized in Table 3; the portions corresponding to the components reducible in the low temperature range (25–400 °C), potentially having relation

Table 1
Content of metal cations in the deposited solid after hydrothermal treatment of Al_2O_3/Al support in aqueous solutions of transition metal nitrates and the lattice parameter *a* of the formed LDH phases.

Cations in solution (molar ratio)	Weight increase[a] (g g^{-1})	Metal content in the deposited solid (wt%)				LDH lattice parameter *a* (10^{-10} m)
		Ni	Co	Cu	Mn	
Co, Mn (2:1)	0.356	–	27.4	–	0.2	3.069
Ni, Co, Mn (1:1:1)	0.443	22.0	13.1	–	1.3	3.050
Ni, Cu, Mn (1:1:1)	0.400	17.7	–	11.2	2.7	3.061
Co, Cu, Mn (1:1:1)	0.247	–	19.6	15.3	0.5	3.068

[a] Difference in sample weight before and after hydrothermal treatment related to final sample weight.

Table 2
Content of metal cations in the supported mixed oxide catalysts obtained by hydrothermal treatment of Al_2O_3/Al supports and grained aluminas (calcined at various temperatures) in aqueous solution of Ni, Co, Cu, and Mn nitrates; samples after deposition were heated at 500 °C.

Catalyst sample	Metal content (wt%)			
	Ni	Co	Cu	Mn
Co–(Mn)–Al[a]	–	11.7	–	0.09
Ni–Co–(Mn)–Al[a]	11.4	6.77	–	0.67
Co–Cu–(Mn)–Al[a]	–	5.57	4.12	0.13
Ni–Cu–(Mn)–Al[a]	7.90	–	5.00	1.20
Ni–Cu–(Mn)–Al/130[b]	8.10	–	10.9	0.83
Ni–Cu–(Mn)–Al/550	5.95	–	6.40	0.64
Ni–Cu–(Mn)–Al/750	3.94	–	2.40	0.19
Ni–Cu–(Mn)–Al/800	4.81	–	1.60	0.09
Ni–Cu–(Mn)–Al/950	3.07	–	1.59	0.20
Ni–Cu–(Mn)–Al/1050	0.83	–	0.38	0.06

[a] Catalysts deposited on Al_2O_3/Al support.
[b] Grained aluminum hydroxide dried at 130 °C was used as support for LDH deposition.

to catalytic oxidation reaction, are presented as well. The measured TPR patterns are shown in Figs. 3 and 4. Major portions of the Ni- and Co-containing species in the deposited mixed oxides were reduced at relatively high temperatures (>400 °C). It could be explained by formation of both the spinel-like phases and high structural ordering of the oxides formed upon calcination of the LDH precursors. The deposited LDHs consisted of relatively large and well developed platy crystals. As it was recently reported [14,15], the better structural ordering and increased crystallite size of hydrothermally treated Ni–Al LDH precursors enhanced the stability of Ni^{II} species in calcination products against reduction.

During reduction of the Co–(Mn)–Al sample the reduction peaks with maxima at about 445, 595, and 695 °C were found (Fig. 3). The first reduction peak was ascribed to reduction of Co_3O_4 (reduction of Co^{III} to Co^{II} followed by reduction of Co^{II} to Co^0) and the reduction peaks observed at higher temperatures were likely connected with reduction of Co in Co–Al spinel-type mixed oxide. The low-temperature reduction peak at 335 °C observed in TPR pattern of the Ni–Co–(Mn)–Al sample could be ascribed to reduction of NiO. The Cu-containing catalysts started to reduce at lower temperatures. The sharp reduction peak with maximum at 220 °C found in TPR pattern of the Ni–Cu–(Mn)–Al sample corresponded to reduction of copper oxide even if no CuO (tenorite) was detected by XRD; an XRD-amorphous copper oxide was evidently present in this sample. The TPR pattern of Co–Cu–(Mn)–Al sample exhibited a broad, low-temperature reduction peak with maximum at about 130 °C, which could be explained by reduction of an amorphous Cu-containing component. The reduction peaks observed in TPR patterns of Ni–Cu–(Mn)–Al and Co–Cu–(Mn)–Al catalysts at higher temperatures were ascribed to reduction of Ni and Co components in the spinel-type mixed oxides.

Table 3
Surface area, amount of consumed hydrogen during TPR measurements, catalytic activity and selectivity of the supported mixed oxide catalysts in the deep oxidation of ethanol (catalyst weight 0.40 g, ethanol concentration in air 1.0 g m^{-3}, space velocity 20 m^3 kg^{-1} h^{-1}, heating rate 2.0 °C min^{-1}), T_{50} and T_{90}: temperatures, at which 50 and 90% conversion of VOC was achieved.

Catalyst sample	S_{BET} (m^2 g^{-1})	H_2 consumption (mmol H_2 g^{-1})		T_{50} (°C)	T_{90} (°C)	CH_3CHO (a.u.)[b]
		(25–1000 °C)	(25–400 °C)			
Co–(Mn)–Al[a]	28	3.57	0.68[c]	242	284	36.2
Ni–Co–(Mn)–Al[a]	84	3.31	0.62[c]	218	262	24.6
Co–Cu–(Mn)–Al[a]	70	0.51	0.30[c]	268	307	8.0
Ni–Cu–(Mn)–Al[a]	37	1.99	1.00[c]	204	228	7.5
Ni–Cu–(Mn)–Al/130[d]	192	2.82	1.14	206	238	2.9
Ni–Cu–(Mn)–Al/550	203	2.35	0.89	223	248	2.4
Ni–Cu–(Mn)–Al/750	55	1.61	0.47	231	264	4.3
Ni–Cu–(Mn)–Al/800	20	1.08	0.37	244	270	9.9
Ni–Cu–(Mn)–Al/950	26	0.91	0.42	233	257	12.7
Ni–Cu–(Mn)–Al/1050	5	0.31	0.13	265	286	14.3

[a] Catalysts deposited on Al_2O_3/Al support.
[b] CH_3CHO peak area at ethanol conversion 95%.
[c] Temperature range 25–500 °C.
[d] Grained aluminum hydroxide dried at 130 °C was used as support for LDH deposition.

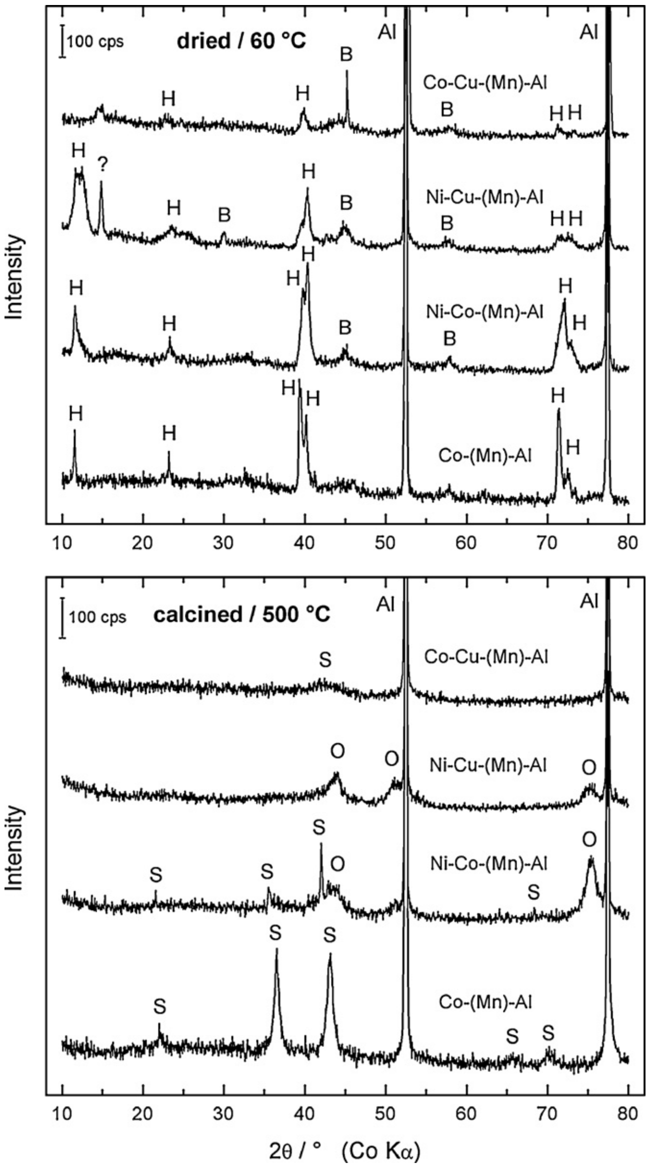

Fig. 1. Powder XRD patterns of the samples obtained after LDH deposition on Al_2O_3/Al support (solution pH of 6.8, 65 h deposition at 140 °C); washed samples dried at 60 °C and calcined at 500 °C for 4 h in air. H – hydrotalcite-like phase, B – AlOOH (boehmite), ? – unidentified; O – NiO-like oxide, S – spinel-type mixed oxide, Al – aluminum (support).

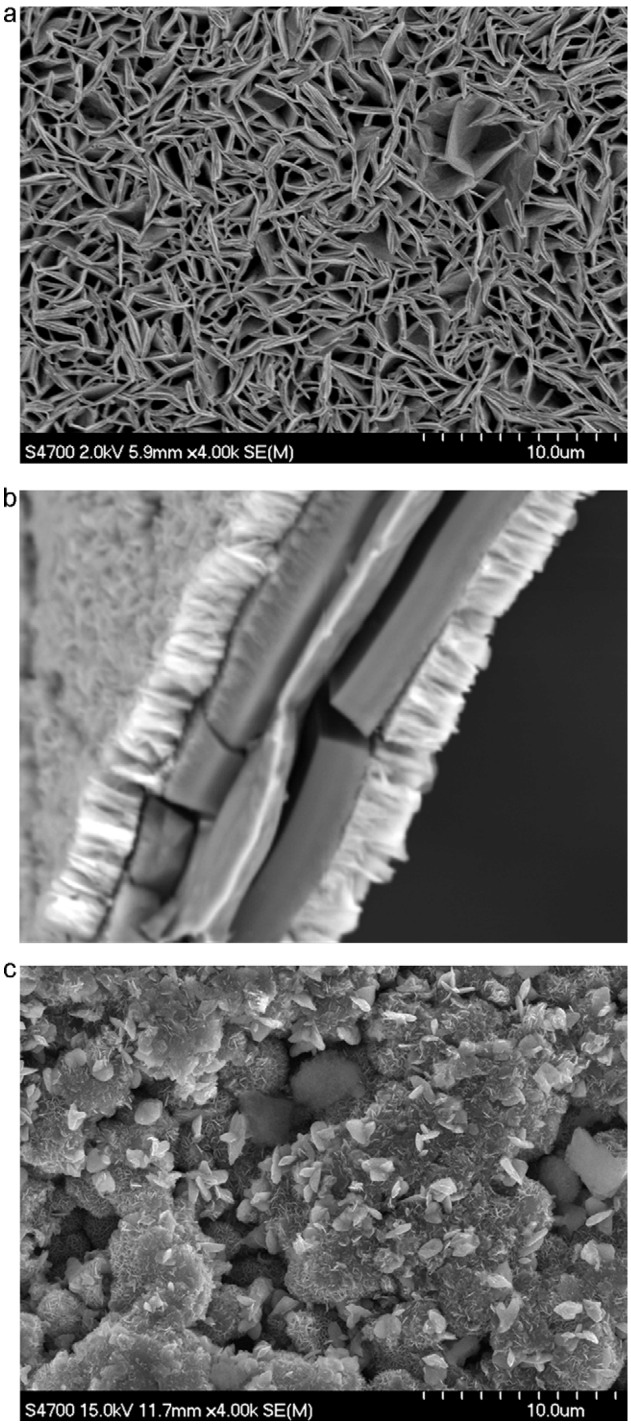

Fig. 2. SEM images of the Co–(Mn)–Al LDH layer formed on Al_2O_3/Al support (a), the profile of the Co–(Mn)–Al sample after calcination at 500 °C (b), and the Ni–Cu–(Mn)–Al product formed on grained aluminum hydroxide support – sample calcined at 500 °C (c).

The grained alumina heated at various temperatures was also used as supporting material. The hydrothermal deposition of LDH precursor was carried out in the aqueous solution of Ni, Cu, and Mn nitrates with Ni:Cu:Mn molar ratio of 1:1:1. Contents of transition metals in the prepared catalysts are presented in Table 2. The amount of deposited active components was strongly affected by heating of the used supports – alumina grains. Among the examined grained supports, the dried aluminum hydroxide was the most suitable for deposition of the LDH precursor as the present Al cations could easily enter the formed LDH phase and, therefore, the obtained catalyst contained the highest amount of LDH-related mixed oxides comprising transition metal cations. Small LDH platelets crystallized on the support surface (Fig. 2c) and formation of LDH precursor in the pores can be also expected. Porous structure of the prepared catalysts resembled the structure of the supports. The incorporated LDH-related mixed oxides only diminished space among the alumina aggregates leading to decrease in pore volume and pore sizes; the pore size distribution copied that of the supports. Slightly lower amount of transition metals was found in the catalyst, when alumina calcined at 550 °C was used as the support. Heating of alumina at higher temperatures resulted in substantial decrease in surface area (Table 3) and, consequently, the amount of deposited active species (Table 2). Decreased amount of reducible components with increasing temperature of alumina heating was confirmed also by TPR measurements (Fig. 4). All catalysts showed distinct peak with maximum at about 260 °C, which was attributed to reduction of CuO to Cu. Decreasing intensity of

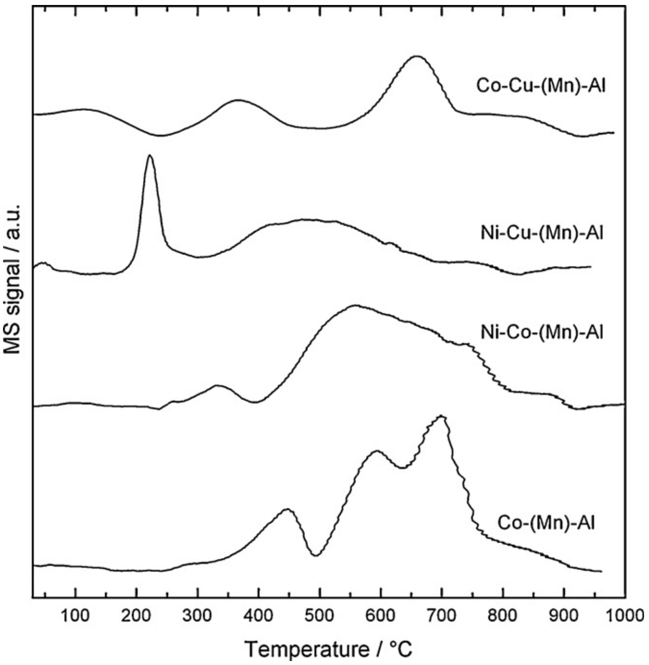

Fig. 3. TPR patterns of LDH-related M^{II}–(Mn)–Al mixed oxides deposited on Al_2O_3/Al supports (catalysts prepared at 500 °C).

the peak with increasing temperature of the support calcination was in accord with decreasing amount of copper oxide in the catalysts. The TPR profiles in temperature region from 350 to 1000 °C resembled a complex reduction peak with two or three non-distinct maxima at about 400, 600, and 900 °C. The peak at 400 °C could be ascribed to the reduction of Ni^{II} to Ni^0 (reference NiO was reduced at 330 °C). Increasing amount of accessible Al cations very likely led to partial incorporation of Al cations into the nickel oxide lattice and nickel aluminate-type phases were likely formed upon heating. It is necessary to note that reduction process is affected by surface area and crystallinity of the samples what can reflect in shifting the temperatures of reduction maxima. Only very low contribution of manganese reduction to over-all reduction patterns was considered due to low Mn contents in the prepared catalysts.

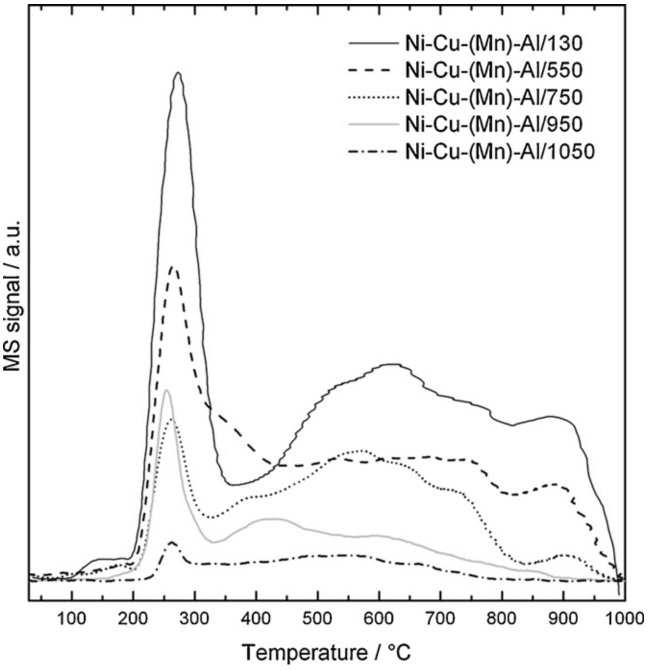

Fig. 4. TPR patterns of Ni–Cu–(Mn)–Al mixed oxides deposited on grained aluminas (alumina supports were calcined at various temperatures, catalysts were prepared at 500 °C).

3.2. Catalytic activity and selectivity of the catalysts in deep ethanol oxidation

Temperatures T_{50} and T_{90}, at which 50 and 90% conversion of ethanol over the examined catalysts was achieved, are compared in Table 3. Among the mixed oxides deposited on Al_2O_3/Al support, the Ni–Cu–(Mn)–Al one was the most active (T_{50} = 204 °C). The Ni–Co–(Mn)–Al catalyst showed only slightly lower activity (T_{50} = 218 °C). The lowest activity was found with the Co–Cu–(Mn)–Al catalyst (T_{50} = 268 °C). The order of catalysts activity correlated well with the amount of easily reducible components determined as H_2 consumption in the temperature range from 25 to 500 °C (Table 3).

The catalytic activity of the Ni–Cu–(Mn)–Al mixed oxides deposited on the grained alumina supports corresponded to both surface area and the amounts of reducible components in the catalysts. The Ni–Cu–(Mn)–Al/130 and Ni–Cu–(Mn)–Al/550 samples obtained after LDH deposition on dried aluminum hydroxide and alumina calcined at 550 °C, respectively, exhibited the highest catalytic activity (T_{50} = 206 and 223 °C, respectively). The catalytic activity of the grained catalysts gradually decreased with increasing temperature of the support calcination. Again, the activity of the catalysts supported on grained aluminas was correlated well with the amounts of hydrogen consumed in the temperature range from 25 to 400 °C (correlation coefficient R^2 = 0.878).

Selectivity of the deep oxidation catalysts is very important as reaction byproducts are often more harmful than the processed VOC. During ethanol oxidation, acetaldehyde, acetic acid, ethylene, ethyl acetate, and carbon monoxide can be formed; the concentration of these harmful compounds at high ethanol conversion is especially important, as such effluent could be emitted from the catalytic unit. Over all studied catalysts, acetaldehyde was found as the main reaction byproduct. In the experiments performed over the Ni–Cu–(Mn)–Al mixed oxides deposited on grained aluminas, the acetaldehyde concentration in the reaction mixture (measured at 95% conversion of ethanol) increased with increasing temperature of the support calcination (Table 3). The activity of mixed oxides deposited on alumina calcined at high temperatures was likely not sufficient to oxidize acetaldehyde to CO_2 in an appropriate rate. Ethylene was the other byproduct detected in the reaction mixture but its concentration was very low and did not change during the reaction. A slight amount of acetic acid was detected during the ethanol oxidation over the Ni–Cu–(Mn)–Al/550 catalyst. No formation of carbon monoxide was found over all examined catalysts.

4. Conclusions

Well-crystallized LDH precursors were prepared on Al_2O_3/Al support during hydrothermal reaction in aqueous solutions containing various divalent metal nitrates. Formation of Al-containing M^{II}–(Mn)–Al LDHs (M^{II} = Co, Ni–Co, Ni–Cu, or Co–Cu) was expected, since only slight incorporation of Mn cations into the deposited solid was found. The deposited solid consisted of relatively large, well-developed thin platelet crystals oriented nearly perpendicular to the support. After heating at 500 °C, when mixed oxides were formed, the same morphology was observed. Higher reduction temperatures (>400 °C) of Ni- and Co-containing species can be explained by formation of spinel-like phases during precursors heating and high structural ordering of the calcination products. Temperature programmed reduction indicated also presence of amorphous copper oxide, which was reduced up to about 260 °C. The Ni–Cu–(Mn)–Al mixed oxide deposited on Al_2O_3/Al support exhibited the highest catalytic activity in the deep oxidation of ethanol. When the grained aluminum hydroxide was used as the support for LDH deposition, the supported mixed oxide catalyst with similar catalytic activity was obtained. The heating of alumina support at high temperatures resulted in strong decrease in amount of deposited active components and catalytic activity. Acetaldehyde was found as the main reaction byproduct during the ethanol deep oxidation over all the examined catalysts. The grained Ni–Cu–(Mn)–Al/130 sample showed both high catalytic activity and selectivity.

Acknowledgements

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