Catalysis Today 179 (2012) 164–169

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Titania supported Co–Mn–Al oxide catalysts in total oxidation of ethanol

Jana Ludvíková[a], Květa Jirátová[a,*], Jan Klempa[a], Vlasta Boehmová[b], Lucie Obalová[c]

[a] *Institute of Chemical Process Fundamentals of the CAS, v.v.i., 165 02 Praha 6, Rozvojová 135, Czech Republic*
[b] *Institute of Geology of the CAS, v.v.i., 165 00 Praha 6, Rozvojová 269, Czech Republic*
[c] *Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic*

ARTICLE INFO

Article history:
Received 27 April 2011
Received in revised form 24 June 2011
Accepted 28 June 2011
Available online 19 August 2011

Keywords:
Mixed oxide catalysts
VOC oxidation
Titania

ABSTRACT

Catalytic activity of the Co–Mn–Al mixed oxide catalysts (Co:Mn:Al molar ratio of 4:1:1) supported over titania was examined in total oxidation of ethanol. The prepared catalysts were characterized by chemical analysis (AAS), surface area measurements, and temperature programmed techniques (TPR, TPD). In ethanol oxidation, the catalysts activity gradually increased with increasing active phase content. Low concentration of Co–Mn–Al oxides in the catalyst negatively affected formation of reaction byproducts: carbon monoxide production steeply increased when Co + Mn metals concentration were lower than 5 wt.%. On the other hand, formation of the second main reaction intermediate, acetaldehyde was limited, when acidity of the catalyst was not high, i.e. concentration of Co–Mn metals over titania was low.

1. Introduction

The catalysts mostly used for the total oxidation of volatile organic compounds comprise noble metals (platinum, palladium) supported on a suitable material, mostly aluminum oxide. Some other supports were studied to obtain very active and stable combustion catalyst [1]. However, the catalysts containing noble metals are very sensitive to poisoning and are rather expensive. The other group of catalysts used in VOC combustion is based on alternative active components, namely various transition metal oxides (V, W, Cr, Mn, and Cu) or their mixtures [2]. Amorphous copper–manganite, $CuMn_2O_4$, called also 'hopcalite', is probably the most known catalyst of this type used in combustion processes [3–5]. Presumably [6], its catalytic effect is based on redox equilibrium $Cu^{2+} + Mn^{3+} \Leftrightarrow Cu^{1+} + Mn^{4+}$. Transition metals, which can attain variable oxidation state, are suitable active components for such catalysts. In addition to oxidizing/reducing properties, the transition metals containing mixed oxides (as prepared or supported on various materials) exhibit different acid–base properties, influencing significantly the activation of reactants [7].

Mixed oxides containing transition metal cations are usually prepared by thermal decomposition of various precursors such as hydroxides, carbonates, nitrates, oxalates. Mixed oxides can be taken as a very efficient model system for studying the relationship between acid–base and oxidizing/reducing properties of solids and their catalytic activity in total oxidation of chemical compounds with various polarity. In recent years, we have found that the most active LDH (layered double hydroxides)-related mixed oxide catalysts are those comprising cations of Ni, Cu, Co, Mn, Mg and/or Al in various molar ratios [8–10]. The most active catalysts for total oxidation of model aromatic (toluene) and oxidic (ethanol) organic compounds were the Ni–Mg–Mn, Ni–Cu–Mg–Mn and Co–Mn–Al mixed oxides. With these catalysts, the similar or higher conversions than that of reference Pt/Al_2O_3 catalysts were achieved in total oxidation of the model VOC. However, some problems are connected with application of the pelletized mixed oxides: (i) troubles accompanying formation of the precursors into larger pellets (5–8 mm), (ii) relatively low mechanical strength, (iii) higher pressure drop, and (iv) low utilization of the pellet volume by the reason of a high influence of internal diffusion during catalytic reaction. The catalytic reaction, taking place in a narrow surface region of the pellets represents very important problem, which should be minimized by applying a thin active layer deposited on the supporting material. Therefore, we are focused on the detailed study of methods suitable for deposition of the active precursors or components on preformed supports of appropriate physical chemical properties. The most common support of the active species is alumina. Apart from it, other oxides can be also used as support of the active species in the structured catalysts. Titania, showing hydrophobic properties, is an extremely interesting support for oxidation of VOC in the presence of steam.

To reduce process costs in catalytic combustion of VOC, it is necessary to achieve an increase in catalyst activity that reflects in a decrease in reaction temperature. However, influencing the catalyst selectivity is also important, often more important than influencing the catalyst activity. During catalytic oxidation of organic compounds, especially oxygenated ones, formation of a group of partially oxidized by-products may occur; it can be more

---

* Corresponding author.
E-mail address: jiratova@icpf.cas.cz (K. Jirátová).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.06.032

harmful for environment than the original reactants. For example, aldehydes and/or organic acids or esters can be formed during oxidation of oxy-compounds; analogously, a formation of alkenes cannot be excluded during oxidation of alkanes. For that reason, knowledge of the relations between surface properties of the catalyst and the spectrum of arising oxidation products is very important. Surface properties of the structured catalyst can be substantially affected by the support as well as by the deposited layer of other material anchoring the active components on the support; a synergic action can proceed among all components of the catalyst.

In pelletized mixed oxide catalysts prepared by calcination of coprecipitated precursors, a considerable part of the pellets is not utilized in case of very fast catalytic reaction, due to the effect of internal and external diffusions. Therefore, deposition of thin active layer on a supporting material is advantageous. Moreover, deposition of the active compounds over a support could contribute to a higher thermal stability of the transition metal oxides during the reaction process.

In this contribution, the effect of the support (titania) on properties and catalytic activity of Co–Mn–Al oxides in ethanol oxidation was examined. The catalysts differed in geometric form (grains and extrudates) and in the distribution of metals in the extrudates.

2. Experimental

2.1. Catalyst preparation

Two geometric forms of titania (anatase) were used for the catalyst preparation: titania extrudates of diameter 3 mm (Eurosupport, Litvínov, Czech Republic) and the grains (0.16–0.315 mm) which were prepared by crushing and sieving from the extrudates. Pore-filling method was applied for the impregnation of the support; aqueous solution of nitrates, i.e., $Co(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$, with Co:Mn:Al molar ratio of 4:1:1 was used to obtain catalysts with nominal amount of 5–25 wt.% of transition metals. To meet uniform distribution of active components in the support, the support was being in a contact with the impregnation solution for half an hour. For comparison, the unsupported grained sample was prepared by drying of the impregnation solution of Co, Mn, and Al nitrates followed by calcination like the other samples. This sample contained about 58 wt.% Co + Mn. The catalysts with non-uniform distribution of active metals in the pelletized support were prepared in a rolling pan where the impregnation solution was sprayed over the extrudates in a regular time interval (1 min). After impregnation, the wet samples were dried 4 h at 130 °C, and then calcined at 500 °C for 4 h in air. All obtained catalysts were denoted by the demanded content of active metals (Co–Mn) in the Co–Mn–Al/TiO_2 catalysts, e.g. 0; 5; . . .25; 58.

2.2. Characterization of the catalysts

The prepared catalysts were characterized by chemical analysis (AAS), microanalysis, surface area measurements, powder X-ray diffraction and temperature programmed techniques (TPR, TPD-NH_3 and TPD-CO_2).

Chemical analysis of the calcined catalysts was performed by atomic adsorption spectrometry (AAS) after milling of the sample and its dissolution in aqueous solution of HCl (1:1).

Distribution of metals in the catalysts pellets were measured using a Vega 3SEM Scanning Electron Microscope of Tescan equipped with SDD (silicon drift detector) XFlash 5010 of Bruker for quantitative analysis of chemical elements. The samples were prepared as polished sections and covered by carbon. Conditions of measurements: chamber pressure $< 10^{-2}$ Pa, accelerating voltage 20 kV, and working distance 15 mm, beam size 2 μm, analyzed area ca 50 μm.

Powder X-ray diffraction (XRD) patterns were recorded using an INEL CPS 120 instrument with Cu Kα radiation ($\lambda = 0.15405$ nm, germanium monochromator), in 2θ range of 10–80°, step size 0.05°. The crystallite size of the phases present in pure and supported solids were determined using the Scherrer equation [11]:

$$d = \frac{K\lambda}{\beta_{1/2}\cos\theta},$$

where d is the mean crystalline diameter, λ the X-ray wave length in nm, K the Scherrer constant (0.89), $\beta_{1/2}$ the full width at half maximum (FWHM) of the main diffraction peak of the crystalline phase present (in radians) and θ is the diffraction angle.

Surface area and mesoporous structure of the catalysts were determined by adsorption/desorption of nitrogen at −196 °C using Micromeritics ASAP 2010 instrument. The BET (Brunauer, Emmet, and Taylor), *t*-plot and BJH (Barret, Joyner, and Hallenda) methods were used for evaluation of surface area, volume of micropores and pore size distribution.

Temperature-programmed reduction (TPR) measurements of the calcined samples (0.025 g) were performed with a H_2/N_2 mixture (10 molar% H_2), flow rate of 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 catharometer. Reduction of the grained CuO (0.16–0.315 mm) was employed to calibrate the catharometer response.

Temperature-programmed desorption (TPD) of NH_3 and CO_2 was carried out to examine acid and basic properties of the catalysts surface, respectively. The measurements were accomplished with 0.050 g of a sample in the temperature range of 20–1000 °C, with helium as a carrier gas and CO_2 or NH_3 as adsorbing gases. Prior to the measurement, each sample was calcined in helium to 500 °C, then cooled to 30 °C and an excess of ammonia (ten doses, each 840 μl) was applied on the sample. Then, the sample was flushed with helium for 1 h to remove physically adsorbed ammonia. The heating rate of 20 °C min^{-1} was applied and a change in ammonia concentration of the gas mixture was registered by a mass spectrometer. During the experiments the following mass contributions m/z were collected: 2-H_2, 18-H_2O, 16-NH_3, and 44-CO_2. The spectrometer was calibrated by dosing the known amount (840 μl) of CO_2 or NH_3 into the carrier gas (He) in each experiment to obtain quantitative desorption data. The TPR and TPD experiments were evaluated using OriginPro 7.5 software with an accuracy of ±5%.

2.3. Catalyst activity and selectivity measurements

The catalytic reaction was carried out in a fixed-bed glass reactor (5 mm i.d.). Reaction was performed in the temperature range from 100 to 400 °C with linearly increased temperature of the furnace by the rate of 2.25 °C min^{-1}. The activity of a catalyst (0.20 g of the sieved grains with the particle size of 0.16–0.315 mm) was examined at 20 $m^3\,kg^{-1}\,h^{-1}$ space velocity (GHSV).

Examination of the catalytic activity of the pelletized catalysts was carried out in a fixed bed glass reactor (28 mm i.d.) in the same temperature range as the catalyst grains. The catalyst extrudates layer (14 ml, layer height 25 mm) were placed in the middle of the furnace. The inlet concentration of ethanol in the air was 1.4 g m^{-3}. Reaction products were analyzed using a gas chromatograph Hewlett-Packard 6890 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). The accuracy of the conversion and selectivity determination was ±2%. Concentration of CO and CO_2 was measured by an IR analyzer (Ultramat 23, Siemens, Germany). Temperatures T_{50}EtOH (the temperature at which 50% conversion

Table 1
Chemical analysis and characteristic values of porous structure of the grained supported Co–Mn–Al/TiO_2 catalysts.

Sample	Co + Mn (wt.%)	Co (wt.%)	V_{meso} ($cm^3 g^{-1}$)	S_{BET} ($m^2 g^{-1}$)	$R = 2V/S_{BET}$ (nm)	C_{BET}	V_{micro} ($mm^3 g^{-1}$)	S_{meso} ($m^2 g^{-1}$)	C_{modif}
0	0	0	0.54	200	4.2	99	47	130	10
5	4.63	3.95	0.39	94	6.8	123	22	56	12
10	8.44	7.14	0.36	93	5.8	90	21	60	10
15	12.80	10.70	0.32	86	5.9	114	20	53	12
20	19.98	15.88	0.27	74	5.4	119	18	44	12
25	24.10	19.50	0.21	71	4.6	96	16	43	12
58	58.30	47.32	0.08	42	4.2	88	9	26	12

of ethanol was observed) and T_{50}VOC (the temperature at which 50% conversion of all organic compounds to CO_2 was observed) were chosen as a measure of the catalyst activity. Selectivity of the catalysts during ethanol conversion was expressed in the form of observed maximum of reaction intermediates recorded by the IR analyzer (CO concentration in ppm) and the GC peak area of the reaction intermediate (acetaldehyde).

3. Results and discussion

3.1. Catalysts in the form of grains

Chemical analysis of the prepared samples showed that concentration of metals (Co and Mn) varied in the range of 0–58 wt.% (Table 1). The sample with the highest amount of active metals was that one prepared by calcination of a mixture of appropriate metal nitrates (Co, Mn, Al) without the support. The Co/Mn molar ratio in all samples was close to value four.

Examination of the porous structure of titania support showed that the support posses high surface area and volume of mesopores ($S_{BET} = 200\,m^2\,g^{-1}$, $V_{meso} = 0.54\,cm^3\,g^{-1}$). Other important characteristic values of its porous structure are summarized in Table 1. Porous structure of the calcined catalysts prepared by impregnation of the support with metal nitrates substantially differed from the support (Table 1). Volume of mesopores decreased with increasing amount of incorporated compounds of active metals, from $0.39\,cm^3\,g^{-1}$ for the catalyst having 5 wt.% of active metal oxides to $0.08\,cm^3\,g^{-1}$ for the mixture of the unsupported Co–Mn–Al oxides. Surface area of the support decreased approximately to a half by introduction of the lowest amount of the metals (5 wt.%). With further increase of the incorporated amounts of metals surface area of the catalysts did not significantly change. The catalyst prepared by calcination of metal nitrates showed the lowest surface area of all ($42\,m^2\,g^{-1}$). Average radius of pores calculated using volume of mesopores and BET surface area decreased with increasing amount of incorporated active metals. As can be seen from the high constants of C_{BET}, all catalysts including the support have to possess some amount of micropores. The *t*-plot method confirmed their presence in all catalysts and Table 1 documents their decreasing amount with increasing concentration of incorporated catalytic components. The lowest portion of micropores showed the unsupported catalyst prepared by calcination of the mixture of Co, Mn, Al nitrates. The decrease of micropores volumes can be explained by filling of micropores with the active components during the support impregnation. Surface of mesopores was calculated using a three-parameter equation [12], and it roughly does two thirds of the BET surface area for all catalysts. Contrary to the C_{BET} constants varying from 88 to 123, the constants C_{modif} obtained from the modified BET equation show practically identical values (around 12) confirming similar adsorption properties of the samples.

Temperature programmed reduction of the grained supported catalysts (Fig. 1) revealed two main reduction peaks, the maximum of the first one was around 425 °C (reduction of Co_3O_4 to CoO and MnO_2 to Mn_3O_4) and the second within the limits 520–580 °C (reduction of CoO, Mn_2O_3 and CoAl spinel) [10,13,14]. Small reduction peak appearing as a shoulder at about 300 °C was slightly increasing with the content of Co–Mn oxides in the catalysts. Oxidation state of manganese in the solids prepared by thermal decomposition of manganese nitrate was studied previously [15], as well as in the solids prepared from manganese nitrate by precipitation [10,16,17]. During calcination in air, following processes occur in the sample:

(i) 145–370 °C – removal of fixed water

$$2MnOOH \rightarrow \gamma\text{-}Mn_2O_3 + H_2O$$

(ii) 395–470 °C – oxidation of γ-Mn_2O_3

$$\gamma\text{-}Mn_2O_3 + 0.5O_2 \rightarrow 2(\beta\text{-}MnO_2)$$

Similarly, the Co^{2+} species are also partly oxidized to Co^{3+} ones during calcination. The Co 2p electron spectra revealed [18] the presence of both Co^{2+} and Co^{3+} species in the ratio Co^{2+}/Co^{3+} of 1.13 in the Co–Mn–Al mixed oxides.

From Fig. 1 it is also noticeable that position of the first main peak does not change with variable Co–Mn concentration, whereas position of the second peak slightly moves with increasing Co–Mn concentration to higher temperature except the peak position of the catalyst having 25 wt.% of Co–Mn metals. In contrast to the catalysts with lower concentration of Co–Mn metals which were impregnated in a single step, this sample was prepared by repeating impregnation of titania in order to gain the catalyst with the highest concentration of active metals. After each impregnation the sample was calcined to 500 °C for 4 h. Different behavior of this sample

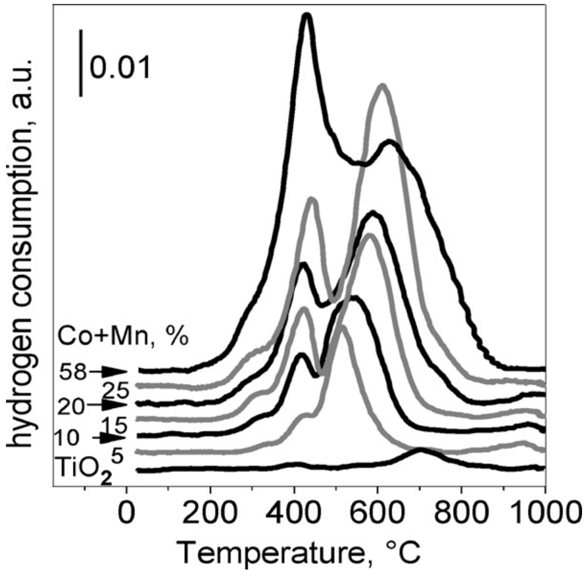

Fig. 1. Temperature programmed reduction curves of the supported Co–Mn–Al catalysts having various amounts of active components (Co + Mn) on titania.

Table 2
Characterization of the supported Co–Mn–Al/titania catalysts – size of crystallites, amount of consumed hydrogen during TPR, amounts of acidic and basic sites, and catalytic activity and selectivity in total oxidation of ethanol.

Sample	Co + Mn (wt.%)	Size (nm)	H_2[a] (mmol g^{-1})	H_2[b] (mmol g^{-1})	NH_3[b] (mmol g^{-1})	CO_2[b] (mmol g^{-1})	T_{50}EtOH (°C)	T_{50}VOC (°C)	CO (ppm)	AcAld (pA s)
0	0.0	0	0.53	0.16	1.15	0.01	203	210	618	18
5	4.6	15.7	1.35	0.59	0.77	0.02	145	180	444	20
10	8.4	16.6	2.34	0.93	0.71	0.03	152	179	425	25
15	12.8	25.7	2.86	1.03	0.68	0.02	135	167	0	20
20	20.0	31.4	3.75	1.39	0.59	0.03	130	165	0	33
25	24.1	35.3	5.36	1.77	0.52	0.03	130	169	0	41
58	58.3	44.1	13.6	6.3	0.22	0.02	174	221	n.dtd	77

n.dtd – not determined.

[a] 25–1000 °C.

[b] 25–500 °C.

during reduction might be explained by different size of the metal compounds, as the repeating calcination could lead to the increase of metal oxides particle size not having such close contact with the support, and, therefore, to the decrease in the reduction temperature. As shown in Table 2, the size of crystalline phases calculated from Scherrer equation gradually increases with increasing concentration of metals in the catalysts, and therefore, such elucidation of the second reduction peak maximum shift cannot be correct. The shift of this peak to lower temperature for the catalyst with 25 wt.% Co + Mn is likely caused by slightly different composition of the catalyst, namely by higher Co/Mn molar ratio. The Co/Mn molar ratio is gradually decreasing from 5.4 for the catalyst with 5 wt.% Co + Mn to 3.7 for the catalyst with 58 wt.% Co + Mn. The catalyst having 25 wt.% Co + Mn shows the Co/Mn molar ratio 4.4 and deviate from the tendency of decreasing Co/Mn molar ratio with increasing Co + Mn concentration in the titania supported catalysts. Higher concentration of Co oxides in this catalyst could manifest itself in the decrease of reduction temperature peak.

Table 2 summarizes quantitative data obtained from TPR and TPD-NH_3, CO_2 measurements. As expected, total amount of reducible compounds increases with the amount of incorporated Co–Mn components. The amount of the easily reducible compounds (amount of hydrogen consumed in the temperature range of 25–500 °C) also increased with increasing amount of active components in the catalysts. From the comparison of the amounts of ammonia and CO_2 desorbed from the catalyst in the temperature range of 25–500 °C follows that the surface of all catalysts is substantially more acidic than basic and that incorporation of Co and Mn oxides on the support leads to decrease in acidity of the samples, due to, very likely, covering of the acidic sites, which are present in the support, by the metal oxides.

Catalytic activity in ethanol oxidation is characterized by the temperatures of T_{50}EtOH and T_{50}VOC that are summarized in Table 2. Pure support, titania, oxidizes ethanol to CO_2 at relatively low reaction temperature (T_{50}VOC = 210 °C). Reason of such high activity is probably in its high surface area. Incorporation of the Co and Mn metal oxides decreased this temperature by ca 50 °C. The temperature T_{50}EtOH is always lower than the temperature T_{50}VOC indicating that ethanol is oxidized to reaction intermediates, mainly acetaldehyde, more easily than the two main intermediates, acetaldehyde and CO, to CO_2. The most active catalysts from the examined set of titania-supported catalysts are those comprising the highest concentration of active components on the support. It was confirmed that oxidation activity of the grained catalysts is proportional to the amount of easily reducible components present in the catalysts. The most active grained catalyst, containing 20 wt.% of active components, oxidized 50% of organic compounds to CO_2 at 165 °C, while the least active catalyst was the one prepared by drying and calcination of metal nitrates likely because of very low surface area.

Selectivity of the ethanol oxidation substantially differed with the amount of active metals in the catalysts (Table 2). Two main reaction intermediates were observed in the reaction mixture in dependence on catalyst composition: CO and acetaldehyde. Over pure titania the main reaction intermediate was CO which reached its maximum value of 618 ppm. The observed maximum in the CO concentration decreased with increasing concentration of Co and Mn oxides in the catalysts. The catalysts with the highest concentration of Co and Mn oxides did not produce CO at all. Concentration of the other reaction intermediate, acetaldehyde, in the reaction mixture expressed as the GC peak area also changed with the concentration of Co + Mn oxides in the catalyst. Observed maximum in concentration of acetaldehyde in the reaction mixtures increased with increasing amount of Co + Mn oxides in the catalysts (from 18 to 77 pA s). As can be seen from Fig. 2, maximum concentration of acetaldehyde formed during oxidation of ethanol decreases with increasing concentration of acidic sites in the catalysts.

3.2. Pelletized catalysts

Titania extrudates (diameter 3 mm) were used for the preparation of the supported Co–Mn–Al catalysts either with uniform or non-uniform active components distribution in the catalyst pellets. Chemical analysis, amount of reducible compounds and characteristic values of the catalyst activity and selectivity are summarized in Table 3. Total amounts of transition metals deposited over the support varied from 1.5 to 12 wt.% depending on the way of catalyst preparation. Pore-filling method and sufficient time (>15 min) used during the spray method of impregnation resulted in higher

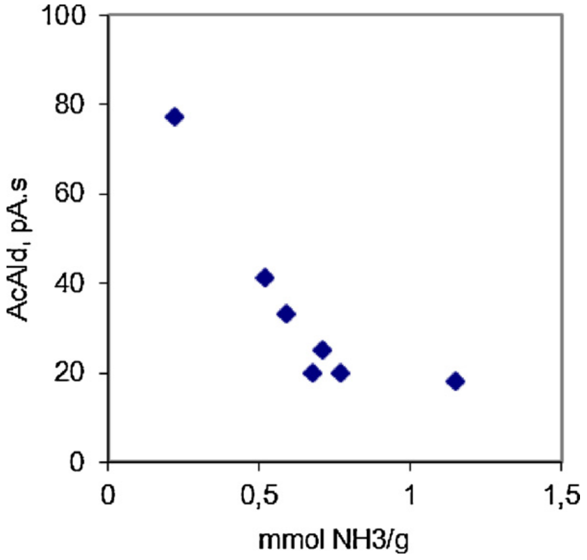

Fig. 2. Dependence of maximum concentration of acetaldehyde formed during oxidation of ethanol on acidity of the catalysts.

Table 3
Chemical analysis, physical–chemical properties and characteristic values of the catalytic activity and selectivity of the pelletized catalysts obtained at oxidation of ethanol.

Sample	Preparation	Co + Mn (wt.%)	Co (wt.%)	H_2[a] (mmol g^{-1})	H_2[b] (mmol g^{-1})	T_{50}EtOH (°C)	T_{50}VOC (°C)	CO (ppm)	AcAld (pA s)
1.5	Spraying	1.28	1.14	0.51	0.18	197	232	614	23
2.5	Spraying	2.48	2.16	0.81	0.45	193	228	400	30
6	Spraying	6.37	5.43	2.39	1.66	179	228	182	22
11	Pore-filling	11.17	9.30	2.46	1.62	186	222	130	25
12	Pore-filling	11.60	9.70	2.56	1.19	175	223	111	26

AcAld – acetaldehyde.
[a] 25–1000 °C.
[b] 25–500 °C.

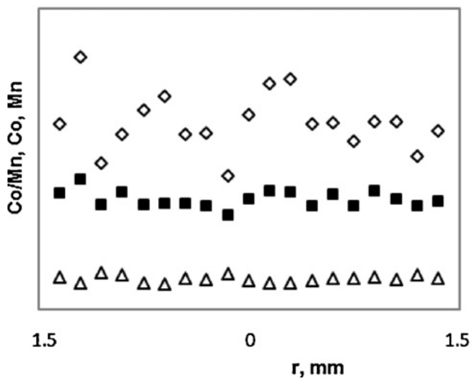

Fig. 3. Concentration profiles of Co and Mn, wt.%, in extrudates of Co–Mn–Al/TiO_2 catalysts. Distribution of Co and Mn in dependence on the total amount of both metals (Co + Mn): (left) uniform, 6.5 wt.% and (right) non-uniform, 1.5 wt.%. Concentration of Co (■), Mn (△), and molar ratio Co/Mn (◊).

concentration of metals and their uniform distribution in the catalysts.

Fig. 3(left) illustrates uniform distribution of metals across the catalyst diameter when the catalysts were prepared by pore-filling method (the catalysts with approximately 11 and 12 wt.% of active metals Co + Mn). The Co/Mn molar ratio throughout the catalyst is near to value 4. On the contrary, the catalyst prepared by spraying of extrudates by an aqueous solution of Co, Mn and Al nitrates in a rotating pan to meet lower concentration of active components (1.5 wt.%) showed non-uniform distribution. Transition metals Co and Mn were concentrated in the outer shell of the extrudates, approximately 0.9 mm thick (Fig. 3, right). Only in this shell, the Co/Mn molar ratio met the value of 4; in the extrudate centre this ratio achieved the value about 1 only. The finding indicates higher affinity of TiO_2 to Mn nitrate than to Co nitrate that reflects in the higher rate of Mn salt adsorption.

The course of the temperature programmed reduction curves of the titania extrudates with various amounts of Co, Mn, Al oxides is shown in Fig. 4. The catalyst with the lowest concentration of reducible transition metal oxides (1.5 wt.% of Co + Mn) exhibits only one low peak with temperature maximum at 492 °C. When the Co + Mn metals concentration was increased to 2.5 wt.%, the T_{max} shifted slightly to lower temperature (440 °C). Position of the formed peak corresponds to the first main reduction peak in the grained Co–Mn–Al/TiO_2 catalysts. The catalysts with more than 10 wt.% of Co + Mn metals exhibited similar reduction peaks as the grained impregnated catalysts (Fig. 1).

Catalytic activities of the pelletized catalysts were examined in the same experimental set-up and under the same reaction conditions as those of the grained catalysts. The only difference was the size of catalyst pellets and the dimension of reactor. The data obtained are summarized in Table 3. It is seen that increasing amount of Co + Mn metals from 1.5 to 12 wt.% leads to decrease in the value of T_{50}EtOH (by 25 °C). Other way of catalyst activity evaluation – examination of the T_{50}VOC temperature – showed also the increase in catalyst activity, but not so high. The difference between the two temperatures was only 11 °C. It indicates the activity of the catalysts with non-uniform distribution of metal oxides in the pellets is higher than that of the catalysts with the uniform distribution (Fig. 5). The observed lower catalytic activity of the pelletized catalysts is likely caused by the influence of lateral back-mixing, wall effect and/or mass transfer (inner and outer) limitation of reaction components during the experiments.

As concerned the selectivity of the pelletized catalysts (Table 3), main observed reaction intermediate was carbon monoxide. Its amount was decreasing with increasing concentration of Co + Mn metal oxides in the catalysts. Formation of the CO (maximum observed concentration in the reaction mixture) depended on the amount of easily reducible compounds in the catalysts, as clearly

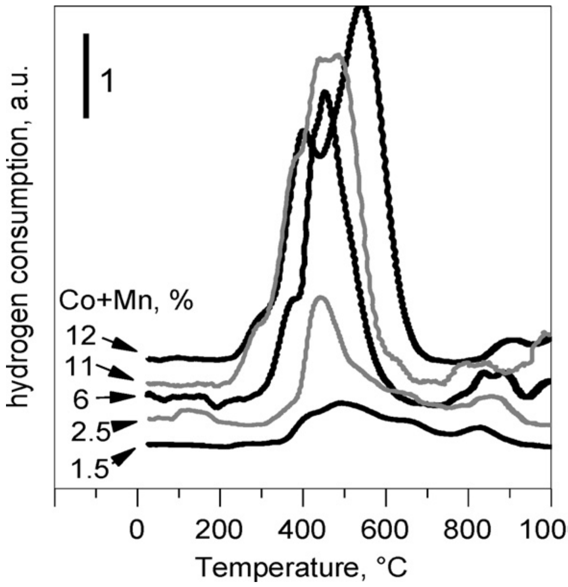

Fig. 4. Temperature programmed reduction curves of the Co–Mn–Al catalysts prepared over titania extrudates.

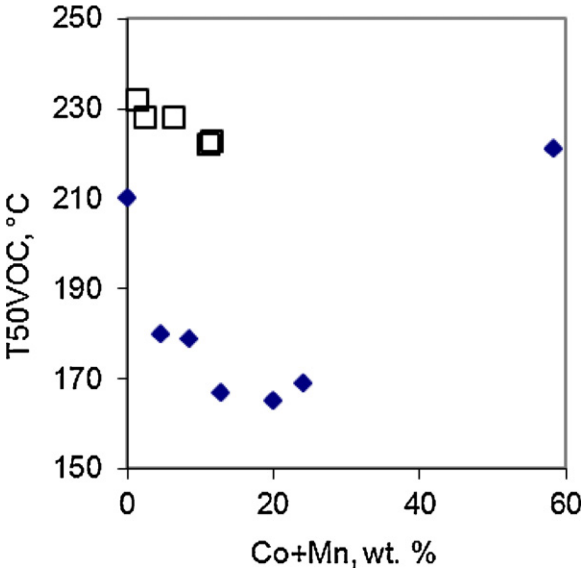

Fig. 5. Catalytic activity (T_{50}VOC) of the Co–Mn–Al/TiO$_2$ catalysts examined in the form of grains (♦) and pellets (□).

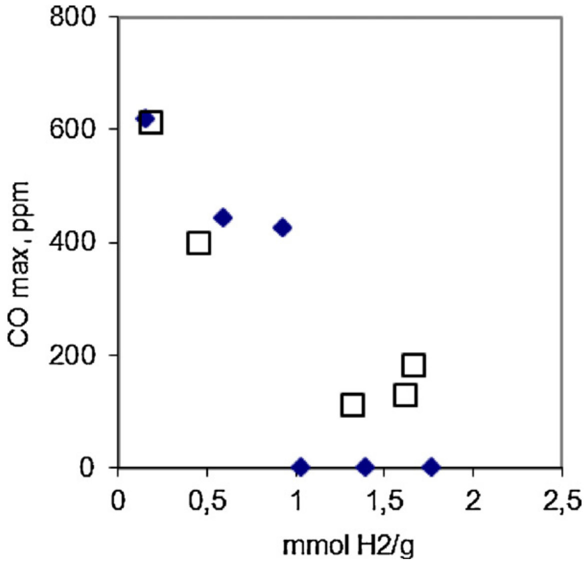

Fig. 6. Dependence of maximum concentration of CO observed in the reaction mixture on the amount of components reducible in the temperature range of 25–500 °C (grains ♦ and pellets □).

shown in Fig. 6. Concentration of CO decreased substantially in case the catalysts possess more than 1.5 mmol H_2 g^{-1} of components reducible in temperature range of 25–500 °C, regardless they are in the form of grains or pellets.

4. Conclusion

Deposition of Co–Mn–Al oxides (molar ratio of metals 4:1:1) over titania caused the increase in catalytic activity in ethanol oxidation, maximum in activity being found for the catalyst with ca 20 wt.% of transition metals oxides Co + Mn. Though titania also oxidized ethanol to CO$_2$, the course of reaction intermediates with increasing reaction temperatures differed from those observed over catalysts containing transition metal oxides: among the reaction intermediates CO was in the highest concentration. On the other hand, the catalysts with the highest concentration of Co and Mn oxides did not produce CO at all. Physical–chemical properties of the catalysts play key role in the selectivity: CO formation proceeds over the catalysts with low concentration of easily reducible oxides and high acidity of the catalyst.

The size of support particles and the way of Co–Mn–Al oxides deposition over the support is also important, especially for catalytic activity. The catalysts pellets showed lower activity than the grains, which is likely caused by the influence of lateral backmixing, wall effect and mass transfer (inner and outer) limitation of reaction components during the catalytic experiments. However, the decrease in activity of the pelletized catalysts, caused by presence of macrokinetic effects during their testing, is lower in case the active components are deposited in the outer shell of the catalyst extrudates confirming more advantageous distribution of active metals in the outer shell of the pellets.

Acknowledgements

This work was supported by the Czech Science Foundation (P106/10/1762 and GD203/08/H032).

References

[1] K.C. Taylor, Catalysis – Science and Technology, vol. 5, Springer, Berlin, 1984, p. 120.
[2] E.S.J. Lox, B.H. Engler, in: G. Ertl, H. Knoezinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 4, VCH, Weinheim, 1997, p. 1664.
[3] H.A. Iones, H.S. Taylor, J. Phys. Chem. 27 (1923) 623.
[4] A.B. Lamb, W.C. Bray, J.C.W. Frazer, Ind. Eng. Chem. 12 (1920) 213.
[5] F.S. Stone, Advances in Catalysis, vol. 13, Academic Press, New York, 1962, p. 1.
[6] B.I. Yang, S.F. Chan, Y.Z. Chen, J. Catal. 130 (1991) 52.
[7] A. Bielanski, J. Haber, Oxygen in Catalysis, Marcel Dekker, Inc., New York, 1991.
[8] F. Kovanda, T. Grygar, V. Dorničák, T. Rojka, P. Bezdička, K. Jirátová, Appl. Clay Sci. 28 (2005) 121–136.
[9] L. Obalová, K. Jirátová, F. Kovanda, K. Pacultová, Z. Lacný, Z. Mikulová, Appl. Catal. B 60 (2005) 289–297.
[10] F. Kovanda, T. Rojka, J. Dobešová, V. Machovič, P. Bezdička, L. Obalová, K. Jirátová, T. Grygar, J. Solid State Chem. 179 (2006) 812–823.
[11] B.D. Cullity, Elements of X-ray Diffraction, second ed., Addison-Wesley Publishing Co., Reading, 1978, pp. 102–105.
[12] P. Schneider, Appl. Catal. A 129 (1995) 157.
[13] K. Jirátová, J. Mikulová, J. Klempa, T. Grygar, Z. Bastl, F. Kovanda, Appl. Catal. A 361 (2009) 106–116.
[14] S. Todorova, H. Kolev, J.P. Holgado, G. Kadinov, Ch. Bonev, R. Pereníguez, A. Caballero, Appl. Catal. B 94 (2010) 46–54.
[15] K.J. Euler, R. Kirchhof, Electrochim. Acta 26 (1981) 1383–1386.
[16] F. Kovanda, T. Grygar, V. Dorničák, Solid State Sci. 5 (2003) 1019–1026.
[17] Ye.V. Kuzminskii, A.A. Andriiko, L.I. Nyrkova, J. Power Sources 52 (1994) 49–53.
[18] L. Obalová, K. Pacultová, J. Balabánová, K. Jirátová, Z. Bastl, M. Valášková, Z. Lacný, F. Kovanda, Catal. Today 119 (2007) 233–238.