

## MODIFICATION OF Co-Mn-Al MIXED OXIDE WITH PROMOTERS AND THEIR EFFECT ON PROPERTIES AND ACTIVITY IN VOC TOTAL OXIDATION

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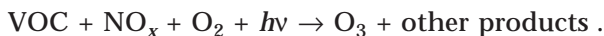
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The activity and selectivity of the Co-Mn-Al mixed oxide catalyst modified with promoters (Pt, Pd, K and La) in total oxidation of volatile organic compounds (toluene and ethanol) were studied. The promoters were introduced at the stage of coprecipitation of a layered double hydroxide (LDH) precursor or impregnation of the mixed oxide obtained by LDH precursor calcination. In total oxidation of toluene, the most active Co-Mn-Al catalysts were those containing low amounts of potassium regardless of the mode of modification, while in total oxidation of ethanol the catalyst impregnated with a higher potassium concentration (3 wt.%) was the most active. Introduction of Pt and Pd in an amount of 0.5 or 0.1 wt.% into the Co-Mn-Al mixed oxide did not improve its catalytic activity. The impregnation method appears to be a more effective mode for preparation of active catalysts than the method using an addition of promoters at the stage of coprecipitation of the LDH precursor. Undesirable reaction intermediate (benzene) was formed when toluene oxidation was carried out over lanthanum- or palladium-containing catalysts. In total oxidation of ethanol, a number of reaction intermediates were produced acetaldehyde being the main one. The catalysts modified at the stage of LDH precursor coprecipitation exhibited a better selectivity (i.e., a lower acetaldehyde formation) than those modified by impregnation. The best results were obtained with the Co-Mn-Al mixed oxide catalyst modified with potassium.

**Keywords:** Catalytic oxidation; Volatile organic compounds; Promoters; Layered double hydroxides; Mixed oxide catalysts.

Volatile organic compounds (VOC) in industrial gases are a serious environmental problem. Some of them exhibit harmful properties, e.g., toxic, carci-

ogenic or narcotic effects. They can react with  $\text{NO}_x$  and oxygen under formation of ozone



Ozone causes human health problems, affects DNA and enzyme functions, its action is toxic for vegetation, impairs quality of some materials, etc. Therefore, an abatement of VOC emissions is considered very desirable.

Concentration of VOC in air can be reduced applying the total catalytic oxidation. Catalysts with noble metals are currently preferred as they are highly active and stable but expensive<sup>1-3</sup>. Platinum is more active in oxidation of saturated and aromatic hydrocarbons, while palladium is more efficient in oxidation of unsaturated hydrocarbons,  $\text{CO}$ <sup>4</sup>, methane<sup>5</sup>, and in oxidation reactions in the presence of water vapor<sup>6</sup>. It is also worth mentioning that palladium is ca. five times cheaper than platinum<sup>7</sup>. Metal oxide alternatives (in particular Cu, Mn, Cr, Co, Mn and Ni oxides) show appreciable activity; they are cheaper but less stable<sup>4,5,8-10</sup>. Mixed oxide catalysts are often obtained by controlled thermal decomposition of the layered double hydroxides (LDH). Chemical composition of LDH can be represented by the general formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}\cdot y\text{H}_2\text{O}]^{x-}$ , where  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  are divalent and trivalent metal cations,  $\text{A}^{n-}$  is an  $n$ -valent anion and  $x$  has usually values between 0.20 and 0.33. After heating at moderate temperatures, LDH give finely dispersed mixed oxides of metals with a sufficiently large surface area and good thermal stability<sup>5</sup>. It was shown previously<sup>10,11</sup> that calcined Co-Mn-Al LDH exhibit very good catalytic activity in total oxidation of toluene and ethanol.

Combination of both groups of active materials, i.e., noble metals and transition metal oxides could give highly active catalysts with a better selectivity and a sufficient stability<sup>12,13</sup>. Very good catalytic properties exhibit also transition metal oxides promoted with potassium<sup>14,15</sup> and lanthanum<sup>16</sup>.

The mode of catalysts modification can also affect the activity of oxide catalysts modified with noble or other metals. The mode of catalyst modification can manifest itself in both the size of active particles and their distribution in the catalyst grain. Modification of oxide catalysts during precursor precipitation makes possible a fine and random distribution of the active metal in the catalyst bulk causing formation of well-dispersed and stable metal particles after calcination<sup>17</sup>.

In the present work, the effect of a small amount of promoters introduced by two methods, impregnation of the mixed oxide catalyst and addi-

tion of promoter during LDH precursor coprecipitation, was studied in order to improve catalytic properties of the parent mixed oxide system. Noble metals (Pd, Pt), La and K were chosen as promoters.

## EXPERIMENTAL

The Co-Mn-Al LDH precursor was prepared by coprecipitation. An aqueous solution (450 ml) of appropriate nitrates,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , with the Co/Mn/Al molar ratio 4:1:1 and total metal ion concentration of  $1.0 \text{ mol l}^{-1}$  was added at a flow rate of  $7.5 \text{ ml min}^{-1}$  into a 1000-ml batch reactor containing 200 ml of distilled water. The flow rate of the simultaneously added solution of  $0.5 \text{ M Na}_2\text{CO}_3$  and  $3 \text{ M NaOH}$  was controlled to maintain reaction pH  $10.0 \pm 0.1$ . The coprecipitation was carried out under vigorous stirring at  $25 \text{ }^\circ\text{C}$ . The resulting suspension was stirred at  $25 \text{ }^\circ\text{C}$  for 1 h, the product was then filtered off, washed with distilled water several times, and dried overnight in air at  $60 \text{ }^\circ\text{C}$ . The dried and powdered product was formed into pellets and calcined in air at  $500 \text{ }^\circ\text{C}$  for 4 h. The obtained catalyst was denoted as parent Co4MnAl sample.

Two modes of modification of Co4MnAl catalyst with promoters were studied:

1) The parent Co4MnAl catalyst, i.e., the calcined LDH precursor was impregnated with aqueous solution of the chosen compound ( $\text{H}_2\text{PtCl}_6$ ,  $\text{La}(\text{NO}_3)_3$  or  $\text{KNO}_3$ ), the solid was dried at  $105 \text{ }^\circ\text{C}$  and then calcined in air at  $500 \text{ }^\circ\text{C}$  for 4 h.

2) Promoters were incorporated into the LDH precursor during coprecipitation, when a corresponding amount of  $\text{H}_2\text{PtCl}_6$ ,  $\text{PdCl}_2$  or  $\text{La}(\text{NO}_3)_3$  was added to the nitrate solution. In the case of catalyst modification with potassium, the washed LDH precursor (filtration cake) was resuspended in a  $\text{KNO}_3$  solution, the concentration of which was adjusted to obtain the desired K content in the calcined product. After 1-h stirring at  $25 \text{ }^\circ\text{C}$ , the solid was filtered off and dried at  $60 \text{ }^\circ\text{C}$  overnight. The dried and powdered precursors containing promoters were formed and calcined in the same way as the parent Co4MnAl catalyst.

The catalysts modified with the following amounts of promoters were prepared (in wt.%): 0.1 and 0.5 Pt, 0.1 Pd, 0.5 and 3 La, 0.5 and 3 K. The modified catalysts were denoted by acronyms with concentration of the promoter and the mode of modification (*im* – impregnation, *co* – incorporation of the promoters at the stage of coprecipitation). For example, 3La-*im* denotes Co4MnAl catalysts containing 3 wt.% La modified by impregnation.

The prepared catalysts were characterized by chemical analysis (AAS), powder X-ray diffraction, thermal analysis, surface area measurements, temperature-programmed reduction (TPR), and temperature-programmed desorption (TPD) of ammonia and  $\text{CO}_2$ .

Powder X-ray diffraction (XRD) patterns were recorded using a Seifert XRD 3000P instrument with  $\text{CoK}\alpha$  radiation ( $\lambda = 0.179 \text{ nm}$ , graphite monochromator, goniometer with the Bragg-Brentano geometry) in the  $2\theta$  range  $10\text{--}80^\circ$ , with steps of  $0.05^\circ$ .

Thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA) were performed using a Setaram Setsys Evolution instrument equipped with the quadrupole mass spectrometer OmniStar (Pfeiffer VakuuM). The heating rate  $10 \text{ }^\circ\text{C min}^{-1}$ , air flow rate  $75 \text{ ml min}^{-1}$  and 50-mg samples were used. Gaseous products were continually monitored for the chosen mass numbers  $m/z$  ( $18\text{-H}_2\text{O}^+$  and  $44\text{-CO}_2^+$ ).

Surface areas and mesoporous structures were determined by adsorption/desorption of nitrogen at  $-196 \text{ }^\circ\text{C}$  using a Micromeritics ASAP 2010 instrument. The BET and BJH (Barret-

Joyner-Hallenda) methods were used for evaluation of surface area and pore size distribution, respectively.

Temperature-programmed reduction (TPR) measurements were carried out to find out reducibility of the catalysts. Experiments were performed with a  $\text{H}_2/\text{N}_2$  mixture (10 mole %  $\text{H}_2$ ), flow rate  $50 \text{ ml min}^{-1}$  and linear temperature increase  $20 \text{ }^\circ\text{C min}^{-1}$  up to  $1000 \text{ }^\circ\text{C}$ . A change in  $\text{H}_2$  concentration was detected with a mass spectrometer Omnistar 300 (Pfeiffer Vakuum). Reduction of the grained  $\text{CuO}$  (0.16–0.315 mm) was repeatedly performed to calculate absolute values of the hydrogen consumed during reduction.

Temperature-programmed desorption (TPD) of  $\text{NH}_3$  and  $\text{CO}_2$  was carried out to examine acid and basic properties of the catalysts, respectively. The measurements were accomplished in the temperature range  $20\text{--}1000 \text{ }^\circ\text{C}$ , with helium as a carrier gas and  $\text{CO}_2$  or  $\text{NH}_3$  as adsorbing gases. The heating rate  $20 \text{ }^\circ\text{C min}^{-1}$  was applied. During the experiments the following mass contributions  $m/z$  were collected:  $2\text{-H}_2$ ,  $18\text{-H}_2\text{O}$ ,  $16\text{-NH}_3$  and  $44\text{-CO}_2$ . The spectrometer was calibrated by dosing an amount ( $840 \mu\text{l}$ ) of  $\text{CO}_2$  or  $\text{NH}_3$  into the carrier gas (He) in every experiment. The TPR and TPD experiments were evaluated using OriginPro software with an accuracy of  $\pm 5\%$ .

The catalytic reaction was carried out in a fixed-bed glass reactor (5 mm i.d.) in the temperature range  $100\text{--}400 \text{ }^\circ\text{C}$  (the furnace temperature linearly increasing at  $3.5 \text{ }^\circ\text{C min}^{-1}$ ). The catalyst (sieved grains with the particle size 0.16–0.315 mm) was examined at  $10 \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1}$  space velocity. The inlet concentration of VOC in air was  $1 \text{ g m}^{-3}$  (toluene and ethanol were chosen as model compounds). The reaction products were analyzed using a Hewlett-Packard 6890 gas chromatograph equipped with a FID detector and a capillary column (HP-5 19091 J-413,  $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ mm}$  with 5% of poly(methylphenylsiloxane). The accuracy of the conversion and selectivity determination was  $\pm 2\%$ . The temperature  $T_{50}$  (the temperature at which 50% conversion of a reactant was observed) was chosen as a measure of the catalyst activity. Inaccuracy in the conversion determination  $\pm 2\%$  manifested itself in ca.  $\pm 3\%$  inaccuracy of  $T_{50}$  values.

## RESULTS AND DISCUSSION

### *Catalytic Activity*

The results of total oxidation of toluene and ethanol over the parent and modified Co4MnAl catalysts are summarized in Table I.

It can be seen that the catalytic activity of the parent Co4MnAl catalyst, expressed as the temperature  $T_{50}$  at which 50% conversion of a reactant is observed, in the oxidation of toluene is relatively high ( $T_{50}$  of  $158 \text{ }^\circ\text{C}$  was measured). An impregnation of the parent catalyst with the chosen promoters did not change its catalytic activity substantially: Potassium and lanthanum slightly improved the catalyst activity (the  $T_{50}$  value decreased to ca.  $150 \text{ }^\circ\text{C}$ ) while an addition of platinum surprisingly decreased the activity ( $T_{50}$  increased to  $169 \text{ }^\circ\text{C}$ ). An introduction of various amounts of potassium into the Co4MnAl catalyst resulted in only slight changes of its activity: the catalyst containing 0.5 wt.% K exhibited  $T_{50}$  lower by  $8 \text{ }^\circ\text{C}$ ,

TABLE I  
Physicochemical and catalytic properties of modified Co<sub>4</sub>MnAl catalysts

Catalyst <sup>a</sup>	Co <sub>4</sub> MnAl	0.5Pt-im	0.5K-im	3K-im	3La-im	0.1Pt-co	0.1Pd-co	0.5K-co	3K-co	0.5La-co	3La-co
Modifier	0	0.45	0.43	2.34	2.60	0.09	0.07	0.48	2.50	0.54	2.54
wt. %											
Na, wt. %	0.11	-0.1	-0.1	-0.1	-0.1	0.11	0.11	0.57	0.55	0.07	0.05
TPR <sup>b</sup> mmol H <sub>2</sub> /g	13.05	15.51	16.51	17.51	14.55	14.60	17.51	13.26	15.39	14.41	15.69
TPR <sup>c</sup> mmol H <sub>2</sub> /g	4.33	10.14	5.73	6.08	5.34	4.10	8.52	4.32	6.77	4.65	5.44
Acidity <sup>c</sup> mmol/g	0.35	0.43	0.25	0.11	0.33	0.42	0.38	0.32	0.13	0.50	0.33
Basicity <sup>c</sup> mmol/g	0.15	0.09	0.08	0.35	0.10	0.16	0.11	0.23	0.21	0.20	0.23
T <sub>50</sub> (toluene) °C	158	169	150	162	152	172	172	135	188	171	170
T <sub>50</sub> (ethanol) <sup>d</sup> °C	172	177	155	131	171	192	189	160	158	185	192
Byproducts <sup>e</sup> a.u.	8.1	10.5	17.3	11.6	8.7	1	0.55	7.6	5.6	1	0

<sup>a</sup> Explanation of the catalyst acronyms see Experimental. <sup>b</sup> 20–1000 °C. <sup>c</sup> 25–500 °C. <sup>d</sup> Conversion of all organics is 50%. <sup>e</sup> Reaction intermediates in ethanol oxidation (expressed as chromatographic peak areas, pA.min, of all determined intermediates when ethanol oxidation was 90%).

while the catalyst containing 3 wt.% K showed  $T_{50}$  higher by 4 °C in comparison with the parent one. On the other hand, introduction of Pt, Pd or La at the stage of precursor coprecipitation decreased the catalyst activity nearly to the same level regardless of the modifying metal ( $T_{50}$  increased by 12–14 °C). Potassium affected the parent catalyst activity in a different way depending on the amount added: low concentration (0.5 wt.% K) led to an essential rise in activity ( $T_{50}$  decreased to 135 °C), while a higher amount (3 wt.% K) caused a substantial activity decrease ( $T_{50}$  of 188 °C).

It is evident that the mode of modification plays a very important role in modification of the catalyst with potassium. Potassium added in a low concentration to a freshly precipitated LDH precursor (at the stage of coprecipitation) is randomly distributed throughout the whole precursor volume, and likely changes efficiently the bond strength of oxygen to transition metal cations and in this way affects oxygen mobility<sup>15</sup>. Higher concentration of potassium (3 wt.%) added to the LDH precursor evidently raised the K content in the calcined product to such a value that caused a substantial decrease in catalyst activity (temperature  $T_{50}$  increased by 53 °C). On the other hand, the effect of potassium concentration added to the parent catalyst at the stage of impregnation is much lower (temperature  $T_{50}$  increased only by 12 °C when concentration of K increased in the same range). Thus, it can be concluded that a non-dried LDH structure is more sensitive to the introduced potassium than a tough structure of the mixed oxide formed in LDH calcination, which is to be modified by impregnation.

In total oxidation of ethanol, some catalysts promoted with Pt, Pd and La exhibited a slight increase in activity (e.g., 3La-*im*), the others a decrease in catalytic activity (Table I) within the limits  $\pm 10$  relative % of the  $T_{50}$  found for the parent catalyst. The catalysts containing higher concentration of potassium modified by both impregnation and coprecipitation, showed the highest activity (the 3K-*im* sample was the most active of all the examined catalysts).

It follows from the experiments in total oxidation of toluene that modification of the Co<sub>4</sub>MnAl catalyst with a low amount of potassium (0.5 wt.% K) is sufficient for obtaining very active catalysts. However, in the case of total oxidation of ethanol it is necessary to add a higher amount of potassium to achieve the highest catalyst activity. An addition of noble metals like Pt or Pd in amounts of 0.5 (Pt) or 0.1 (Pd) wt.% to the parent Co<sub>4</sub>MnAl catalyst did not improve its catalytic activity at all. Comparing both modes of the catalyst modification from the catalytic activity point of view, modification of the fresh Co<sub>4</sub>MnAl precipitate with potassium is better in tolu-

ene oxidation, while impregnation gives a more effective catalyst in ethanol oxidation.

### *Catalyst Selectivity*

Knowledge of reaction intermediates arising in total oxidation of VOC is important for industrial applications of the catalysts, as the intermediates can impair the quality of air more extensively than the original waste VOC.

Total catalytic oxidation of toluene over the parent and modified catalysts did not lead to a measurable amount of reaction intermediates except the catalysts modified with lanthanum (3La-*im*, 3La-*co*) and palladium (0.1Pd-*co*), over which some amounts of benzene in the effluent were detected. The following reaction mechanism can explain formation of benzene in toluene oxidation: In the presence of a heterogeneous catalyst, breaking of the C-C bond between the methyl group and benzene ring can proceed as the first step of toluene oxidation, followed by oxidation of the forming intermediates to CO<sub>2</sub> and H<sub>2</sub>O<sup>18</sup>.

In total oxidation of ethanol, a considerable amount of reaction intermediates was produced over the examined catalysts, especially at lower ethanol conversions. Acetaldehyde was found as the main reaction intermediate. Small amounts of acetic acid were detected in some cases at low conversions of ethanol (<50%). We determined the amount of the reaction intermediates as a function of ethanol conversion (Fig. 1), in order to classify more precisely the effect of the chosen promoter on catalyst selectivity. Great differences in the selectivity of the examined catalysts were observed when ethanol conversion was higher than 50%. When we take the selectivity of the parent Co4MnAl catalyst as a reference, we can conclude that the modifiers (Pt, Pd, La and 0.5 wt.% K) introduced by impregnation into the parent catalyst affected its selectivity only slightly. Very likely, all such modified catalysts are not sufficiently active to oxidize acetaldehyde, which needs higher reaction temperatures to be transformed into CO<sub>2</sub> and H<sub>2</sub>O. On the other hand, the catalysts containing the same promoters (Pt, Pd, La and 0.5 wt.% K) but modified at the stage of coprecipitation were much more selective in CO<sub>2</sub> formation and exhibited similar results: very low concentrations of reaction intermediates were observed in a wide range of ethanol conversion (35–95%). A higher amount of K (3 wt.%) in the catalyst improved its selectivity regardless of the mode of catalyst modification, very likely, as a result of lower catalyst activity. But again, the impregnated catalyst exhibited a worse selectivity in the formation of final oxidation products than that modified at the stage of precursor coprecipitation, as

very high acetaldehyde concentrations were observed even at high ethanol conversions (>90%). It follows from the obtained results that in oxidation of ethanol, the most selective catalysts for the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  formation have to possess optimum physicochemical properties necessary for fast oxidation of acetaldehyde.

### *Physicochemical Properties of the Prepared Precursors and Catalysts*

Differential thermal analysis of the parent  $\text{Co}_4\text{MnAl}$  LDH showed two major endothermic effects characteristic of hydrotalcite-like compounds. The first with a minimum at  $178^\circ\text{C}$  was ascribed to release of interlayer water and the second one at  $233^\circ\text{C}$ , accompanying  $\text{H}_2\text{O}$  and  $\text{CO}_2$  evolution, was associated with complete dehydroxylation of hydroxide layers and decomposition of interlayer carbonate. According to XRD, the  $\text{Co}_4\text{MnAl}$  LDH precursor was transformed<sup>10</sup> to a spinel-like mixed oxide at ca.  $200^\circ\text{C}$ . The addition of promoters to the  $\text{Co}_4\text{MnAl}$  LDH precursor slightly decreased its thermal stability; the endothermic minima on DTA curves as well as maxima of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  evolution were shifted to lower temperatures. Modification of the LDH precursor with promoters did not change the

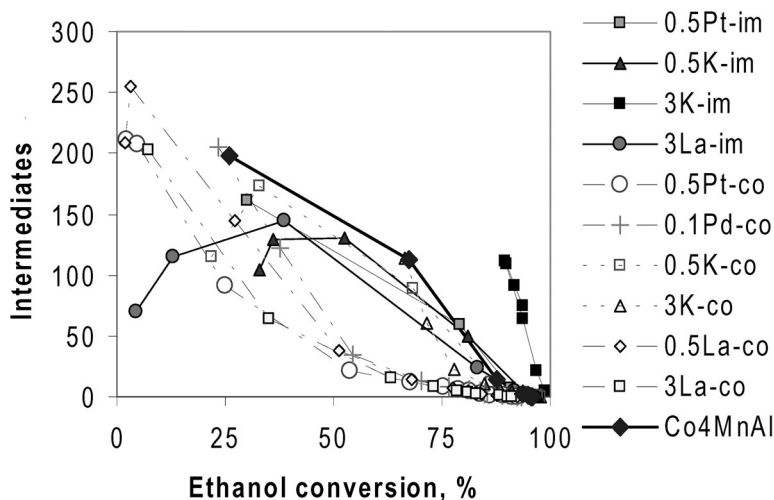


FIG. 1

Dependence of relative concentration of intermediates in the reaction mixture (expressed as the area of the corresponding GC peaks) at ethanol conversion over the modified  $\text{Co}_4\text{MnAl}$  catalysts



phase composition of the calcined products. In the powder XRD patterns of the prepared catalysts, only a spinel-like mixed oxide was found.

The surface area of the parent and modified Co<sub>4</sub>MnAl catalysts (Table II) do not much differ. The impregnated catalysts showed slightly lower  $S_{\text{BET}}$  values (80–93 m<sup>2</sup> g<sup>-1</sup>) than the parent (96 m<sup>2</sup> g<sup>-1</sup>), while the catalysts modified during coprecipitation exhibited slightly higher surface areas (96–111 m<sup>2</sup> g<sup>-1</sup>). In view of these findings, we can state that the mode of modification of the Co<sub>4</sub>MnAl catalyst does not cause any significant change in the surface area and that the determined  $S_{\text{BET}}$  values of the modified samples vary in the range  $\pm 15\%$ .

Modification of the Co<sub>4</sub>MnAl catalyst with Pt, Pd and La by impregnation did not affect the mesopore volume of the catalysts, as the porous structure of the calcined LDH precursor is likely sufficiently tough and, thus, more resistant to the forces acting during drying the impregnated catalysts and the following calcination procedure. On the other hand, catalyst modification at the stage of LDH precursor coprecipitation led to a substantial increase in the catalyst mesopore volume. Only the catalysts modified with potassium showed a decreasing mesopore volume with increasing po-

TABLE II  
Surface area and porous structure of the parent and modified Co<sub>4</sub>MnAl catalysts

Catalyst	$S_{\text{BET}}$ m <sup>2</sup> /g	$V_{\text{micro}}^a$ mm <sup>3</sup> /g	$S_{\text{meso}}$ m <sup>2</sup> /g	$C_{\text{m}}$	Pore volume $V^b$ cm <sup>3</sup> /g	$d_{\text{av}}^c$ nm	$\rho_{\text{He}}$ g/cm <sup>3</sup>
Co <sub>4</sub> MnAl	96.2	24.0	60.5	8	0.40	16.5	4.5
0.5Pt- <i>im</i>	80.3	19.7	52.4	10	0.33	15.7	4.9
0.5K- <i>im</i>	80.7	20.2	51.2	10	0.36	17.3	4.8
3K- <i>im</i>	87.9	24.1	49.0	10	0.36	16.0	4.6
3La- <i>im</i>	93.4	23.3	59.6	10	0.40	16.7	4.9
0.1Pt- <i>co</i>	81.0	19.5	52.4	8	0.47	23.4	4.5
0.1Pd- <i>co</i>	100.5	27.0	65.2	7	0.57	21.9	4.7
0.5K- <i>co</i>	95.8	22.4	60.7	10	0.35	14.5	4.8
3K- <i>co</i>	95.6	23.7	60.3	8	0.29	12.3	4.6
0.5La- <i>co</i>	110.9	29.8	68.5	8	0.69	24.1	4.7
3La- <i>co</i>	97.7	23.7	63.1	8	0.55	22.5	4.7

<sup>a</sup> Volume of liquid nitrogen. <sup>b</sup> Evaluated from N<sub>2</sub> adsorption using Barret–Joyner–Hallenda (BJH) method. <sup>c</sup> Calculated from  $4V/S_{\text{BET}}$ .

tassium concentration. Sintering processes very likely proceed to some extent during calcination of these catalysts and negatively affect their porous structure. This process is more pronounced with the catalysts containing higher concentrations of potassium.

The TPR pattern of the parent Co<sub>4</sub>MnAl catalyst exhibited two broad peaks with a  $T_{\max}$  of 389 and 790 °C (Fig. 2) that can be ascribed to reduction of Co and Mn oxides, the low-temperature peak to reduction of Co<sub>3</sub>O<sub>4</sub>, the high-temperature one to the reduction of Mn oxides and Co aluminate. Modification of the parent catalyst with 0.5 wt.% Pt (sample 0.5Pt-*im*) similarly as its modification with 0.1 wt.% concentration of Pt and Pd (added during coprecipitation) shifted the maxima of the high-temperature peak to lower temperatures (Figs 2 and 3). As both noble metals catalyze, in general, reduction processes<sup>19</sup>, they certainly facilitate reduction of some components (Mn oxides, Co aluminate) present in the catalyst. The effect of 0.1 wt.% Pt and Pd added at the stage of coprecipitation on positions of the low-temperature peak differed: Palladium substantially decreased the temperature while platinum practically did not change it. Very likely, palladium is more finely dispersed than platinum, and therefore a more intimate contact of Pd species with particles of Co oxides results in an easier reduction. In contrast to palladium, which was added as Pd<sup>2+</sup> cation in the solution used for coprecipitation, platinum was added in the form of [PtCl<sub>6</sub>]<sup>2-</sup> complex anion. In an alkaline medium, less soluble platinum-containing compounds are formed and the distribution of Pt in the coprecipitated product is probably not as fine as in the product modified with Pd; therefore, the mixed oxide modified with Pt exhibited a worse reducibility in comparison with that modified with Pd. To achieve the same effect of platinum as that of Pd added at the stage of impregnation, it would be necessary to add substantially higher amount of Pt into the coprecipitated sample.

Modification of the parent catalyst with 0.5% K, 0.5% La or 3% La did not affect substantially their TPR pattern. Higher amounts of potassium (3 wt.%) caused splitting of the low-temperature reduction peak. Therefore, we assume two-step reduction of Co oxides, i.e., Co<sup>III</sup> → Co<sup>II</sup> and Co<sup>II</sup> → Co<sup>0</sup>.

It follows from the hydrogen consumptions determined in the temperature range 20–1000 °C (Table I) that all modifiers (excluding low concentration of K) caused more complete reduction of the oxide components than was observed with the parent catalyst. More facile reduction of the modified catalysts in the low-temperature region is documented in Table I by consumptions of hydrogen observed within temperature range 25–500 °C.

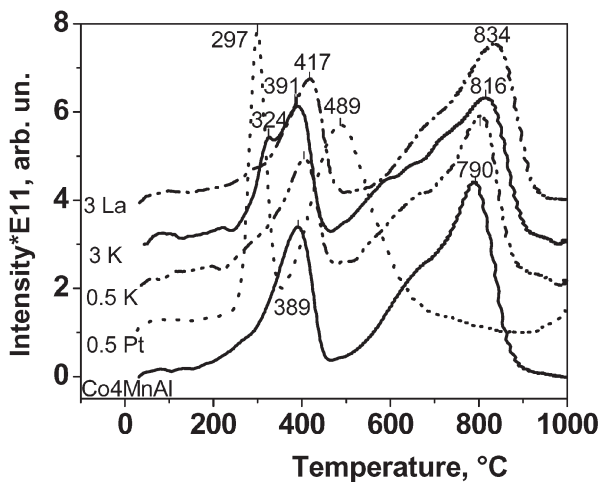


FIG. 2  
TPR patterns of the impregnated  $\text{Co}_4\text{MnAl}$  catalysts

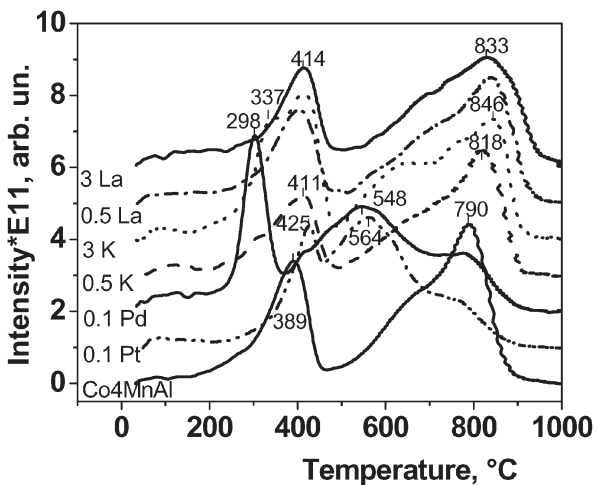


FIG. 3  
TPR patterns of the  $\text{Co}_4\text{MnAl}$  catalysts modified during precursor coprecipitation



Acidity of the catalysts determined from the temperature-programmed desorption of ammonia pre-adsorbed on the catalysts, modified by both methods, changed to greater extent than basicity (ranging from 0.11 to 0.50 mmol  $\text{NH}_3$   $\text{g}^{-1}$ , the acidity of the catalyst impregnated with 3 wt.% K being the lowest and that of the one coprecipitated with 0.5 wt.% La being the highest).

On the basis of the chemical analysis of the catalysts, the electronegativity of assumed oxide mixtures in the catalysts was calculated<sup>20,21</sup>. The electronegativity of corresponding metal ions was taken into account, on the assumption of additive behavior and using mole fractions of the oxides as weights. As it can be seen from Fig. 4, a direct linear dependence between acidity and catalyst electronegativity, and linear, but indirect dependence between basicity and electronegativity were found.

### Correlations

Oxidation-reduction and acid-base properties play an important role in the oxidation of organics over mixed-oxide catalysts<sup>7</sup>. In this work, we attempted to correlate the observed catalytic activity and selectivity in total oxidation of toluene and ethanol total oxidation with some physico-chemical properties of the catalysts modified with noble, alkali or rare earth metals.

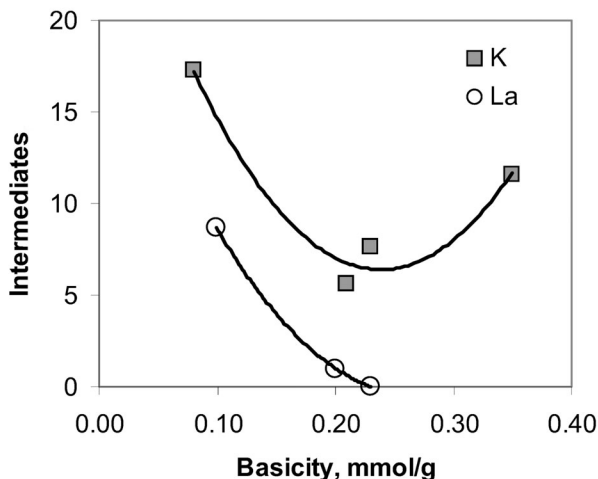


FIG. 5

Dependence of the amount of reaction intermediates (expressed as the area of GC peaks) produced in total oxidation of ethanol at 90% conversion on the total amount of basic sites

We have found no general correlation between catalytic activity of the all modified catalysts and some physicochemical properties. Only partial correlations were found within a group of the catalysts of similar chemical composition. As far as the catalysts modified with La are concerned, in oxidation of both toluene and ethanol their catalytic activity increased (temperature  $T_{50}$  decreased) with increasing amount of compounds reducible in the interval 100–400 °C.

The total oxidation of ethanol was facilitated, when the acidity of catalysts surface was relatively low, i.e., the catalysts were more basic. The catalyst selectivity in the reaction was influenced by their acid-base properties, but to greater extent than total oxidation of toluene. The amount of reaction intermediates (observed at ethanol conversion 90%) over both La- and K-modified catalysts in dependence on total concentration of basic sites showed a minimum at about 0.2 mmol CO<sub>2</sub> g<sup>-1</sup> (Fig. 5). Neither too acid nor too basic catalysts are optimal in order to achieve minimum formation of undesirable reaction intermediates.

## CONCLUSION

Modification of the Co<sub>4</sub>MnAl mixed oxide catalyst with Pt, Pd, La or K promoters and testing of the prepared catalysts in total oxidation of toluene and ethanol led to the following results.

In total oxidation of toluene, the most active catalysts were those containing low concentrations of potassium regardless of the mode of modification (0.5K-*im* and 0.5K-*co*). On the other hand, in total oxidation of ethanol the catalyst with a higher content of potassium (3 wt.%) was the most active, in particular that modified by impregnation. Introduction of Pt and Pd in an amount of 0.5 or 0.1 wt.% into the Co<sub>4</sub>MnAl catalyst did not improve its catalytic activity. Based on the obtained results, the impregnation method was more effective in preparation of active catalysts compared with the method using addition of promoters at the stage of coprecipitation of the LDH precursor.

As far as the catalyst selectivity is concerned, an undesirable reaction intermediate (benzene) was formed when total oxidation of toluene was performed over the catalysts modified with lanthanum and palladium. Therefore, such catalysts cannot be recommended for catalytic combustion of toluene. In total oxidation of ethanol, a considerable amount of reaction intermediates was produced, acetaldehyde being the main one. The catalysts modified at the stage of LDH precursor coprecipitation showed better

selectivity (lower acetaldehyde formation) than those modified by impregnation.

The best results were obtained with the Co<sub>4</sub>MnAl catalyst modified with potassium. Addition of potassium in a low concentration (0.5 wt.% K) afforded the catalyst highly active in total oxidation of toluene, while additions of potassium in higher concentrations were advantageous in total oxidation of ethanol. From the selectivity point of view, potassium concentration in the Co<sub>4</sub>MnAl catalysts must be carefully adjusted in order to achieve optimum acid-base properties, which leads to prevention of formation of harmful reaction intermediates.

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