

ANNA MUSIALIK-PIOTROWSKA*, KRYSZYNA SYCZEWSKA*, EBERHARD SCHUBERT**

OXIDATION OF VOCs OVER MONOLITHIC PEROVSKITE CATALYSTS

Three monolithic perovskite catalysts, one bulk LH and two WK coated on cordierite support, and one basing on Cu-Co-Mn oxides on cordierite monolith, were manufactured. They were tested for oxidation of selected hydrocarbons (toluene and *n*-hexane) and oxyderivatives (acetone, ethyl acetate and butyl acetate). LaMnO₃ perovskite was used as active phase in preparation of WK catalysts, with La³⁺ ions partially exchanged for Ag⁺ ions (25 and 50%). Hydrocarbons were oxidized with lower than oxyderivatives efficiency, but they underwent oxidation to CO₂ and water over all catalysts investigated. Oxidation of oxyderivatives ran via intermediates, first of all aldehydes, typical products of incomplete oxidation. The concentration of yielded intermediates decreased with the rise in the reaction temperature. The addition of silver enhanced catalytic activity and improved the reaction selectivity with respect to CO₂ and water.

1. INTRODUCTION

Volatile organic compounds (VOCs) are recognized as important contributors to air pollution. They are emitted as a result of applying variety of industrial processes and technologies. Chemical industry and pharmaceutical industry are considered to be main producers of VOCs which can also originate during plastics and synthetic resin production and enameling or varnishing processes of various industrial products. Solvent vapours generally include aromatic hydrocarbons, alkanes as well as oxyderivatives – alcohols, acetates and ketones. Catalytic combustion of VOCs presented in industrial effluents is a promising way of their destruction and offers several advantages over thermal oxidation, first of all fuel savings resulting from much lower reaction temperature. Platinum group metal catalysts (Pt, Pd) on alumina granular support (in the form of pellets, balls, rings) or on monolithic (cordierite or metallic – both with alumina washcoat) supports are widely used in this technology. Noble metal

*Institute of Environmental Protection Engineering, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

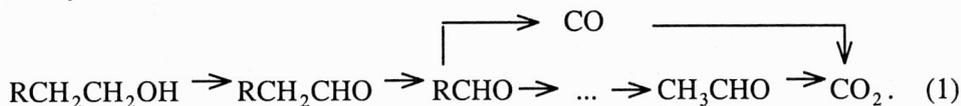
**University of Applied Technology, Dresden, Department of Chemical Technology, Friedrich-List-Platz 1, 01069 Dresden, Germany.

catalysts are highly active, thermally and chemically resistant, and they can be used effectively for a long time.

Because of the high price of noble metals such as platinum or palladium the scientists from many research centers are looking for cheaper catalysts basing on metal oxides as active phase. These days a majority of metal oxide catalysts are being prepared on the bases of copper, chromium, cobalt, manganese, iron or nickel oxides. The only criterion for the choice of metal oxide, suitable for active phase of oxidative catalysts, is the presence of oxygen weakly bounded to metal surface. A mixture of metal oxides in the form of perovskite seems to be a particularly interesting active phase. It has been found that LaMO_3 -perovskite type catalysts, where $M = \text{Mn, Co or Ni}$, are particularly suitable for the oxidation of VOCs in air [1]–[3].

Manufacture of massive or supported metal oxide catalysts in granular form is a well-known process. Recently, monolithic catalyst supports because of their shapes have been considered as an alternative to conventional packed beds of pellets [4], [5]. Noticeable advantages of monolithic structure are as follows: very low pressure drop, uniform flow distribution within the honeycomb matrix, easier accessibility of catalytic active centers on the monolithic walls for the reaction gases which results in faster reaction rate. Therefore, the monolith system provides for more flexible reactor design. The technology of monolithic metal oxide catalysts manufacturing is very complicated. The mechanical strength of bulk catalysts, in which an active ingredient is mixed with binder, is usually too small. The addition of inert binding material results in the reduction of a catalyst activity. The impregnation of ceramic cordierite monolithic support seems to be more efficient way for these catalysts preparation, but the contents of active phase should amount to 20% mass, while the contents of noble metals in catalyst reach 0.05–0.3% only. That is why the metal oxide catalysts are not produced in monolithic form, actually.

Catalytic oxidation of organic air pollutants, particularly oxyderivatives, yields not only the desired total oxidation products – CO_2 and H_2O – but also partially oxidized intermediates. It is important to know that the legal emission or imission limits of yielded intermediates, first of all aldehydes, are much lower than that of primary air pollutants such as acetone or acetates [6]. The general mechanism of oxidation of alcohols with ^{14}C tracer in the air over metal oxide catalysts involves the initial formation of aldehyde molecule with the same carbon skeleton, which, via consecutive steps of CO extraction, converts to shorter chain aldehydes, and finally to CO_2 [7]:



Analysis of the mechanism of ethyl acetate oxidation over $\text{Pt/Al}_2\text{O}_3$ catalyst allows the statement that acetic acid and ethanol are the primary reaction products [8]. Our earlier investigations of the oxidation of ethanol in the air showed that acetaldehyde was yielded as the incomplete oxidation product both over platinum and mixed metal oxides catalysts [9]. Catalytic activity and selectivity depend strongly on the

nature of oxidized compound and the process parameters such as reaction temperature and space velocity of reacting gases.

The purpose of the research was to prepare three perovskite monolithic catalysts and one basing on mixed metal oxides and to investigate their activities and reaction selectivities in the oxidation of selected hydrocarbons and oxyderivatives.

2. CATALYSTS

Four monolithic catalysts were prepared for the purpose of the study. The bulk catalyst LH was extruded from a mixture of LaMnO_3 perovskite slurry and Al_2O_3 as binder in mass proportion of 3:1, at HITK Hermsdorf (Germany). The two WK catalysts were prepared in a laboratory scale by wet impregnation of monolithic cordierite

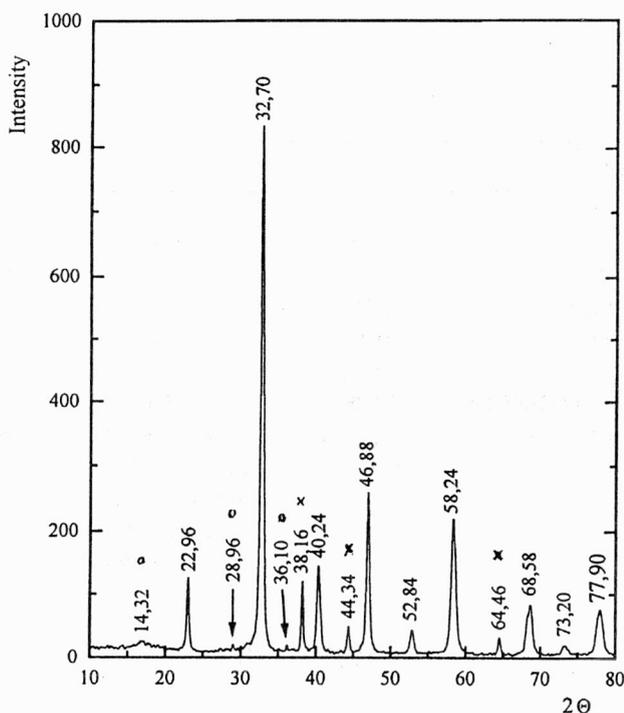


Fig. 1. X-ray analysis of perovskite structure;
 x – metallic silver, o – Mn_2O_3 phase or Ag-Mn-O phase

support with a slurry of Ag^+ -modified LaMnO_3 -perovskite mixed with aluminum oxyhydrate (PSB, Leuna-Werke) in mass proportion of 2:1, and dried at 120 °C. In both catalysts, La^{3+} ions were partially substituted for Ag^+ ions – in 25 and 50% for WK-3 and WK-5, respectively. The perovskite active phase was prepared by precipitation of La^{3+} and Mn^{2+} ions in desired proportion from nitrate solutions with ammo-

nia carbonate. The deposit, after drying at 120 °C and calcination at 450 °C, was impregnated with a silver nitrate solution. After drying and calcination at 600 °C, the specific surface of perovskite powder reached 26 m²/g. X-ray diffraction analysis of Ag-containing perovskite showed the pattern of a LaMnO_{3+x}-phase, metallic silver and some traces of unidentified oxide phases (figure 1). The content of active phase amounted to 16 and 12.5% mass. for WK-3 and WK-5, respectively. Our earlier study showed that the activity of the catalyst WK-1 with content of the active phase, i.e. La_{0.75}Ag_{0.25}MnO₃ (the same as that of WK-3), reduced to 9% mass only was very poor, distinctly lower than that of WK-3 [10].

KO-1 was manufactured also over cordierite support, with γ -Al₂O₃ washcoat and Cu–Co–Mn oxides as active phase collected from the solution of adequate metal nitrates. Description of catalysts is presented in table 1.

Table 1

Description of catalysts

Parameter	LH	WK	KO-1
Shape of catalyst			
Cell geometry]	square	square	square
Cell density [cm ⁻²]	32	28	32
Cell dimension [mm]	1.45	1.6	1.45
Wall thickness [mm]	0.3	0.3	0.3
Open area [%]	67	72	67
Geometric surface area [m ² /m ³]	1856	1790	1856
Catalyst dimension [mm]	$h = 73, \phi = 21$	$h = 76, \phi = 20$	$h = 74, \phi = 21$
Active phase	LaMnO ₃	La _{0.75} Ag _{0.25} MnO ₃ 16% mass (WK-3) La _{0.5} Ag _{0.5} MnO ₃ 12.5% mass (WK-5)	Cu–Co–Mn (5% mass)

3. METHODS

Activity of the catalysts was tested during oxidation of two hydrocarbons (toluene and *n*-hexane) and three oxyderivatives (acetone, ethyl acetate and butyl acetate). Tests were carried out in a flow reactor electrically heated. Reaction temperature varied from 200 to 500 °C and was measured inside the catalytic monolith. The reaction mixtures were prepared by mixing the vapour of investigated compound with the air to obtain the desired concentration of oxidized component (1 g/m³). Catalyst activity in the oxidation of each compound was measured as its conversion efficiency, being the difference between the inlet and outlet concentrations of oxidized compound. Selectivity of the catalytic reaction was estimated in terms of conversion to

partially oxidized intermediates detected in the reaction gases. Reactions proceeded at the space velocity of reaction mixture of 10000 h^{-1} .

The qualitative and quantitative analyses of oxidized compounds and potentially yielded intermediates were carried out by gas chromatographic method with Perkin-Elmer GC (FID; 1.8 m column packed with 10% PEG on Chromosorb W). The parameters of analysis allowed a good separation of peaks of each compound detected. The temperature of the column amounted $73 \text{ }^\circ\text{C}$, and that of injector and detector – $100 \text{ }^\circ\text{C}$.

4. ACTIVITY OF CATALYSTS

The efficiencies of catalytic conversion of each oxidized compound in the presence of the catalysts investigated are shown in figures 2 and 3.

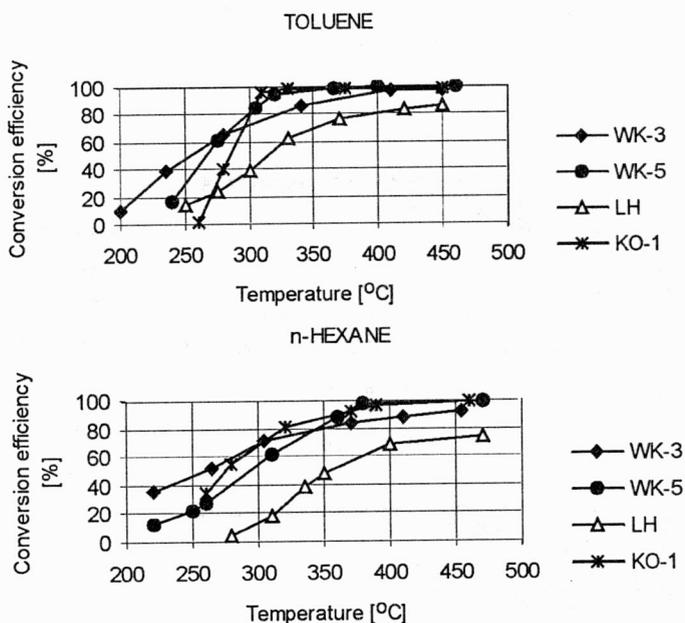


Fig. 2. Conversion efficiency of hydrocarbons over the catalysts investigated

The reactivity of oxidized compounds decreased as follows:

acetone = butyl acetate > ethyl acetate > toluene > *n*-hexane.

The activity of the catalysts investigated during oxidation of both hydrocarbons was lower compared to that during oxidation of oxyderivatives, but toluene and *n*-hexane are oxidized to CO_2 and H_2O only. Independently of the reaction parameters, no other organic compounds were found in the reaction gases. Catalysts WK-5 and KO-1 showed the highest activity during hydrocarbons oxidation. 50 and 90%

conversion efficiencies of toluene over these catalysts were obtained at 270–280 °C and 305–315 °C, respectively. Hexane was more resistant to oxidation, because for its 90% conversion efficiency a temperature of 360–370 °C was necessary. In the presence of WK-3, toluene and *n*-hexane were oxidized with 90% efficiency at 360 °C and 425 °C, respectively. LH catalyst was distinctly less active in hydrocarbon oxidation.

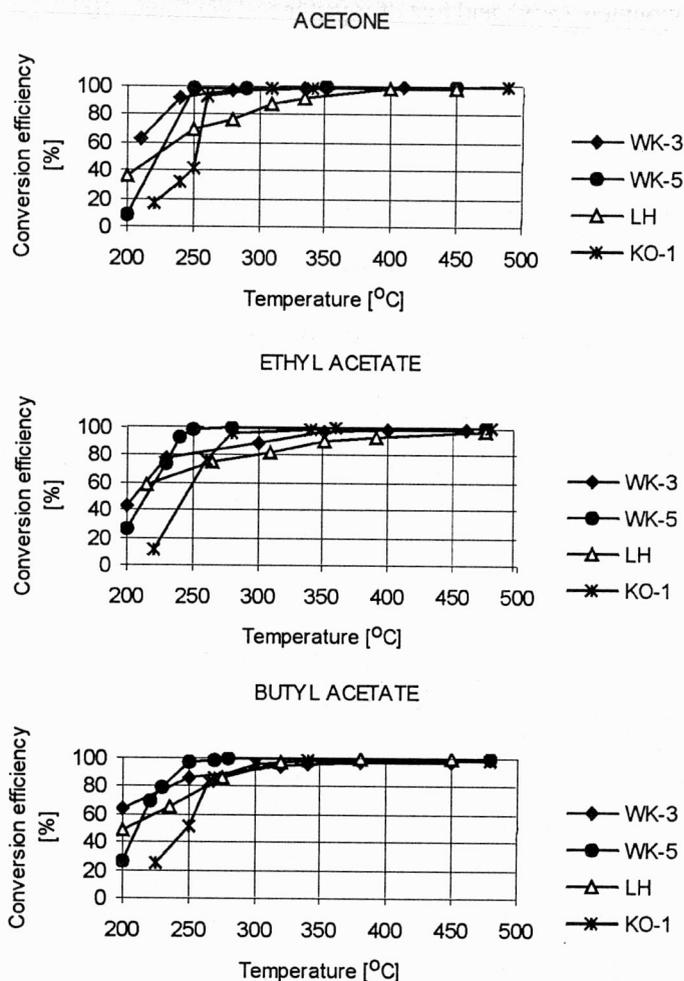


Fig. 3. Conversion efficiency of oxyderivatives over the catalysts investigated

In the presence of each catalyst under investigation, the conversion efficiencies of all oxyderivatives were higher than those of hydrocarbons, but oxidation of oxyderivatives was more complicated and ran via series of parallel and consecutive reactions. WK-5 was the most active in these reactions. The temperature of 90% conversion efficiency of acetone, ethyl acetate and butyl acetate reached 240–245 °C only. In the

presence of WK-3 and KO-1, the temperature of 90% conversion efficiency of oxyderivatives should be about 20° (for acetone) and 40° (for acetates) higher than that for WK-5. It is necessary to note that WK-5 shows the highest activity despite a lower content of active phase (12.5% mass) compared to WK-3 (16% mass). But perovskite of WK-5 contains more silver atoms than perovskite of WK-3; La³⁺ ions in 50% are substituted for Ag⁺ ions (in WK-3 in 25% only). Addition of silver results in higher mobility of oxygen atoms adsorbed on the active sites of the catalyst. It was found that on Ag–Mn catalysts the amount of desorbed oxygen was 2.9 times as much as that desorbed from manganese oxide. The combination of silver and manganese is effective in increasing the oxygen adsorbed on the catalyst surface. Consequently, the activity and reaction selectivity of Ag–Mn catalyst to CO₂ and water remained higher than in the case of pure LaMnO₃ perovskite structure [11].

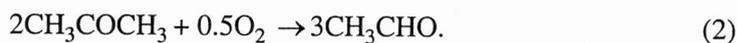
The activity of bulk catalyst LH was lower in the oxidation of each compound under investigation, particularly in oxidation of hydrocarbons. The temperature of 50% conversion efficiency of toluene and *n*-hexane reached 320 and 350 °C, respectively; 90% process efficiency needed temperature higher than 500 °C. Lower activity of this catalyst resulted from its composition. LH was extruded from the mixture of perovskite (without silver) slurry and γ -Al₂O₃ as a binder. In such a catalyst, a significant amount of the active ingredient is located deep in the matrix, some of it can be closed deep inside the pores. The diffusion path to the active sites becomes longer, decreasing their accessibility to reactants, and consequently, inhibiting the overall reaction rate.

5. SELECTIVITY OF CATALYTIC OXIDATION OF OXYDERIVATIVES

The reaction of oxyderivatives oxidation yielded products of incomplete oxidation. In the reaction gases, the following intermediates were detected:

- acetaldehyde – in acetone oxidation,
- acetaldehyde and ethanol – in ethyl acetate oxidation,
- butanol and aldehydes: acetaldehyde, propionaldehyde and butyraldehyde – in butyl acetate oxidation.

The acetone oxidation, except its direct oxidation to CO₂ and water, can undergo according to the following scheme:



Oxidation of both acetates was much more complicated. Probably, as the first step partial hydrolysis of acetate took place – ethyl or butyl acetate was converted to ethanol or butanol, respectively. Alcohols, via aldehydes, were next oxidized to CO₂ and H₂O. One of the reaction paths of ethyl acetate conversion can be presented as follows:





and for *n*-butyl acetate:

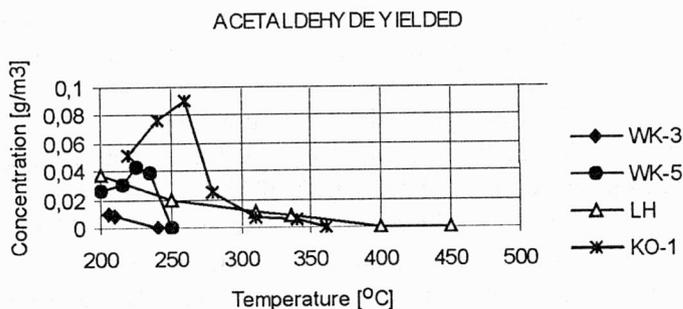


Fig. 4. Concentration of acetaldehyde yielded in the course of acetone oxidation over the catalysts investigated, detected in the outlet gas

Next, the consecutive reactions of butyraldehyde decomposition, via shorter chain aldehydes (reaction (1)), brought to CO_2 and H_2O , according to the known reaction mechanism [7].

The concentration of acetaldehyde yielded in oxidation of acetone over each catalyst investigated is shown in figure 4. The concentrations of ethanol and aldehydes yielded during oxidation of acetates, related to reaction temperature and reaction efficiency, are presented in tables 2 and 3.

When acetone was oxidized, the highest concentration of yielded acetaldehyde was determined in reaction gas over KO-1, Cu-Co-Mn oxides' catalyst. The maximum acetaldehyde concentration (0.09 g/m^3) was measured at 260°C , the temperature of 92% conversion of acetone. Beginning from 360°C , acetone was completely oxidized in the presence of KO-1. Over WK-5 the acetaldehyde concentration was distinctly lower than that over KO-1. Its maximum was detected at 225°C when conversion of acetone reached 50%. At reaction temperatures higher than 250°C no aldehyde was detected in reaction gas.

In the course of ethyl acetate oxidation, ethanol and acetaldehyde were detected in reaction gas when both WK catalysts and KO-1 were used. The intermediates were yielded at the highest concentrations over WK-5. Maximum concentration of acetaldehyde (0.29 g/m^3) was measured at 230°C , the temperature of 74% conversion of acetate, but at 260°C (99% acetate conversion) the concentration of aldehyde decreased to 0.008 g/m^3 . Beginning from 280°C , ethyl acetate was oxidized to CO_2 and water. Over WK-3, the products of incomplete oxidation were detected in lower con-

centrations. In the presence of LH, no traces of ethanol were found in flue gas, only acetaldehyde was detected, even at the highest reaction temperature of 475 °C.

Table 2

Conversion efficiency of ethyl acetate and the concentration of yielded intermediates in the outlet gas, depending on the reaction temperature

Catalyst	Temperature [°C]	Conversion efficiency [%]	Concentration of intermediate yielded [g/m ³]	
			Acetaldehyde	Ethanol
WK-3	400	98.1	0	0
	350	98.0	0.0023	0.003
	300	89.5	0.0136	0.004
	230	78.0	0.010	0.007
	200	42.3	0.042	0.020
WK-5	280	100	0	0
	260	99.0	0.008	0.0014
	250	98.3	0.076	0.0048
	240	92.5	0.190	0.028
	230	74.0	0.290	0.060
	205	40.3	0.130	0.074
	200	27.0	0.127	0.075
LH	475	97.5	0.007	0
	390	92.0	0.018	0
	350	90.2	0.026	0
	310	82.3	0.030	0
	265	73.5	0.048	0
	215	58.0	0.082	0
KO-1	360	100	0	0
	340	99.0	0.005	0
	280	96.5	0.050	0.023
	260	77.0	0.126	0.012
	220	11.0	0.082	0.030

The oxidation of butyl acetate yielded acetaldehyde, propionaldehyde and butyraldehyde. Only over WK-5, traces of butanol were found in flue gas, but at a temperature lower than 230 °C. Like for ethyl acetate, the highest concentration of aldehydes was measured in the presence of WK-5. At 220 °C, the temperature of near 70% butyl acetate conversion, the concentration of acetaldehyde reached 0.16 g/m³. But at temperature higher than 270 °C, no intermediates were found in flue gas. High concentration of acetaldehyde was measured over KO-1, too. Maximum concentration of acetaldehyde of 0.07 g/m³ was detected at 265 °C, when oxidation efficiency of butyl acetate reached 83%.

Table 3

Conversion efficiency of butyl acetate and the concentration of intermediates yielded in the outlet gas, depending on the reaction temperature

Catalyst	Temperature [°C]	Conversion efficiency [%]	Concentration of intermediates [g/m ³]		
			Acetaldehyde	Propionaldehyde	Butyraldehyde
WK-3	350	96.1	0	0	0
	320	94.5	0.002	0	0.003
	250	87.6	0.005	0.003	0.0064
	200	63.6	0.020	0.007	0.011
WK-5	270	99.8	0	0	0
	250	97.5	0.053	0.0084	0.0072
	230	80.3	0.075	0.019	0.025
	220	68.7	0.160	0.043	0.046
	200	27.0	0.067	0.034	0.047
LH	450	98.0	0	0	0
	380	97.1	0	0.004	0
	320	82.2	0.0065	0.003	0.009
	275	61.7	0.0045	0.003	0.010
	235	47.3	0.017	0.015	0.039
	200	31.0	0.026	0.014	0.052
KO-1	300	96.3	0	0	0
	270	86.5	0.006	0	0
	265	83.0	0.030	0.004	0.011
	250	51.1	0.070	0.012	0.050
	225	25.0	0.050	0.016	0.070

The analysis of the results shows that for determination of the optimum parameters of catalytic reaction it is necessary to know not only the temperature of required reaction efficiency, but also the composition of post-reaction gas. In Poland, the legal imission concentration of acetaldehyde is much lower than that of primary air pollutants such as acetone or ethyl and butyl acetates. These values are listed in table 4.

Table 4

Legal imission concentration of VOCs in Poland

VOC	MAC* [µg/m ³]		
	30 min	24 h	Annual
Acetone	350	150	30
Ethyl and butyl acetates	100	43	8.7
Acetaldehyde	20	10	2.5

*MAC – maximum admissible concentration.

6. CONCLUSIONS

The selected hydrocarbons (toluene and *n*-hexane), over all catalysts investigated, were oxidized to CO₂ and H₂O; no other organic compounds were detected in the reaction gas. On the other hand, oxidation efficiency of hydrocarbons was lower than the efficiency of the oxyderivatives' conversion. Catalytic oxidation of oxyderivatives ran via intermediates, first of all aldehydes, typical products of incomplete oxidation. Concentration of yielded intermediates decreased with rising temperature, particularly over more active catalysts.

Two of the catalysts investigated, La_{0.5}Ag_{0.5}MnO₃ perovskite WK-5 and KO-1 basing on Cu–Co–Mn oxides (5% mass), presented very high activity in the oxidation of oxyderivatives, comparable to that of platinum catalyst with a platinum content reduced below 0.1%.

The addition of silver atoms to perovskite structure enhanced the catalyst activity. WK-5 with lower active phase content (12.5%) was more active than WK-3 with higher active ingredient content (16% mass), but in WK-3 perovskite only 25% of La³⁺ atoms were exchanged for silver atoms. Modification of the perovskite with Ag⁺ ions enhanced its catalytic properties in terms of improved reversible exchange of gas-phase oxygen.

Bulk catalyst LH extruded from the slurry of perovskite (without silver) and γ -alumina as binding material was less active than other catalysts investigated and its mechanical strength was very poor.

WK-5 seems to be the best for technical application to destruction of the organic air pollutants, particularly when oxyderivatives are present in a reaction mixture. At the temperature higher than 280 °C, the efficiency of oxyderivatives' conversion reached 99%, and they were oxidized to CO₂ and water.

ACKNOWLEDGEMENT

The financial support of the State Committee for Scientific Research, Grant no. 3T09 B 026 11, is greatly appreciated.

REFERENCES

- [1] SEIYAMA T., *Total oxidation of hydrocarbons on perovskite oxides*, Catal. Rev.-Sci. Eng., 1992, Vol. 34, 281–300.
- [2] OTAMIRI J.C., ANDERSSON S.L.T., *Kinetics of CO oxidation over Y–Ba–CuO perovskites*, Applied Catal., 1991, Vol. 73, 267–280.
- [3] SCHNEIDER R., KIESSLING D., WANDT G. et al., *Perovskite-type oxide monolithic catalysts for combustion of chlorinated hydrocarbons*, Catal. Today, 1999, Vol. 47, 429–435.
- [4] FLYTZANI-STEPHANOPOULOS M., VOECKS G.E., CHARNG T., *Modeling of heat transfer in non-adiabatic monolithic reactors and experimental comparisons of metal monolith with packed beds*, Chem. Eng. Sci., 1986, Vol. 41, 1203–1212.

- [5] CYBULSKI A., MOULIJN J., *Monoliths in heterogeneous catalysis*, Catal. Rev.-Sci. Eng., 1994, Vol. 36, 179–270.
- [6] LINZ H.-G., WITTSTOCK K., *Catalytic combustion of solvent containing air on base metal catalysts*, Catal. Today, 1996, Vol. 29, 457–461.
- [7] ISMAGILOV Z.R., *Catalytic combustion related reactions and catalysts for environmentally safe technologies*, Proceed. I World Congress on Environmental Catalysis, G.Centi SCI Publ. Rome, 1995, 145–148.
- [8] PAPAETHIMIOU P., IOANIDES T., VERYKIOS X.E., *Performance of doped Pt/TiO₂(W⁶⁺) catalysts for combustion of VOCs*, Applied Catal. B: Environmental, 1998, Vol. 15, 75–92.
- [9] MUSIALIK-PIOTROWSKA A., SYCZEWSKA K., *Catalytic combustion of selected hydrocarbons*, Environ. Prot. Eng., 1986, Vol. 12, 71–80.
- [10] MUSIALIK-PIOTROWSKA A., SYCZEWSKA K., *Volatile organic compounds oxidation over metal oxide catalysts*, Environ. Prot. Eng., 1999, Vol. 25, 105–114.
- [11] WATANABE N., YAMASHITA H., MIJADERA H., TOMINAGA S., *Removal of unpleasant odor using an Ag-Mn catalyst*, Applied Catal. B: Environmental, 1996, Vol. 8, 405–415.

UTLENIANIE LOTNYCH ZWIĄZKÓW ORGANICZNYCH NA MONOLITYCZNYCH KATALIZATORACH PEROWSKITOWYCH

Wytworzono trzy monolityczne katalizatory perowskitowe, jeden masowy LH oraz dwa WK na nośniku kordierytowym, oraz jeden na bazie tlenków Cu–Co–Mn, które również naniesiono na monolit kordierytowy. Aktywność katalizatorów określano na podstawie wydajności katalizowanej przez nie reakcji utleniania wytypowanych węglowodorów (toluenu i *n*-heksanu) oraz połączeń tlenopochodnych (acetonu, octanu etylu i octanu butylu). Katalizatory WK wytworzono na bazie perowskitu LaMnO₃, w którym atomy lantanu częściowo zastąpiono atomami srebra (w 25 i 50%). Na wszystkich katalizatorach węglowodory utleniały się z mniejszą wydajnością niż połączenia tlenowe, ale produktami reakcji były CO₂ i woda. Połączenia tlenowe utleniały się z wytworzeniem produktów pośrednich, głównie aldehydów, typowych produktów niepełnego spalania. Stężenia tych produktów malały ze wzrostem temperatury reakcji. Dodatek srebra zwiększał aktywność katalizatorów i poprawiał selektywność reakcji względem CO₂ i wody.

utlenianie
węglów lotnych
węglów organicznych
katalizatory perowskitowe