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Combustion of volatile organic compounds in two-component mixtures over monolithic perovskite catalysts

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Abstract

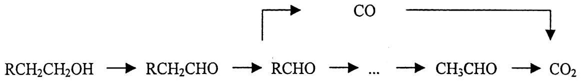
Activity of monolithic perovskite catalysts in oxidation of selected hydrocarbons and oxy-derivatives, oxidized individually and in two-component mixtures, as well as the reaction selectivity were investigated. One bulk perovskite ($LaMn_2O_3$) catalyst and two catalysts based on $LaMn_2O_3$ with addition of silver (25 at.%) coated on cordierite support were prepared for the study. The efficiency of oxy-derivatives oxidation was higher than that of hydrocarbon oxidation, but some by-products (first of all aldehydes) were detected in the flue gases. Addition of silver to the active phase improved catalyst activity and selectivity to CO_2 and water. The "mixture effect" on catalyst activity and selectivity depended on composition of the reaction mixture and the catalyst used. The presence of oxy-derivative in the reaction mixture inhibited oxidation of hydrocarbons. Toluene inhibited the process of oxy-derivatives conversion and increased the concentration of incomplete oxidation products. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Volatile organic compounds; Monolithic perovskite catalysts; Oxidation

1. Introduction

Volatile organic compounds (VOCs) are recognized as still increasing contributors to air pollution. The main portion of VOC emissions in Poland results from stationary sources from the processes of enameling or varnishing of various industrial products. Solvent vapors generally include aromatic hydrocarbons, alkanes, as well as oxy-derivatives — alcohols, acetates and ketones. Catalytic combustion is a common way of reducing this emission, since VOC oxidation over a catalyst takes place at temperatures much lower than that required for thermal destruction. Noble metal catalysts (Pt, Pd), resting on alumina granular pellets or monolithic (cordierite or metallic — both with alumina washcoat) supports, are widely used in this technology.

Catalytic oxidation of organic air pollutants, particularly oxy-derivatives, yielded not only the desired total oxidation products, CO_2 and H_2O, but also partially oxidized intermediates [1,2]. The general mechanism of alcohol oxidation in air over metal oxide catalysts observed with ^{14}C tracer involves the initial formation of aldehyde molecule with the same carbon skeleton, which, via consecutive steps of CO extraction, converts to smaller chain aldehydes, and finally to CO_2 [1]:



The mechanism of alcohol oxidation over platinum catalysts involves also the formation of acids:

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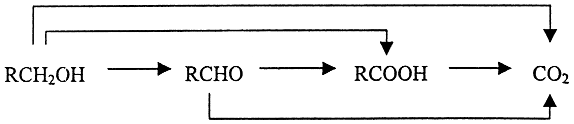


Studying the mechanism of ethyl acetate oxidation over Pt/Al_2O_3 catalyst, acetic acid and ethanol were found as the primary reaction products [3]. Our earlier investigations of the oxidation of ethanol in air showed that acetaldehyde was yielded as the incomplete oxidation product, both over platinum and mixed metal oxide catalysts [4]. Catalytic activity and selectivity depend strongly on the nature of the oxidized compound, and the process parameters such as reaction temperature and space velocity of the reacting gases.

The search for much cheaper substitutes of noble metal catalysts has led to the study of various mixed metal oxides like perovskites. It has been found that $LaMO_3$-perovskite type catalysts, where M=Mn, Co or Ni, are particularly effective for total oxidation of VOCs in air [5–7]. Manufacture of bulk or supported metal oxide catalysts in granular form is a well-known process. Recently, monolithic supports have been considered as an alternative geometry to conventional granular catalysts [8,9]. Noticeable advantages of monolithic structure include very low pressure drop, uniform flow distribution within the honeycomb matrix, easier accessibility of catalytic active centers of the monolithic walls for the reacting gases, resulting in the faster reaction kinetics. Therefore, the monolith system provides for more flexible reactor design. The technology of preparing monolithic metal oxide catalysts is very complicated. Mechanical strength of bulk catalysts is usually too low, while addition of any inert binder results in catalyst activity abatement. The impregnation of ceramic cordierite monolithic support seems to be a more efficient way for the preparation of catalysts, but the contents of the active phase should amount to at least 20% of the support mass.

Organic air pollutants emitted in industrial exhaust gases usually present mixtures of volatile organic compounds of different chemical character. Therefore, it should be of interest to test the catalyst activity not only in the reaction of one organic compound oxidation in the air stream, but also in the oxidation of multi-component mixtures. The “mixture effect” is very difficult to predict a priori, usually an inhibiting effect [10–13], and very rarely promoting effect (e.g. halogenated hydrocarbons oxidation in the presence of VOCs over platinum catalysts) was observed when two-component mixtures were oxidized [14].

The purpose of the study was the preparation of three perovskite monolithic catalysts, and investigation of their activity and selectivity in the oxidation of selected hydrocarbons and oxy-derivatives, oxidized separately and in two-component mixtures.

2. Catalysts

Three 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 γ-Al_2O_3 (binder) in mass proportion of 3:1 at HITK Hermsdorf (Germany). The two WK catalysts were prepared in laboratory scale by wet impregnation of monolithic cordierite support with a slurry of Ag^+-modified $LaMnO_3$-perovskite and aluminum oxy-hydrate (PSB, Leuna-Werke), in mass proportion of 2:1, and dried at 120°C. La^{+3} ions were partially substituted by Ag^+ ions (25 at.%). The perovskite active phase was prepared by precipitation of La^{3+} and Mn^{2+} ions in desired proportion from nitrate solutions with ammonia 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 m^2/g. X-ray diffraction analysis of Ag-containing perovskite showed the pattern of an $LaMnO_{3+x}$-phase, silver both in Ag–Mn–O and metallic form, as well as some traces of unidentified oxide phases. The contents of the active phase amounted to 9 and 16% mass, for WK-1 and WK-3, respectively. Catalyst WK-3 was impregnated twice.

Description of catalysts is presented in Table 1.

3. Experimental

The activity of the catalysts was tested in the oxidation of two hydrocarbons and three oxy-derivatives. Tests were carried out in a typical cross-flow fixed bed reactor, of “tube-in-tube” type, electrically heated. The construction of reactor enables uniform heat distribution in reaction mixture stream. The reaction temperature was measured inside

Table 1
Description of manufactured catalysts

Parameter	LH	WK-1, WK-3
Shape of catalyst		
Cell geometry	Square	Square
Cell density (cm^{-2})	32	28
Cell dimension (mm)	1.45	1.6
Wall thickness (mm)	0.3	0.3
Open area (%)	67	72
Geometric surface area (m^2/m^3)	1856	1790
Catalyst dimension (mm)	h=73, ϕ=21	h=76, ϕ=20
Active phase	$LaMnO_3$	$La_{0.75}Ag_{0.25}MnO_3$; 9% mass (WK-1), 16% mass (WK-3)

the catalytic block, after the reaction ignition zone, and ranged from 200 to 500°C. Gas flow space velocity amounted to $10\,000\,h^{-1}$. The reaction mixtures were prepared by mixing of the investigated compound vapor with air to the desired concentration of the oxidized component — $1\,g/m^3$. Catalyst activity was estimated as conversion efficiency of each compound under investigation measured from the inlet and outlet concentrations of the oxidized compound. Tests were carried out in the following order:

- oxidation of each hydrocarbon (toluene, *n*-hexane) and oxy-derivative compound (acetone, ethyl acetate, butyl acetate) separately,
- oxidation of each oxy-derivative compound in two-component mixture, at first with toluene and next with *n*-hexane.

The qualitative and quantitative analysis of the oxidized compounds and of the reaction products was performed by gas chromatography, with Perkin-Elmer GC (FID; column of 1.8 m/2.7 mm packed with 10% PEG on Chromosorb W). The parameters for gas analysis were selected so as to separate each investigated compound (as well as potential intermediates — first of all aldehydes and light hydrocarbons C_1–C_4). The column temperature was set at 73°C, while that of the injector and detector — at 100°C.

4. Catalysts activity and selectivity in the oxidation of single compound in air

The activity of investigated catalysts in the oxidation of selected compounds, oxidized separately, is plotted in Fig. 1.

Generally, the efficiency of oxy-derivative oxidation was higher than that of the hydrocarbons over each catalyst under investigation. The reactivity of the oxidized compounds decreased as follows:

$$\text{acetone} = \text{butyl acetate} > \text{ethyl acetate} > \text{toluene} > n\text{-hexane}$$

The activity of perovskite catalysts in the reaction of hydrocarbon oxidation was lower when compared with their activity in the oxidation of oxy-derivatives, but the reaction of toluene or *n*-hexane oxidation ran to typical products of complete oxidation — CO_2 and H_2O. Irrespective of the reaction parameters, no organic intermediates of hydrocarbon oxidation were found in the reaction gases. The process of oxy-derivative oxidation was much more complicated and ran via series of consecutive reactions.

The WK-3 catalyst was the most active in the oxidation of every compound under investigation. Fifty percent conversion efficiency of oxy-derivatives oxidation was achieved only at 200°C; with 90% efficiency, acetone, butyl acetate and ethyl acetate were converted at the temperatures of 235, 280 and 300°C, respectively. Both selected hydrocarbons were oxidized with 50% efficiency at 250–255°C, but 90% conversion of toluene and *n*-hexane needed the reaction temperatures of 360 and 425°C, respectively. The conversion efficiency of every oxidized compound over LH was lower than that over WK-3, and for 50 and 90% oxidation efficiency that catalyst demanded higher temperatures as WK-3, particularly when hydrocarbons were oxidized. Catalyst WK-1 was less active in the oxidation of each compound under investigation; content

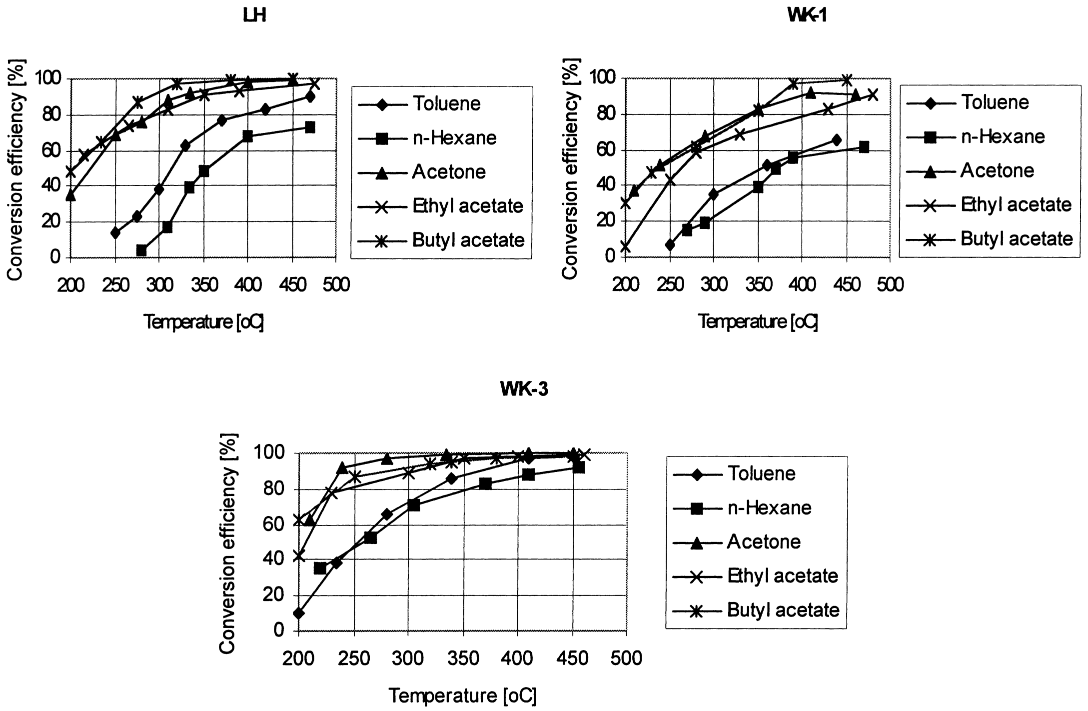


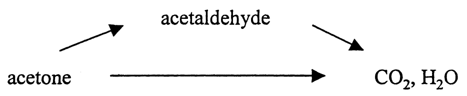
Fig. 1. Conversion efficiency selected compounds over LH, WK-1 and WK-3.

of the active phase amounting to 9% of support mass seems to be insufficient.

The oxidation of oxy-derivatives yielded incomplete reaction products. In the post-reaction gases some intermediates were detected:

acetaldehyde: in the reaction of acetone oxidation,
acetaldehyde and ethanol: in ethyl acetate oxidation,
butanol and aldehydes: acetaldehyde, propionaldehyde and butyraldehyde — in the course of butyl acetate oxidation.

The reaction of acetone oxidation can run according to the following scheme:

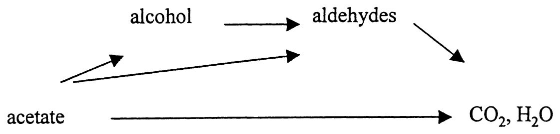


thus

$$2CH_3COCH_3+0.5O_2 \rightarrow 3CH_3CHO$$

Consequently, acetaldehyde is oxidized to CO_2 and water.

The oxidation of both acetates was much more complicated. Probably, in the first step, acetates were partially hydrolyzed — to ethanol or butanol, for ethyl or butyl acetate, respectively. Alcohol, via aldehydes, was next oxidized to CO_2 and H_2O. Generally, the scheme of these reactions can be presented as follows:



The scheme of ethyl acetate reaction pathway via alcohol is

$$CH_3COOCH_2CH_3+H_2O \xrightarrow{\text{hydrolysis}} CH_3COOH + CH_3CH_2OH$$

$$CH_3CH_2OH + 0.5O_2 \rightarrow CH_3CHO + H_2O$$

and that of *n*-butyl acetate reaction is

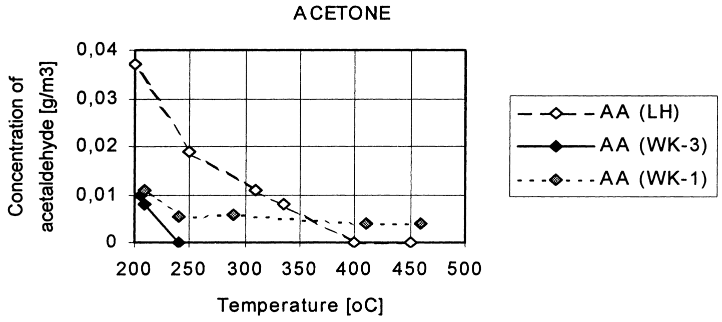


Fig. 2. Concentration of AA yielded during acetone oxidation over LH, WK-1 and WK-3.

$$CH_3COO(CH_2)_3CH_3+H_2O \xrightarrow{\text{hydrolysis}} CH_3COOH + CH_3(CH_2)_3OH$$

$$CH_3(CH_2)_3OH + 0.5O_2 \rightarrow CH_3(CH_2)_2CHO + H_2O$$

Further consecutive reaction of butyraldehyde decomposition, via smaller chain aldehydes, yielded CO_2 and H_2O, according to the known reaction mechanism [1].

Reaction selectivity to the intermediates in the process of oxy-derivative oxidation is plotted in Figs. 2–4.

The highest concentration of the intermediates yielded in the oxidation of each oxy-derivative was measured for bulk catalyst LH (without Ag^+ ions). In the course of acetone oxidation, the concentration of acetaldehyde reached 0.038 g/m^3 at 200°C, and only at temperatures higher than 400°C acetone was oxidized to CO_2 and H_2O. Over this catalyst the highest concentration of intermediate compound was measured in the reaction of ethyl acetate oxidation; the concentration of acetaldehyde decreased from 0.082 g/m^3 at 210°C to 0.008 g/m^3 at 475°C. Catalytic combustion of butyl acetate over LH yielded acetaldehyde (AA), propionaldehyde (PA) and butyraldehyde (BA). At 200°C the concentration of aldehydes reached 0.052, 0.026 and 0.014 g/m^3 for BA, AA and PA, respectively. At temperatures higher than 380°C only traces of PA were detected in the reaction gas. In the course of oxidation of acetates over LH, no traces of alcohol (ethanol or butanol, when ethyl acetate or butyl acetate were oxidized, respectively) were found in the flue gases, even at the lowest reaction temperature of 200°C.

Over WK-1, the catalyst of lower than LH activity, with a thin coat of active phase (perovskite with lanthanum partially substituted by Ag^+ ions), the concentration of every yielded intermediate was lower than that formed over LH. The addition of silver to the active phase improved the selectivity of catalytic reaction to CO_2 and water.

The lowest concentrations of each compound found in the flue gases were detected in the presence of

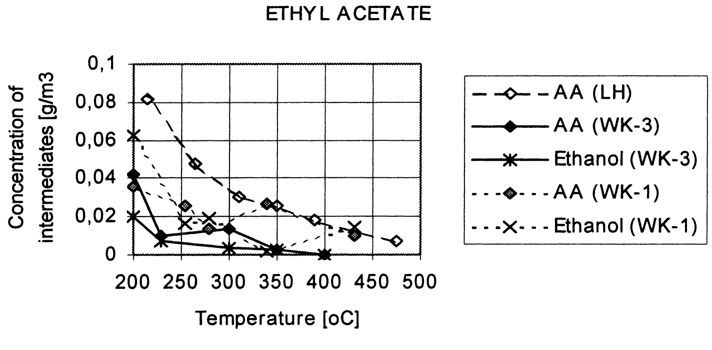


Fig. 3. Concentration of AA and ethanol yielded during ethyl acetate oxidation over LH, WK-1 and WK-3.

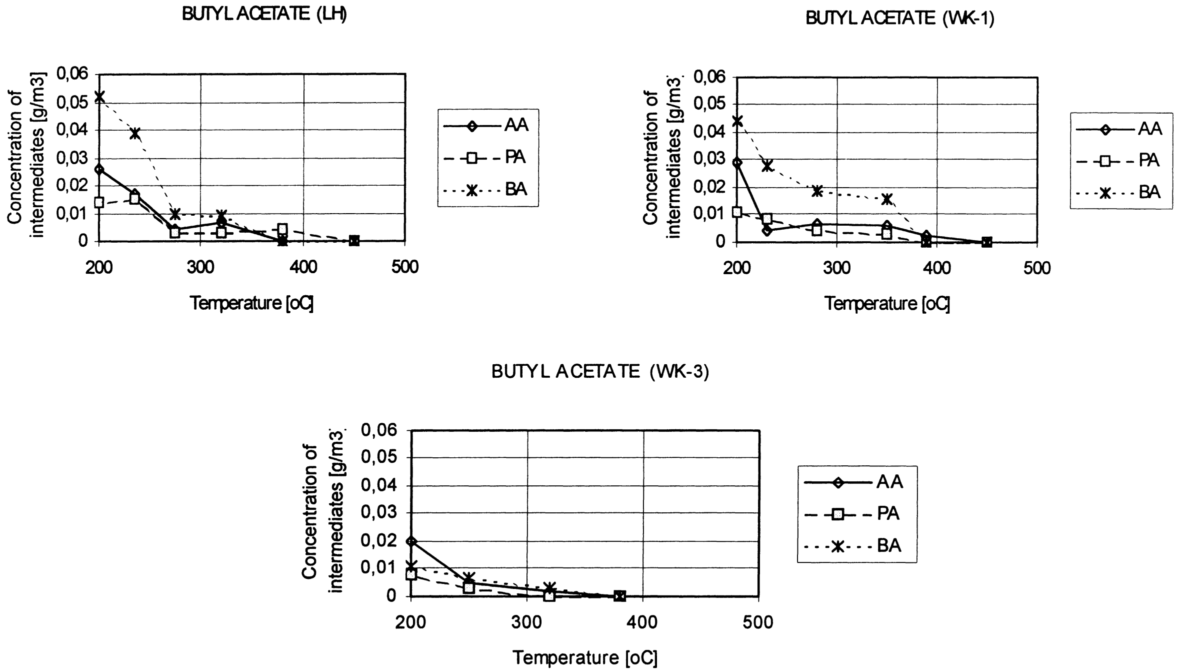


Fig. 4. Concentration of intermediates yielded during butyl acetate oxidation; AA: acetaldehyde, PA: propionaldehyde, BA: butyraldehyde.

WK-3, which was impregnated twice with the same active phase as was WK-1. In the process of acetone oxidation, the concentration of acetaldehyde reached 0.01 g/m^3 at 200°C; once the reaction temperature of 240°C has been achieved, acetone was oxidized to CO_2 and H_2O. Also over WK-3, the highest concentration of the intermediate products was detected in course of ethyl acetate oxidation; at 200°C ethanol and acetaldehyde were present in the flue gas at the concentration of 0.02 and 0.04 g/m^3, respectively. At the same temperature, the concentration of aldehydes yielded during butyl acetate oxidation did not exceed 0.02 g/m^3. Traces of butanol were found in the effluent after WK-1 and WK-3 only at lowest reaction temperatures (200–230°C). In the oxidation of the two acetates, no intermediates were detected in the reaction gas above 380°C.

The results of the study showed relatively low activity of bulk catalyst LH and coated catalyst WK-1. The low activity of WK-1 results from too small amount of the active ingredient. In bulk catalyst, a significant amount of the active component is located deep in the matrix, and some of it can be placed inside the closed pores. The diffusion path to the active sites becomes longer, decreasing their accessibility for reactants and inhibiting the overall reaction rate. Thin catalytic layer in monolithic coated catalysts and a corresponding, short diffusion length, improves the access of reactants to the catalyst surface and consequently speed up reaction of internal diffusion-limited processes. This phenomenon was observed for WK-3.

The high activity of WK-3 results also from the composition of active phase. It was found that on Ag–Mn catalysts the amount of desorbed oxygen was 2.9 times as much as that desorbed from Mn_2O_3. The combination of Ag and Mn was effective in increasing the amount of the oxygen adsorbed on the surface. It was suggested that manganese oxide supplied oxygen to silver, maintaining high oxidative state of silver. This resulted in the efficient donation of oxygen over the whole catalyst [15]. Consequently, the activity and selectivity to CO_2 and water remained higher than in pure $LaMn_2O_3$ perovskite structure. From this finding it can be inferred that, in the presence of WK-3 the oxidation of oxy-derivatives yields lower concentrations of the intermediates than those observed for LH (without silver).

5. Oxidation of two-component mixtures

Tests of catalyst activity in the oxidation of selected organic compound separately showed very poor activity of WK-1. So, the next tests of two-component mixture oxidation were performed for LH and WK-3 only. The temperatures of 50 and 90% conversion efficiency for each compound oxidized separately and in the mixtures are presented in Table 2.

The presence of oxy-derivatives in the reaction mixture inhibited the rate of hydrocarbon oxidation over both catalysts. In the presence of LH, addition of each hydrocarbon to ethyl acetate and acetone in the reaction mixtures had no influence on the conversion efficiency of the oxy-derivatives. Only butyl acetate oxidation was strongly inhibited, particularly when *n*-hexane was present in the reaction mixture. Over WK-3, toluene had an inhibiting effect on the reaction efficiency of each oxy-derivative; *n*-hexane had a slight influence on the oxidation of each oxy-derivative compound.

Table 2
Temperatures (°C) of 50 and 90% conversion efficiencies of selected compounds oxidized individually and in the mixtures

Compound	Catalyst			
	LH (%)		WK-3 (%)	
	50	90	50	90
Toluene	320	460	250	360
With acetone	310	500	280	410
With ethyl acetate	350	480	275	400
With butyl acetate	330	480	265	400
n-Hexane	350	>500	255	425
With acetone	380	>500	270	>500
With ethyl acetate	380	>500	290	500
With butyl acetate	440	>500	270	500
Acetone	220	320	200	235
With toluene	220	320	230	300
With *n*-hexane	220	330	<200	250
Ethyl acetate	200	350	205	300
With toluene	200	325	250	345
With *n*-hexane	200	325	215	300
Butyl acetate	200	285	<200	280
With toluene	225	335	200	325
With *n*-hexane	310	385	200	280

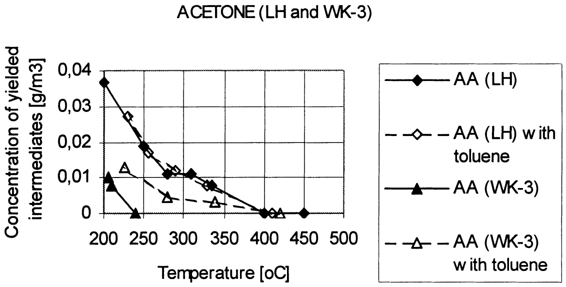


Fig. 5. Concentration of AA yielded during acetone oxidation.

The concentration of the intermediates yielded over LH and WK-3 (when oxy-derivatives were oxidized separately and in a two-component mixture) are presented in Figs. 5–7.

Over LH, the presence of toluene had no influence on reaction selectivity to acetaldehyde production when acetone and ethyl acetate were oxidized. In the course of every other reaction over the two catalysts, when toluene was added to the reaction mixtures, the concentration of the intermediates was higher as compared to that when oxy-derivatives were oxidized separately. The concentration of acetaldehyde yielded during acetone oxidation with toluene over WK-3 ranged from 0.013 g/m^3 at 220°C to 0.0035 g/m^3 at 340°C. Much higher concentration of acetaldehyde was detected when ethyl acetate was oxidized, and these concentrations varied from 0.087 to 0.01 g/m^3 at reaction temperatures of 230 and 380°C, respectively. Maximum concentration of ethanol reached 0.03 g/m^3 and was measured at 230°C, the lowest of the reaction temperatures studied. In the presence of each catalyst, no intermediates were detected in the flue gas when *n*-hexane was added to acetone and ethyl acetate.

In the course of butyl acetate oxidation over LH, addition of toluene increased the concentration of aldehydes — AA, PA and BA. At 335°C (the temperature of 90% butyl acetate conversion efficiency), the concentration of aldehydes varied from 0.007 to 0.014 g/m^3, while aldehydes concentration for butyl acetate oxidized separately with 90% efficiency (at 280°C) ranged from 0.003 to 0.01 g/m^3. Hexane strongly inhibited butyl acetate oxidation, but at

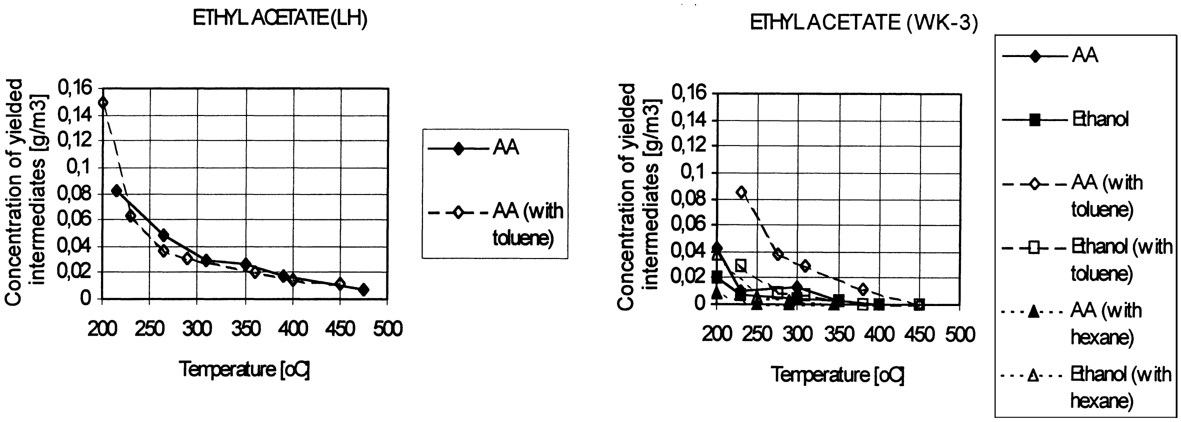


Fig. 6. Concentration of AA and ethanol yielded during ethyl acetate oxidation.

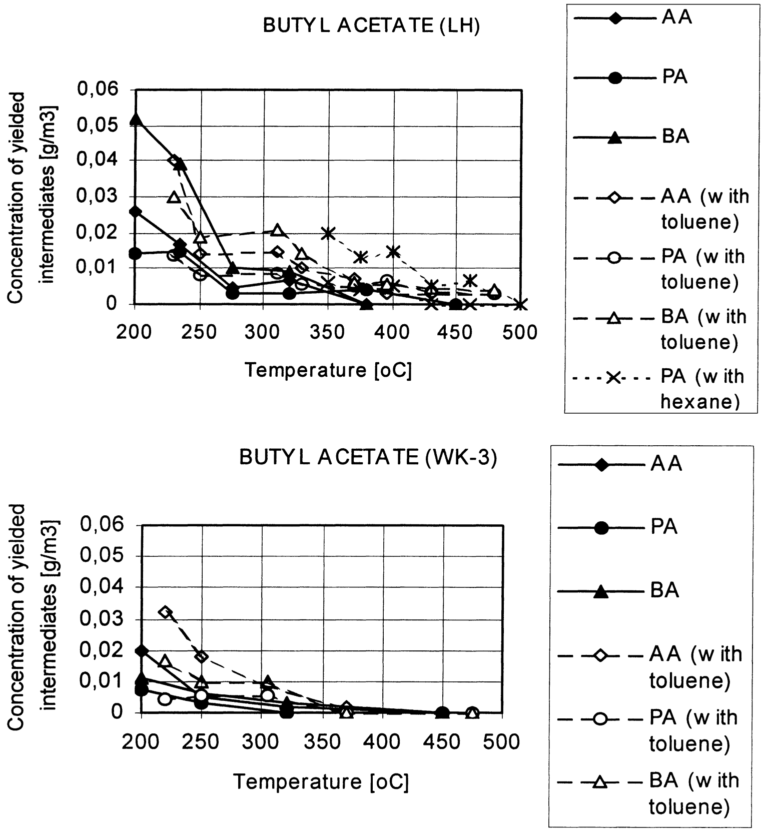


Fig. 7. Concentration of intermediates yielded during butyl acetate oxidation; AA: acetaldehyde, PA: propionaldehyde, BA: butyraldehyde.

385°C (temperature of 90% acetate conversion) only BA (0.013 g/m^3) and PA (0.005 g/m^3) were detected in the flue gas. Over WK-3, butyl acetate oxidation was inhibited in the presence of toluene in the reaction mixture, but the concentration of aldehydes was lower, as compared to LH. When butyl acetate was oxidized with *n*-hexane over WK-3, no by-products were detected in the flue gas, even at 200°C (the lowest investigated reaction temperature).

The results of investigations showed that the "mixture effect" on catalyst activity and reaction selectivity of each component, depend both on the reaction mixture composition and the catalyst used. As it was reported earlier, the inhibiting effect on some hydrocarbons (benzene, toluene, *n*-heptane and *n*-hexane) oxidation in two-component mixture with the oxy-derivative compounds was observed even for noble metal catalysts [11,13]. On the other hand, enhanced reactivity of ethyl acetate, butyl acetate and butanol was observed when these compounds were oxidized in the mixture with selected hydrocarbons. This effect was noticeable poorer for the less active catalyst, with reduced to 0.05% mass platinum content. The selectivity of ethanol oxidation to acetaldehyde depended also on the overall catalyst activity. The concentration of acetaldehyde when ethanol was oxidized individually (as compared to that detected for ethanol oxidized with toluene and *n*-heptane in the reaction mixture) was lower for the more active catalyst (0.1% Pt), but higher for the catalyst with reduced (0.05% Pt) noble metal content [13].

6. Conclusions

Over each perovskite catalyst hydrocarbons oxidation efficiency was lower than the efficiency of the oxy-derivative compounds conversion. Selected hydrocarbons (toluene and *n*-hexane) were oxidized to CO_2 and H_2O; no intermediates were detected in the reaction gas.

Catalytic combustion of oxy-derivatives yielded partially oxidized intermediates. Acetone oxidation runs via acetaldehyde. Mechanism of acetate oxidation is more complicated; probably acetate partially hydrolyzed to alcohol, and next in the course of the consecutive reaction of alcohol oxidation, via aldehydes, it is oxidized to CO_2 and H_2O. The concentration of intermediates decreased in the presence of the more active catalyst.

The perovskite (La^{3+} ions partially substituted with Ag^+ ions) catalyst on a monolithic cordierite support (WK-3) was more active in the oxidation of the selected VOCs than the monolithic bulk catalyst (LH) prepared from a mixture of $LaMnO_3$ slurry with addition of γ-Al_2O_3 as binder. The cordierite support also provided higher mechanical strength than that of the bulk catalyst LH. The active phase of coated metal oxide catalyst should amount to at least 16% mass. The low activity of WK-1 resulted from insufficient amount of the active ingredient accounting for 9% mass only. Modification of the perovskite active phase with Ag^+ ions enhanced catalytic properties in terms of improved catalyst overall activity and selectivity to CO_2 and water. To determine the influence of silver content on the catalytic properties of $LaMn_2O_3$ perovskite, further investigations will be carried on.

After ca. 500 h of the oxidation tests carried out over WK-3, no decrease of catalyst activity was observed, in spite of a slight lost of active phase (small amount of dust recovered at the reactor outlet).

The reaction of hydrocarbon oxidation over each catalyst was evidently inhibited by the oxy-derivative compound in the reaction mixtures. The presence of hydrocarbon in the reaction mixture influenced in different way catalyst activity in oxy-derivative compound oxidation. Generally, toluene strongly inhibited the oxy-derivatives oxidation and increased the concentration of yielded by-products. With *n*-hexane in the reaction mixture, oxidation of oxy-derivatives yielded by-products at lower concentration. When acetone and butyl acetate were oxidized over WK-3 with *n*-hexane, no products of incomplete oxidation were found in the reaction gas.

The practical application of metal oxide catalyst in air pollution control demanded the careful selection of the optimum parameters of its work, both in term of high conversion efficiency of combusted compounds and the quality of post-reaction gases. The legal emission limit in Poland for acetaldehyde (typical product of incomplete oxidation) reached 20 μg/m^3. This limit is lower as for the solvent itself (for acetone — 350 μg/m^3 and for ethyl or butyl acetate — 100 μg/m^3), and even very small amount of yielded by-product can be more harmful as the primary air pollutant.

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