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VOLATILE ORGANIC COMPOUNDS OXIDATION OVER METAL OXIDE CATALYSTS

Catalytic oxidation is an efficient method for the control of organic pollutants in air. Actually, in industrial systems noble metal catalysts of high activity and stability are used. High prize of platinum group metals (PGM) involves the search for cheaper substitutes for noble metals and has led to the tests of various metal oxide systems, including perovskites. Four three-component metal oxide catalysts and three perovskite catalysts basing on $La_{1-x}Ag_xMnO_3$, all on a cordierite monolithic support, were manufactured for the purpose of the study. Their activities and selectivities were tested during oxidation of two hydrocarbons (toluene and n-hexane) and three oxy-derivatives compounds (acetone, ethyl acetate, and butyl acetate). Oxy-derivatives were oxidized easier than hydrocarbons, but the reaction ran via intermediates, first of all aldehydes detected in the flue gas. Catalyst KOW-4 (Cu–Co–Mn oxides on γ-alumina washcoat) and WK-5 ($La_{0.5}Ag_{0.5}MnO_3$ perovskite) were most active, their activity was comparable to activity of platinum catalyst with the content of platinum reduced below 0.1%.

1. INTRODUCTION

Volatile organic compounds (VOCs) in waste gases are considered as significant atmospheric pollutants due to their toxicity and their contribution to smog generation. The major sources of VOC emission in urban environment can be itemized as follows: transport and various industrial activities – chemical plants including crude oil refineries, synthetic fiber plants, pharmaceutical plants, food processing as well as painting and coating operations. Catalytic combustion of VOCs and other oxidizable compounds, e.g. CO, in effluent streams is a promising way of reducing their emission. New catalytic technology in air pollution control allows us to protect the ozone layer, to create environmentally safer transport and to solve environmental problems of energy production.

Catalytic oxidation offers several advantages over thermal combustion. Catalytic reaction takes place typically at temperatures between 300 and 600 °C, while thermal

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oxidation needs temperatures higher than 800 °C. The residence time for catalytic reaction is usually shorther than that for thermal combustion. The advantages lie in fuel savings and lower NO_x formation resulting from lower operating temperatures as well as in higher reaction selectivity to CO_2 and H_2O formation. Thermal combustion of hydrocarbons carried out at too low temperature or too short residence time yields often products of incomplete oxidation – carbon monoxide or aldehydes, while the halogenated hydrocarbons' oxidation accounts for the formation of another toxic products, i.e. phosgene. Catalytic oxidizer can be applied in a wide range of effluent flows and organic pollutant concentrations. A variety of organic components can be destroyed in this way: hydrocarbons, their oxy- and nitrogen-derivatives as well as halogenated hydrocarbons.

Industrial systems for flue gas treatment make use of the catalysts basing on platinum group metals (PGM). They are highly active, resistant to poisons and thermally durable [1], [2]. Typically they are prepared by impregnation of supports in the form of balls, pellets, rings or monolithic blocks with a solution of chloroplatinic acid or palladium and rhodium chlorides. Monolithic honeycomb blocks are widely used in automobile converters. Monoliths have many advantages compared to conventional granular form catalyst. They are as follows:

very low pressure drop, up to 2 orders of magnitude lower than in packed bed,

uniform flow distribution and mass/heat transfer conditions for the whole cross-section of monolith,

high surface-to-volume ratio,

thin layer of active phase which effected in short diffusion length and easier accessibility of catalytic active centers to reactants [3].

Therefore, the wide use of monolithic catalysts for industrial waste gas treatment is likely to be their main domain in the near future.

Monolithic supports are usually produced as metallic (heat-resistant steel with additives, alumina–titania alloy, etc.) or ceramic extruded blocks. The most important ceramic material used for extruded monolithic substrate is a synthetic cordierite, $2\ MgO \cdot 2\ Al_2O_3 \cdot 5\ SiO_2$. Cordierite has a very high resistance to thermal shock due to a low thermal expansion coefficient, as well as porosity and pore size distribution suitable for ease washcoat application [4]. Both support substrates, metallic or ceramic, are characterized by very low specific surface. Hence, the monolithic catalysts are manufactured via an intermediate step – washcoating, which consists in depositing the layer of extended-surface-area material of washcoat (usually γ-Al_2O_3) on the support surface. The final step of catalyst preparation is an impregnation of washcoat with the solution of active ingredients, its drying and calcination at adequate temperatures.

The search for much cheaper substitutes for noble metals has led to the examination of various mixed metal oxides as Cu, Co, Cr, Zn, Mn, Fe. It has been found that perovskite-type catalysts in the form of $LaMO_3$, where M = Mn, Co or Ni, are particularly suitable for the oxidation of VOCs in air [5], [6]. Generally, base metal

catalysts are considered as not so active, particularly in the reaction of aromatic hydrocarbon oxidation, and not so chemically and thermally durable as PGM catalysts. But some metal oxide catalysts can be more active than noble metal contacts in the process of oxy-derivatives' oxidation and more resistant to chlorine during oxidation of halogenated hydrocarbons. It was found that a metal oxide catalyst (Cu–Cr–Mn) was as active as platinum catalyst in the reaction of nitrogen-derivatives' oxidation, but its selectivity with respect to NO_x formation was very poor – the concentration of nitrogen oxides detected in the flue gases was much lower than that when platinum catalyst was used [7]. Nitrogen was the main reaction product.

The Research Group of Environmental Catalysis, Wrocław University of Technology, has been working for many years on the development and preparation of new oxidation catalysts and their application in the treatment of organic air pollutants from industrial flue gases and motor exhaust. Since several years the Research Group has been collaborated with the colleagues from the Technical University of Dresden and the Technical High School of Dresden. Recently, some perovskite catalysts on monolithic support were developed at Dresden Technical High School, and tested at Wrocław University of Technology for the oxidation of typical solvent vapours. At the Wrocław University of Technology, the variety of noble metals and base metal catalysts, generally on monolithic support, were manufactured and tested in the process of solvent vapour (including nitrogen-, oxy- and halogen-derivatives) oxidation. Some of them were tested for automotive emission control. The aim of this paper is a review of the results of authors' recent investigations.

2. CATALYSTS

The catalysts manufactured for the purpose of the study were in the monolithic form on cordierite supports. The cordierite monolithic blocks were produced at the Institute of Glass and Ceramics in Warsaw. The description of cordierite support is presented below:

Cell shape, square.
Cell density, $32/cm^2$.
Cell size, 1.45 mm.
Wall thickness, 0.35 mm.
Open front area, 64%.
Specific surface area, $1856 \ m^2/m^3$.

Because of a very small specific surface area of cordierite support substrate, it needs a washcoat deposition between the support and an active phase. The best material developed at our laboratory for the washcoat consists of γ-Al_2O_3 with an addition of rare earth elements, generally lanthania, up to 10 mass% of alumina. After drying and calcination the washcoat includes 1.5–2% of the support mass. The active ingre-

dients were deposited on the washcoat by its immersion in the solution of nitrates of adequate active metal (Co, Cr, Cu, Mn, Ni) or $LaMnO_3$ perovskite slurry with La^{+3} ions partially exchanged for Ag^+ ions. The active phase of coated metal oxide catalysts should amounted at least to 5–20 mass%, so the monolithic supports needed the twice impregnation. For the purpose of solvent vapours' oxidation, seven metal oxide catalysts were manufactured; their description is shown in table 1.

Table 1

Description of the catalysts tested in solvent vapour oxidation

Catalyst	Support	Active phase
KOW-1	Cordierite	Cu–Cr–Mn (ca. 5%)
KOW-2	Cordierite	Cu–Cr–Ni (ca. 5%)
KOW-3	Cordierite	Cu–Co–Mn (ca. 5%)
KOW-4	Cordierite + alumina + lanthania washcoat	Cu–Co–Mn (ca. 5%)
WK-1	Cordierite + lanthania washcoat	$La_{0.75}Ag_{0.25}MnO_3$ (9%)
WK-3	Cordierite + lanthania washcoat	$La_{0.75}Ag_{0.25}MnO_3$ (16%)
WK-5	Cordierite + lanthania washcoat	$La_{0.5}Ag_{0.5}MnO_3$ (12.5%)

3. METHODS

The test reactions of solvent vapours' oxidation proceeded over metal oxide catalysts on a cordierite monolithic support – KOW-1, KOW-2, KOW-3 and KOW-4, as well as over perovskite catalysts – WK-1, WK-3 and WK-5. The tests were carried out in an electrically heated laboratory-scale glass reactor of "tube-in-tube" type. Every compound was combusted separately. The solvent vapours were mixed with air to an inlet concentration of ca. 1 g/m^3. The reaction temperatures ranged between 200 and 500 °C. Gas flow space velocity of 10000 h^{-1} was typical of metal oxide catalysts.

Concentrations of reagents in the reaction gases were measured using gas chromatography (Perkin-Elmer GC with integrator, FID, and column of 1.8 m/2.7 mm packed with 10% PEG 2000 on Chromosorb W). The conditions of analysis were selected in such a way as to separate every investigated compound as well as potentially yielded intermediate products – first of all aldehydes and light hydrocarbons (C_1–C_4). Temperature of the column reached 73 °C, while the temperature of injector and detector amounted to 100 °C. The analysed gas samples were taken by means of a gas syringe and injected directly into a chromatograph.

4. RESULTS AND DISCUSSION

The activities of the catalysts investigated were measured based on the conversion efficiency of oxidized compounds, i.e. from their inlet and outlet concentrations. The selectivity of the reaction was estimated from the concentration of yielded intermediates detected in flue gases.

Table 2

Temperatures of 50% and 90% conversion efficiencies of oxidized compounds

Catalyst	Toluene		n-Hexane		Acetone		Ethyl acetate		Butyl acetate	
	50%	90%	50%	90%	50%	90%	50%	90%	50%	90%
KOW-1	415	460	430	>500	290	360	315	375	300	360
KOW-2	430	490	>500	>500	315	375	–	–	310	500
KOW-3	295	360	300	370	240	265	250	290	265	315
KOW-4	280	305	275	360	250	260	240	270	250	275
WK-1	350	>500	370	>500	230	400	260	500	240	370
WK-3	255	360	255	425	240	350	210	300	210	280
WK-5	270	315	290	370	230	245	215	240	215	240

The temperatures of 50 and 90% conversion efficiencies of every oxidized compound are presented in table 2. Generally, the oxidation efficiencies of oxy-derivatives were higher than those of hydrocarbons over all metal oxide catalysts tested. The reactivity of oxidized compounds can be arranged in the following descending order:

oxy-derivatives > toluene > n-hexane.

Depending on the active phase composition, a catalyst activity changed markedly. In the presence of the most active catalysts – WK-5 (perovskite) and KOW-4 (Cu–Co–Mn oxides on alumina–lanthania washcoat) – toluene and n-hexane were oxidized with 90% efficiency at the temperatures of 315 and 370 °C (WK-5), and 305 and 360 °C (KOW-4), respectively. The other catalysts needed much higher temperatures for 90% oxidation efficiency of toluene and n-hexane. Over each catalyst under investigation, oxidation of hydrocarbons ran to CO_2 and water, no other organic compounds were detected in the flue gases.

The reaction of oxy-derivatives oxidation was much more complicated and yielded by-products, including products of incomplete oxidation. In the flue gases, the following intermediates were detected:

acetaldehyde – in course of acetone oxidation,

acetaldehyde and ethanol – in ethyl acetate oxidation,

acetaldehyde, propionaldehyde, butyraldehyde and butanol – in butyl acetate oxidation.

The scheme of acetone oxidation could be presented as follows:

$$acetaldehyde$$

$$acetone \longrightarrow CO_2$$
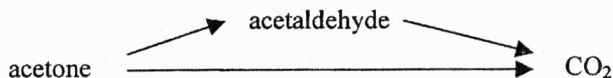
Acetate oxidation could be shown according to the scheme:

$$alcohol \longrightarrow aldehydes$$

$$acetate \longrightarrow CO_2$$
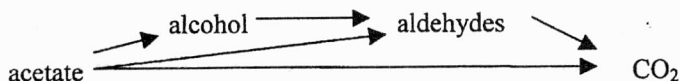
In the first step of acetate oxidation, acetate yields an adequate alcohol (ethanol or butanol for ethyl and butyl acetate oxidation, respectively), due to partial hydrolysis. Next, ethanol was partially oxidized via acetaldehyde to CO_2 and water. Butanol, partially oxidized to butyraldehyde, due to consecutive reactions of butyraldehyde decomposition via smaller chain aldehydes, yielded CO_2 according to the reaction mechanism presented by ISMAGILOV [8]:

$$RCH_2CH_2OH \longrightarrow RCH_2CHO \longrightarrow RCHO \longrightarrow ... \longrightarrow CH_3CHO \longrightarrow CO_2$$
$$CO$$

The results of oxy-derivative conversion efficiency versus reaction temperature over the most active catalysts – WK-5 and KOW-4 – are presented in figure 1.
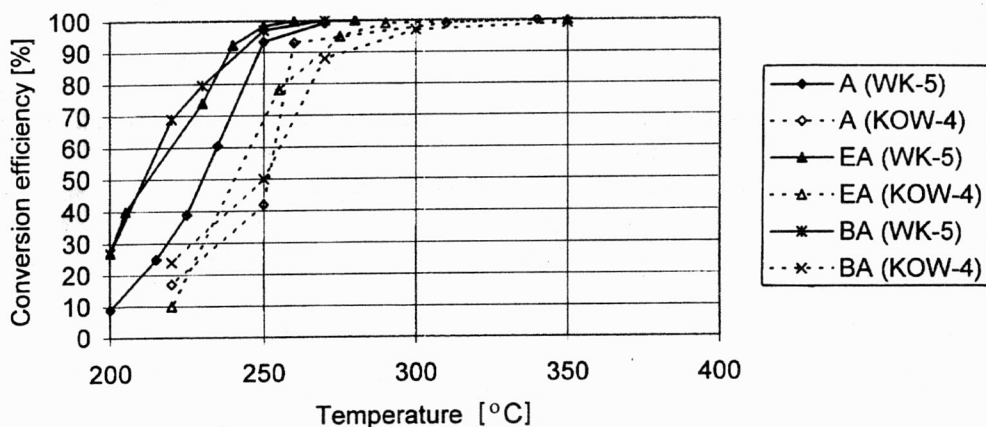

Fig. 1. Conversion efficiencies of the oxy-derivatives tested
over the most active catalysts WK-5 and KOW-4;
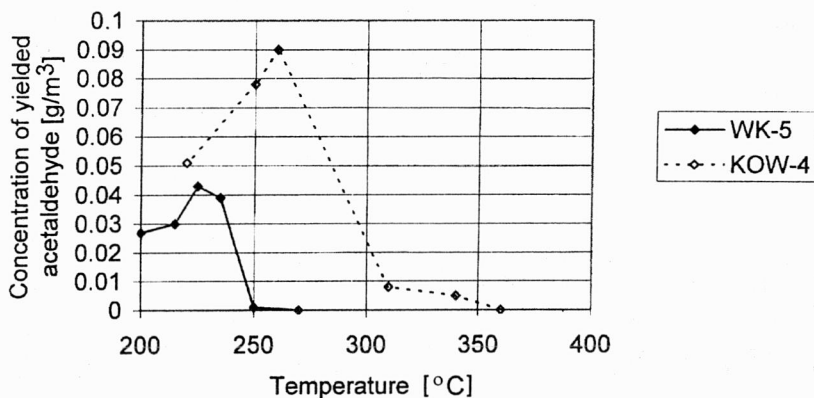A – acetone, EA – ethyl acetate, BA – butyl acetate

Fig. 2. Selectivity of acetone oxidation to acetaldehyde over WK-5 and KOW-4
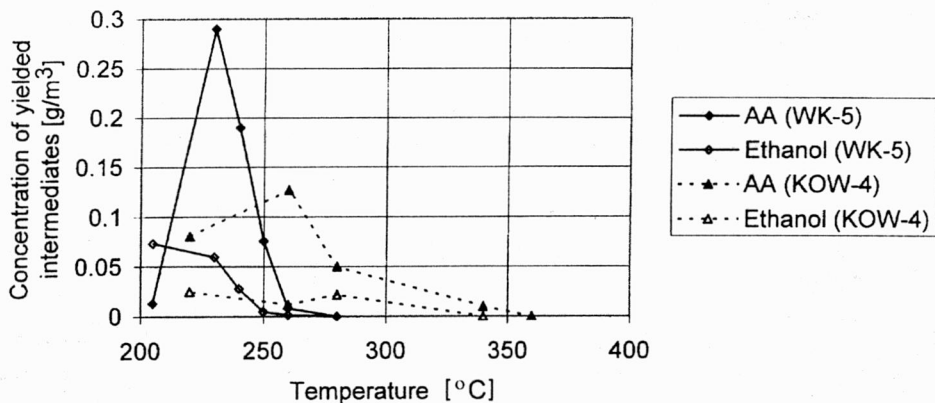

Fig. 3. Selectivity of ethyl acetate combustion to ethanol and acetaldehyde (AA)
over WK-5 and KOW-4

Figures 2–5 represent the selectivity of oxy-derivatives oxidation expressed as a concentration of the intermediates yielded.

Perovskite catalyst WK-5 was most active in the oxidation of each compound under investigation. Acetone and acetates were oxidized with 90% efficiencies at the temperatures of 245 and 240 °C, while KOW-4 needed the reaction temperatures of 260, 270 and 275 °C, for the respective 90% conversion efficiencies of acetone, ethyl acetate and butyl acetate. Acetone oxidation over WK-5 at lower oxidation temperatures yielded acetaldehyde; its maximum concentration of 0.042 g/m^3 was observed at 225 °C. Acetaldehyde was completely oxidized above 250 °C. In the presence of KOW-4, acetaldehyde was produced in much higher concentration. The highest concentration of aldehyde (0.09 g/m^3) was measured at 260 °C – the temperature of 90%

acetone conversion efficiency. Even at 310 °C acetaldehyde concentration reached 0.009 g/m^3; only beginning from the temperature of 360 °C aldehyde was not detected in the flue gas.
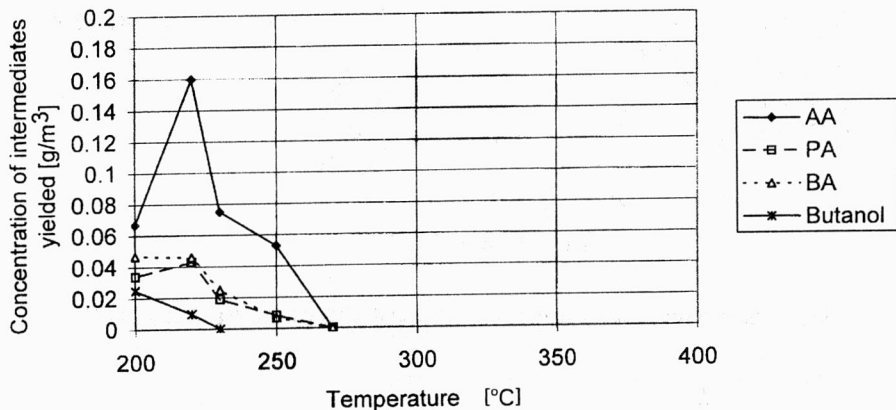

Fig. 4. Selectivity of butyl acetate combustion to acetaldehyde (AA), propionaldehyde (PA), butyraldehyde (BA) and butanol over WK-5
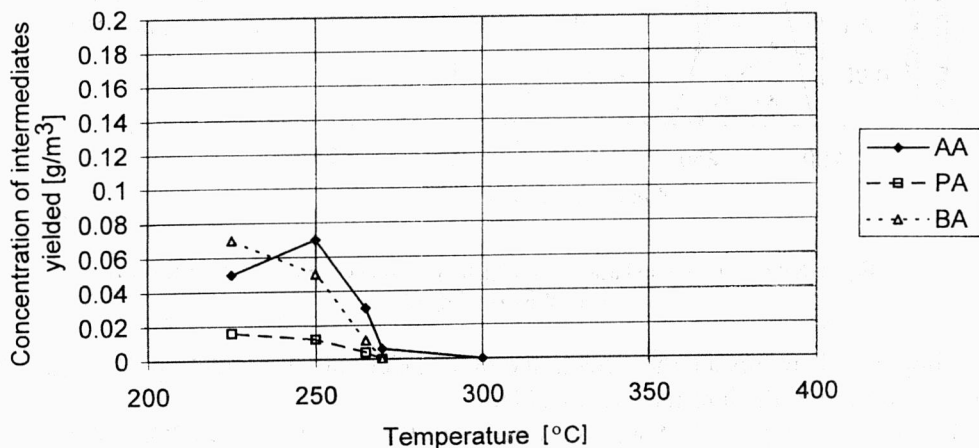

Fig. 5. Selectivity of butyl acetate combustion to acetaldehyde (AA), propionaldehyde (PA) and butyraldehyde (BA) over KOW-4

When acetates were oxidized, the concentration of by-products yielded over WK-5 was lower than over KOW-4. In the presence of WK-5, the highest concentration of acetalde-hyde, typical product of incomplete oxidation, was measured at 220–230 °C, and reached

0.16 and 0.29 g/m^3, respectively, when butyl acetate and ethyl acetate were oxidized. The other intermediates were detected at much lower concentration; when butyl acetate was oxidized maximum concentration of propion- and butyraldehyde reached 0.043 g/m^3 at 220 °C. The concentration of ethanol yielded in the course of ethyl acetate oxidation reached 0.075 g/m^3 at 205 °C and systematically decreased with the rising temperature of reaction. Beginning from 275 °C, no by-products were found in the flue gas.

In the presence of KOW-4, acetaldehyde at the highest concentration of 0.07 and 0.125 g/m^3 was detected at 250 and 260 °C, respectively, when butyl and ethyl acetates were combusted. In the course of butyl acetate oxidation, aldehydes were oxidized completely beginning from 300 °C, while ethyl acetate required 360 °C for total oxidation of intermediates.

Over other catalysts of lower activity than WK-5 and KOW-4, the concentrations of yielded by-products were similar to those observed for KOW-4, but they were detected in the flue gas even at the highest reaction temperature of 450–500 °C.

5. CONCLUSIONS

• In the presence of metal oxide catalysts, the hydrocarbon oxidation efficiency was lower compared with oxy-derivative conversion. The selected hydrocarbons were oxidized only to CO_2 and water, no other compounds were found in the flue gas.

• Oxidation of oxy-derivatives run via intermediates, such products of incomplete oxidation as acetaldehyde in the course of acetone and ethyl acetate oxidation and acet-, propion- and butyraldehydes when butyl acetate was combusted. It is particularly important when the aldehyde yielded (first of all acetaldehyde) has a concentration limit lower than the primary oxy-derivative compound (e.g. acetates). When the optimum reaction temperature is chosen the reaction selectivity to the products of incomplete oxidation should be taken into account.

• WK-5 perovskite catalyst, with La^{3+} ions partially exchanged for Ag$^+$ ions (50 atom %), and KOW-4 (Cu–Co–Mn oxides on a γ-alumina washcoat) were most active in the oxidation of every tested compound. Their activities were similar or, in the case of oxy-derivatives oxidation, even higher than those of noble metal catalysts with platinum contents lower than 0.1 mass %. The other metal oxide compositions, e.g. Cu–Cr–Ni or Cu–Cr–Mn, were of lower activity and higher selectivity to the products of incomplete oxidation than Cu-Co-Mn oxides. Over less active catalysts the yielded by-products were detected in the flue gas even at high reaction temperatures (450–500 °C).

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UTLENIANIE LOTNYCH ZWIĄZKÓW ORGANICZNYCH
W OBECNOŚCI KATALIZATORÓW TLENKOWYCH

Utlenianie katalityczne stanowi skuteczną metodę ograniczania emisji organicznych zanieczyszczeń powietrza. W instalacjach przemysłowych są zwykle stosowane katalizatory na bazie metali szlachetnych z grupy platynowców, charakteryzujące się wysoką aktywnością i stabilnością pracy. Aby otrzymać tańsze katalizatory, prowadzi się badania nad wytworzeniem katalizatorów tlenkowych, również o strukturze perowskitu. Do badań wytworzono cztery katalizatory na bazie trójskładnikowych tlenków metali oraz trzy kontakty perowskitowe typu La$_{1-x}$Ag$_x$MnO$_3$, wszystkie na monolitycznym nośniku kordierytowym. Ich aktywność i selektywność przebadano w reakcji utleniania dwóch węglowodorów – toluenu i *n*-heksanu, oraz trzech połączeń tlenowych – acetonu, octanu etylu i octanu butylu. Połączenia tlenopochodne utleniały się łatwiej niż węglowodory, jednak reakcja przebiegała poprzez produkty pośrednie, głównie aldehydy, wykrywane w gazach poreakcyjnych. Katalizatory KOW-4 (tlenki Cu–Co–Mn na warstwie pośredniej γ-Al$_2$O$_3$) i WK-5 (perowskit La$_{0.5}$Ag$_{0.5}$MnO$_3$) wykazały najwyższą aktywność, porównywalną z aktywnością kontaktów platynowych o zredukowanej poniżej 0,1% mas. zawartości platyny.