

Preparation and testing of cordierite monolithic catalysts for oxidation of aromatic volatile organic compounds

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This work reports the results of catalytic oxidation of aromatic volatile organic compounds (VOCs). A gaseous mixture of benzene, toluene, ethylbenzene, and o-xylene (BTEX) in nitrogen was used as representative of VOCs. Reactions were carried out in a monolithic reactor at different temperatures, with a constant initial concentration of reactants and a constant ratio of BTEX and oxidant (synthetic air). Analysis of the oxidation products was carried out on-line before and after reaction using gas chromatography. The work involves the preparation of catalysts and their application on an inert cordierite monolithic carrier, using different combinations of mixed manganese oxides (manganese with copper, iron, and nickel) and palladium as a representative of noble metals. The prepared cordierite monolithic catalysts showed great mechanical stability and high performance regarding oxidation of the mixture of aromatic compounds. High conversion values (90 %) of all components of the mixture were achieved at temperatures below 200 °C, depending on the chemical composition of the catalytic layer. A comparison with the activity of a commercial monolithic catalyst (Purelyst PH-304), which contains Pt and Pd as catalytically active components, using toluene as a model component. A comparison of the prepared manganese oxides showed that $MnFeO_x$ and $MnCuO_x$ had the best catalytic activity. When Pd was used in combination with $MnFeO_x$ in a form of a single monolith, where Pd was applied to $\frac{1}{4}$ of the overall monolith length and $MnFeO_x$ to $\frac{3}{4}$ of overall length, achieved 90 % conversions (T_{90}) were up to 20 °C lower when compared with the same $MnFeO_x$ monolithic catalysts without Pd. Based on the comparison of the prepared ceramic monolithic catalysts with a commercial catalyst and because the comparison was made only based on toluene conversion, it was concluded that the prepared catalysts can be considered as alternatives to commercial monolithic catalysts by introducing a low concentration of Pd.

1. Introduction

Volatile organic compounds (VOC) due to their use in industry (oil refineries and petrochemical plants), transport and households, are present in an aquatic environment, soil and atmosphere. Although biogenic sources are a large source of volatile organic compounds in the atmosphere, the impact of emissions from human activities is much more significant. This is a major environmental and sociological problem today, as it not only leads to many detrimental impacts on human health and living standards but also disrupts the state of ecosystems and causes global climate change.

There are many exhausts and waste gas after-treatment technologies. One of the most suitable processes concerning environmental and economic criteria is catalytic oxidation. Given the great interest in expanding existing areas of application of monoliths, great attention of researchers is focused on improving existing and developing new procedures for the preparation of monolithic catalysts. In catalytic reaction engineering, the monolith represents a structure with well-defined and constant geometry, which most often serves as a carrier of catalytic material, through whose channels reactants and products are transferred by convection. There are also so-called integral versions of monoliths that do not contain an inert carrier but consist entirely of a catalytically active component or mixtures of active components. The geometry of the channels determines the total active surface area and therefore affects the mass and heat transfer processes and thus the catalytic efficiency. There is no ideal channel geometry, but it depends on the specific problem and the chemical

reaction. The first step in the preparation of monolithic catalysts usually involves a selection of basic structural material, so-called carrier (e.g. cordierite). Sometimes it is necessary to apply a second layer (support) between the carrier and catalyst layer which improves adhesion and application properties of monolithic catalysts (most often Al₂O₃ and zeolites). It may itself contain catalytically active components. The third (outer) layer contains catalytically active components (e.g. noble metals and transition metal oxides) that participate in chemical reactions and have the greatest impact on obtained conversions.

This work aims to prepare ceramic monolithic catalysts for catalytic oxidation of aromatic compounds using mixed oxides of transition metals (manganese, copper, iron, and nickel) and a noble metal (palladium) as catalytically active components. In this study, a mixture of benzene, toluene, ethylbenzene, and o-xylene (BTEX) was chosen as a representative of volatile organic compounds. The reactions were carried out in a monolithic reactor. The main advantages of such catalytic reactor design are a small pressure drop, ease of construction, and specificity of the reactor design itself which ensures favorable hydrodynamic operating conditions and transfer to a larger scale (scale-up). The work includes devising a monolithic catalyst, which includes the preparation of mixed metal oxides and the development of a method for applying such a catalytic layer to an inert ceramic monolithic carrier. Testing of catalytic properties of the monolithic catalyst thus prepared was carried out at different temperatures, with a constant initial concentration of reactants (BTEX), a constant ratio of reactants, and oxidant (synthetic air) with an approximately constant mass/thickness of the catalyst layer.

2. Experimental part

2.1. Characterization of catalytically active components

Characterization of used mixed manganese oxides was performed by Duplancic et al (2020). It included differential scanning calorimetry, nitrogen adsorption-desorption analysis, scanning electron microscopy with energy-dispersive X-ray spectroscopy, temperature-programmed reduction of hydrogen, X-ray diffraction, and X-ray photoelectron spectroscopy.

2.2. Preparation of monolithic catalysts

Monolithic catalysts were prepared by applying catalytically active components to the walls of an inert monolithic cordierite structure using the impregnation method. Two types of square-shaped monoliths were used that differed in channel size. Monolith channel dimensions were 1 mm x 1 mm for smaller channels (SCC) and 2 mm x 2 mm for larger channels (LCC). The length of the monolithic catalysts was 40 mm. When the combination of transition metal oxides and palladium oxide was used, the length of the monolith containing manganese oxides was 30 mm ($\frac{3}{4}$ of overall length) while the length of the monolith containing palladium oxide was 10 mm ($\frac{1}{4}$ of overall length). After the cordierite substrate was cut to the desired shape and size suitable for experimental measurements, it was washed in ethanol to remove impurities, and then dried at 120 °C for 1 hour. For applying mixed metals on the cordierite carriers 1 M water solutions (initial solutions) of manganese (II) nitrate tetrahydrate, copper (II) nitrate trihydrate, iron (III) nitrate nonahydrate, and nickel (II) nitrate hexahydrate were prepared. To compare the efficiency of mixed metal oxides with noble metals, monolithic catalysts containing palladium were prepared using palladium (II) nitrate hydrate (0.1 M). Solutions for impregnation were prepared by mixing initial solutions in volume ratio 1:1. When the combination of all transition metals was used volume ratio was Mn: Fe: Cu: Ni = 3: 1: 1: 1. Carriers were submerged in impregnation solutions for 30 minutes. This was followed by drying at 120 °C for 1 h and then calcination at 500 °C for 2 h.

2.3. Adhesion test

Testing of the mechanical stability of the catalytic layer (adhesion test) was performed by exposing the prepared monolithic catalysts to ultrasonic vibrations and measuring the weights before and after the procedure, similar to how it is shown by Barbero et al. and Wu et al. An Elmasonic S 30 H ultrasonic bath with an ultrasonic frequency of 37 kHz and a working volume of 1.9 L was used. The monolithic catalyst was immersed in petroleum ether and then exposed to ultrasonic vibrations for 30 minutes at room temperature. Drying was then carried out at 120 °C for 1 h after which monoliths were cooled to room temperature and weighted.

2.4. Catalytic oxidation of BTEX compounds

Catalytic oxidation of BTEX was tested at atmospheric pressure, at different temperatures, and with a constant total flow of the reaction mixture ($92 \text{ cm}^3\text{min}^{-1}$). During the experiment, the reaction mixture was passed from bottom to top of the reactor, and the monolithic catalyst was placed between two layers of quartz wool. The initial concentration of benzene, toluene, ethylbenzene, and o-xylene was 52.1, 52.4, 49.9, and 55.4 ppm, respectively in nitrogen. The temperature inside the reactor was controlled using a thermocouple located in the central part of the reactor above the catalyst. Analysis of the reaction mixture at the reactor outlet was performed by on-line gas chromatography. The course of the reaction was monitored by determining the total conversion of BTEX components after reaching steady-state conditions. The economic goal was to achieve as high conversions as possible at the lowest possible temperatures, and therefore the possibility to catalytically oxidize volatile organic compounds.

3. Results and discussion

3.1. Mechanical stability of prepared monolithic catalysts

The results of performed adhesion test are summarized in Table 1. As can be seen, the adhesion of the catalytic layer is excellent due to the mass loss ranging between 0 and 0.018 %. Such a low amount of lost catalyst suggests great mechanical stability of the prepared monolithic catalysts which is one of the key properties that monoliths must have before further tests. Significant loss of catalyst would suggest that catalyst and carrier are not compatible and that the application of support layer, a different combination of carrier and catalytically active components, or using additives for enhancing adhesion could be mandatory.

Table 1: Mechanical stability of monolithic catalysts

Catalyst	Mass [g]		Mass loss [%]
	Before ultrasound	After ultrasound	
MnFeOx	0.6621	0.6220	0.016
MnCuOx	0.5609	0.5608	0.018
MnNiOx	0.6095	0.6094	0.016
MnFeCuNiOx	0.5994	0.5994	/

3.2. Catalytic oxidation of BTEX

The results of the measurements are showed in Figures 1 and 2 and summarized in Table 2.

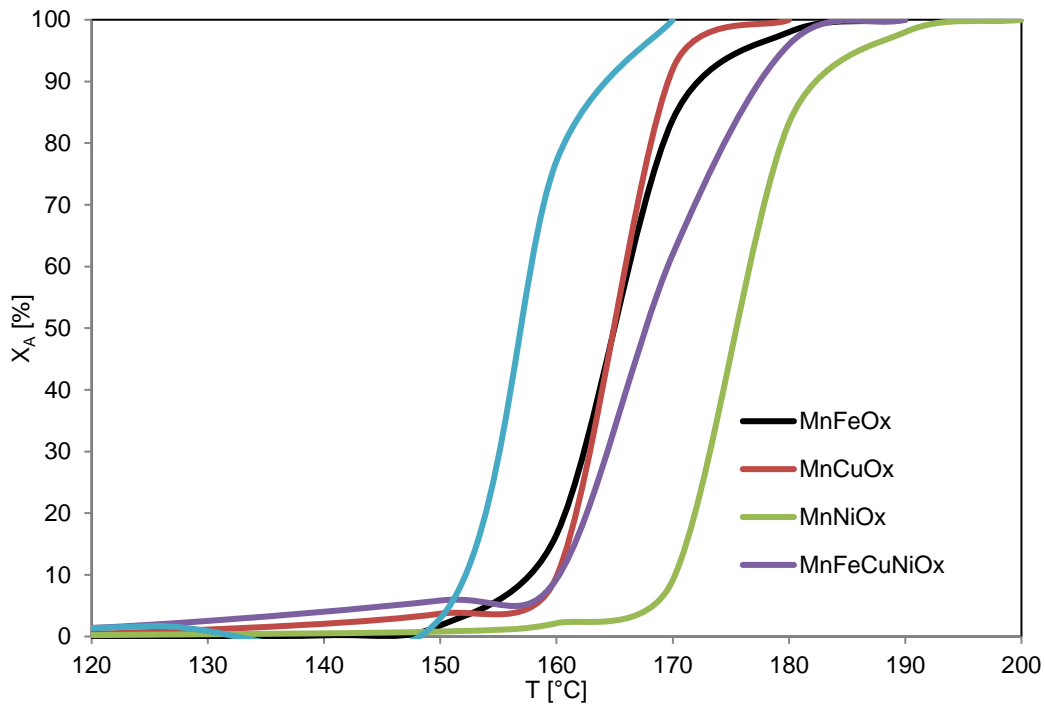


Figure 1. Comparison of tested SCC monolithic catalysts with mixed manganese oxides and palladium

Based on the measurements made, it can be seen that the curves showing the dependence of the conversion on temperature took on a characteristic S-shape. Such curves are common for the oxidation of related compounds, such as CO and various hydrocarbons, and are also known as self-ignition or self-heating curves.

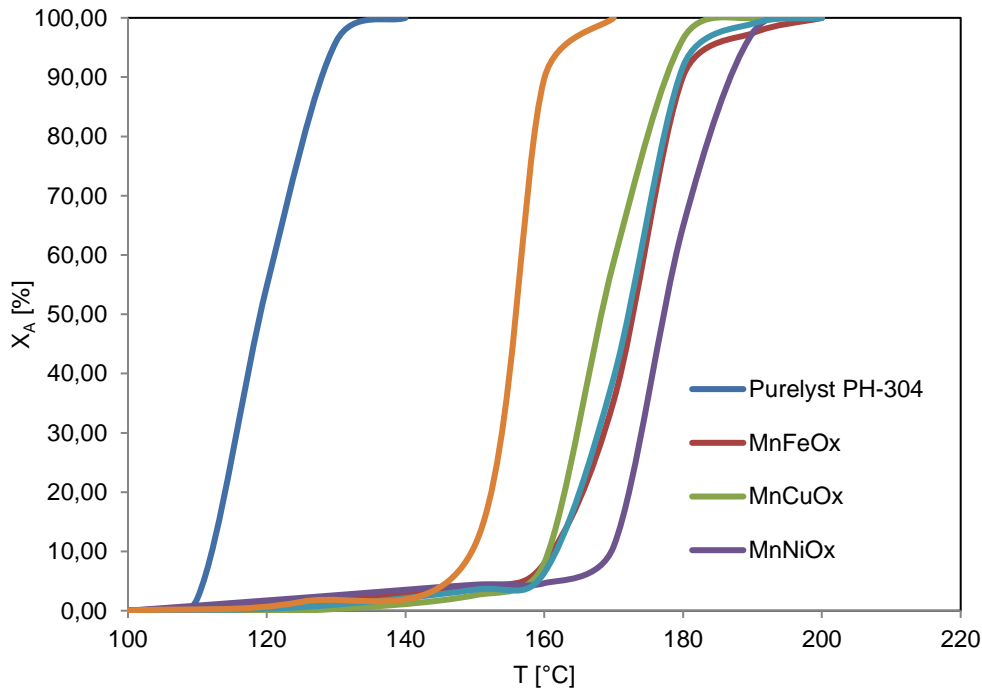


Figure 2. Comparison of conversions achieved on tested LCC monolithic catalysts

In the preliminary part of the study, the possibility of homogeneous oxidation in the gas phase at different temperatures without the presence of catalytically active components was investigated. For this purpose, measurements were performed in an empty reactor and measurements with inert monolithic support (without a previously applied catalytic layer).

Common parameters that indicate the efficiency of catalytic systems are the temperatures at which 50 % (T_{50}) and 90 % (T_{90}) conversion is achieved. When comparing catalysts on that basis, lower values of T_{50} and T_{90} indicate a catalyst with better efficiency.

Table 2. Temperatures at which T_{90} and T_{50} were reached for all BTEX components

Catalyst	T_{90} [°C]				T_{50} [°C]			
	B	T	E	o-X	B	T	E	o-X
Empty reactor	>400	347	333	312	395	305	279	271
Carrier without catalyst	398	342	336	334	332	308	286	280
SCC MnFeOx	184	174	169	169	173	165	158	158
LCC MnFeOx	190	180	178	178	178	173	168	168
SCC MnCuOx	179	170	168	169	174	165	161	161
LCC MnCuOx	190	178	171	170	178	168	162	162
SCC MnNiOx	192	185	179	179	183	175	171	171
LCC MnNiOx	196	188	183	184	186	177	174	174
SCC MnFeCuNiOx	180	178	172	172	175	168	164	164
LCC MnFeCuNiOx	190	180	177	176	180	172	164	164
SCC MnFeOx/Pd	182	166	164	165	161	156	156	156
LCC MnFeOx/Pd	182	160	160	160	159	155	155	155
LCC Purelyst PH-304	-	128	-	-	-	119	-	-

From the obtained results it can be seen that complete homogeneous oxidation of the mixture of benzene, toluene, ethylbenzene, and o-xylene occurs only at temperatures higher than 300 °C. In the case of oxidation in an empty reactor, complete conversion of only o-xylene was achieved at a temperature of 350 °C, while at the same temperature in the reactor with inert monolithic support, complete conversion of ethylbenzene, o-xylene, and toluene were achieved. That is expected because the reaction mixture stays at operating temperature in the reactor for a longer time when passing through a filled reactor. The lowest conversions were obtained for benzene, which can be attributed to its stable aromatic structure.

The maximum conversion of BTEX components is achieved at temperatures up to 200 °C. In both types of ceramic monolithic catalysts concerning the size of the channels, it was observed that the best catalyst was the one with a catalytically active layer containing a combination of Pd and transition metals ($\frac{1}{4}$ Pd and $\frac{3}{4}$ MnFeOx), and the one with the highest T_{90} values with the active layer of MnNiOx. Of the two-component and three-component mixed metal oxides that did not contain Pd, MnFeOx and MnCuOx proved to be the best, followed by MnFeCuNiOx and MnNiOx.

In line with expectations, monoliths with smaller channels, regardless of the chemical composition of the catalytic layer, showed better results, i.e. lower temperature values at which 50 % and 90 % conversion are achieved. This can logically be explained by the larger outer or geometric surface area of the monolithic support, which results in a larger specific surface area of the catalytic layer available for the oxidation of the model components. It can be seen that the effect of a larger surface area in monoliths with smaller channels was not significant, from which it follows that the oxidation of BTEX components is probably very fast.

When results thus obtained are compared with the same catalysts in form of powders and immobilized on a metallic carrier, conversions are similar. As shown in Duplančić et al. were MnNiOx in a form of powder had higher conversions when compared with the same catalyst that was applied on a surface of a metallic monolith, but when the conversions were expressed per unit mass of catalyst it was shown that the monolith had 9 times higher conversions using 20 times smaller amount of catalyst.

4. Conclusions

The catalytic oxidation of BTEX mixture on ceramic monolithic catalysts with two characteristic channel sizes and different composition of the catalytically active layer was investigated. Mixed oxides of manganese with copper, iron, and nickel, and palladium were used as catalytically active components.

Ceramic monolithic catalysts have been successfully prepared, and it has been confirmed that the catalytic layer shows great mechanical stability. Complete conversion of all components of the BTEX mixture on all ceramic monolithic catalysts was achieved at a temperature of 200 °C or less. Due to the larger total surface area on ceramic monolithic catalysts with smaller channels (SCC), complete conversions of the BTEX mixture were achieved at lower temperatures in comparison with monolithic catalysts with larger channels (LCC). A combination of manganese and copper, followed by manganese and iron, proved to be the most efficient for

the oxidation of BTEX. Monolith containing a mixed metal oxide of manganese and iron ($\frac{3}{4}$ monolith) with palladium ($\frac{1}{4}$ monolith) improved the catalyst activity, reducing T_{90} for all components of the BTEX mixture compared to a catalyst to which only mixed metal oxide of manganese and iron was applied. Future work will include further improvement of activities of the tested metal oxides and proposing of kinetic and reactor models with varying degrees of complexity using the basic methodology of chemical engineering.

5. References

- Avila P., Montes M., Miró E. E., 2005, Monolithic reactors for environmental applications: A review on preparation technologies. *Chemical Engineering Journal*, 109, 11-36, DOI: 10.1016/j.cej.2005.02.025
- Barbero B. P., Costa-Almeida L., Sanz O., Morales M. R., Cadus, L. E., Montes M., 2008, Washcoating of metallic monoliths with a MnCu catalyst for catalytic combustion of volatile organic compounds, *Chemical Engineering Journal*, 139, 430-435, DOI: 10.1016/j.cej.2007.12.033
- Berenjian A., Chan N., Malmiri H. J., 2012, Volatile Organic Compounds Removal Methods: A Review, *American Journal of Biochemistry and Biotechnology*, 4, 220-229, DOI: 10.3844/ajbb.2012.220.229
- Duplančić M., Tomašić V., Gomzi Z., 2017, Catalytic oxidation of toluene: comparative study over powder and monolithic manganese-nickel mixed oxide catalysts, *Environmental Technology*, 39, 2004-2016, DOI: 10.1080/09593330.2017.1346713
- Duplančić M., Gomzi V., Pintar A., Kurajica S., Tomašić V., 2020, Experimental and theoretical (ReaxFF) study of manganese-based catalysts for low-temperature toluene oxidation, *Ceramics International*, In Press, DOI: 10.1016/j.ceramint.2020.09.147
- Evuti A. M., 2013, A Synopsis on Biogenic and Anthropogenic Volatile Organic Compounds Emissions: Hazards and Control, *International Journal of Engineering Sciences*, 2, 145-149
- Guo H., Lee S. C., Chan L. Y., Li W. M., 2004, Risk Assessment of exposure to volatile organic compounds in different indoor environments, *Environmental Research*, 94, 57-66, DOI: 10.1016/s0013-9351(03)00035-5
- Govender S., Friedrich H. B., 2017, Monoliths: A review of the basics, preparation methods and their relevance to oxidation, *Catalysts*, 7, 62-91, DOI: 10.3390/catal7020062
- Nijhuis T. A., Beers A. E. W., Vergunst T., Hoek I., Kapteijn F., Moulijn J. A., 2001, Preparation of monolithic catalysts, *Catalysis Reviews*, 43, 345-380, DOI: 10.1081/CR-120001807
- Rusu A. O., Dumitriu E., 2003, Destruction of Volatile Organic Compounds by Catalytic Oxidation, *Environmental Engineering and Management Journal*, 2, 273-302
- Tomašić V., Jović F., 2006, State-of-the-art in the monolithic catalysts/reactors, *Applied Catalysis A: General*, 311, 112-121., DOI: 10.1016/j.apcata.2006.06.013
- Wu D., Kong S., Zhang H., 2014, Mechanical Stability of Monolithic Catalysts: Factors Affecting Washcoat Adhesion and Cohesion During Preparation, *Particle Technology, and Fluidization*, 60, 2765-2773, DOI: 10.1002/aic.14480
- Zemankova K., Brechler J., 2010, Emissions of biogenic VOC from forest ecosystems in central Europe: Estimation and comparison with anthropogenic emission inventory, *Environmental Pollution*, 158, 462-465, DOI: 10.1016/j.envpol.2009.08.032

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