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*Original research paper*

# Comparison of the powder and monolithic Mn-Ni catalyst in toluene combustion

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## Summary

One of the major air pollutants that give rise to harmful health and environmental effects are volatile organic compounds (VOCs) emitted from many of anthropogenic sources. Among existing destructive VOCs removal methods, catalytic combustion is the most convenient one due to low reaction temperatures that lead to lower $NO_x$ and CO emissions. Catalysts usually used in this process are supported or unsupported noble metals and transition metal oxides or their combinations. Recently, many efforts have been made on the utilization of the low-cost and environment-friendly raw materials, such as manganese oxide combined with nickel, which have been investigated in this research. In this study toluene has been chosen as a representative volatile organic compound, since it contains aromatic ring which cannot be easily degraded.

Catalysts based on the mixed manganese oxides were synthesized by the co-precipitation method and characterized using different instrumental techniques (such as DSC, FTIR, SEM, etc.) Monolithic Mn-Ni catalyst was prepared using the washcoating method. Catalytic combustion of toluene was carried out both in the fixed bed reactor (catalyst in the powder form) and in the metallic monolith reactor. Reaction was performed at different reaction temperatures and different total flow rates of the reaction mixture (23-100 $cm^3$/min). It was revealed that the manganese-nickel mixed oxide catalysts show good catalytic activity, achieving a complete oxidation of toluene in the temperature range of 230-350 °C, depending on the space time inside the reactor, toluene inlet concentration and the type of catalyst used.

*Keywords:* VOC, toluene combustion, Mn-Ni oxides, metallic monolith

## Introduction

Volatile organic compounds attracted great attention of researchers in the field of environmental protection, because of their high toxicity contribution to the air, water and soil pollution, as well as due to their participation in the emergence of the greenhouse effect, acid rain formation and the destruction of stratospheric ozone. A majority of VOCs emissions are result of antrophogenic activities, such as fuel combustion, industrial processes, non and on-road vehicles (Ihm, 2000). When there is no interest in recovering VOCs, they are usually destroyed by catalytic oxidation, which is more preferable than thermal one, due to lower reaction temperatures that lead to lower $NO_x$ and CO emissions.

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In the commercial combustion processes, noble metal catalysts (mainly Pt and Pd) are mostly used, because of their high activity and good stability. In terms of economical and practical consideration, other materials that present alternative to noble metals, have been studied. Among examined catalytic materials, catalysts based on transition metal oxides (such as Ni, Co, Cu, Cr, Mn and Fe) showed good activity in comparison to noble metals. Besides, they are less expensive and less sensitive to poisoning (Huang et al., 2016; Andersson et al., 1996; Bernier et al., 1998). The single oxide of $MnO_x$ was proved to exhibit high activity in VOCs conversion, which can be attributed to the capability of manganese to form oxides with different oxidation states and to their oxygen storage capacity (Armaroli et al., 1999).

In an attempt to develop more efficient catalyst formulations for VOCs combustion, many investigations were focused on the study of catalytic performance of binary mixtures of different transition metal oxides (Barbero et al., 2006, 2007; Banu et al., 2015; Jiang et al., 2009). For instance, catalytic activity of a series of binary mixtures of copper, manganese and cerium oxides supported on high surface area $\gamma$-$Al_2O_3$ for toluene oxidation has been studied in comparison with the corresponding single metal oxide components. Optimal results were obtained for 10 CuO-60 MnO, 30 MnO-50 $CeO_2$ and 15 CuO-75 $CeO_2$ catalysts (e.g. 10 CuO-60 MnO refers to a catalyst consisting of 10% of CuO, 60% of MnO and 30% of $Al_2O_3$, by weight), with complete oxidation at temperatures around 280 °C, i.e., considerably lower than those of the corresponding single oxide catalysts (Kondarides et al., 2011). The obtained results reveal that the improved performance of mixed oxide catalysts is not due to formation of solid solutions or new mixed-oxide phases, but due to facile spreading of one $M_xO_y$ species onto the other, which results in materials with increased surface area. Another example of the improved catalytic activity of combined metal oxides in comparison to single ones are manganese copper mixed oxide catalysts (Mn-Cu, respectively), prepared by co-precipitation varying the aging time for 4, 18 and 24h (Barbero et al., 2006). These catalysts showed better catalytic performance in propane and ethanol total oxidation than $Mn_2O_3$ and CuO pure oxides (prepared by the same method as Mn-Cu catalysts), respectively. It was also found that the increase of the aging time increased the catalytic activity and the selectivity to $CO_2$. The same trend was shown in the catalytic evaluation in ethanol and propane combustion over Mn-Ni, Mn-Fe and their pure oxides (Barbero et al., 2007). In order to apply these alternative catalysts in catalytic combustion of VOCs at the industrial level, they should be deposited on a structured support that allows treating large gas flows under the low pressure drop. The most popular structured supports used in the practice are ceramic or metallic monoliths.

Monolithic catalysts and/or reactors are representatives of the system in which common differences between a catalyst and a reactor disappear relevant to the micro and meso-scale level (Jović et al., 2006). The largest application of the monoliths is in the automotive industry for the cleanup of exhaust gases. Other widespread applications are the selective catalytic reduction of off-gases of the power stations and the ozone destruction in airplanes (Beers et al., 2001). Also, many researchers consider the application of monoliths as a replacement for a conventional reactor in multi-phase reactions (Hoek et al., 2004; Heiszwolf et al., 1999). As we know, till now there is only one example of the large-scale industrial application of monolithic catalysts in a multiphase process - the production of hydrogen peroxide using the anthraquinone process.

Recently, metallic monoliths have become very popular due to their high thermal conductivities, lower heat capacities, greater thermal and mechanical shock resistance and smaller wall thickness,

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allowing the higher cell density and lower pressure drop than ceramic ones (Avila et al., 2005). Different metalls and alloys are investigated for the manufacture of monolithic structures in the search for mechanical, chemical and thermal stability and availability in thin foils, e.g. Ni-Cr alloys, AISI 304 stainless steel, ferritic steel containing alumina (FeCrAlloy[®]) and aluminum coated by $Al_2O_3$ produced by anodization (Barbero et al., 2011). There are few well-developed procedures for coating of the active phase on the metallic monolithic support, for instance ion-exchange, homogeneous deposition-precipitation, impregnation and washcoating, which were explained in detail by Beers et al. (2001). In the study of Burgos et al. (2000) $Al/Al_2O_3$ monoliths impregnated with noble metal (Pt or Pd) have been evaluated in the catalytic oxidation of toluene. The resulting impregnated monoliths have shown high activity in the complete oxidation of toluene, even higher than the same catalyst supported on powder $Al_2O_3$. Considering that transition metal oxides are a more economical alternative, and, moreover, they demonstrated excellent catalytic behavior in oxidation reactions, the aim of this work was to develop an optimized Mn-Ni catalyst on a metallic monolith support by means of washcoating. Monolithic catalyst was then compared to Mn-Ni catalyst in powder form in the catalytic oxidation of toluene and obtained results were compared and discussed.

## Materials and Methods

The preparation procedures for powder and monolithic Mn-Ni oxide catalysts, together with instrumental techniques applied for catalyst characterization were presented. Also, experimental set-up and method of toluene determination were described.

*Catalyst preparation*
The powder catalyst was synthesized by the co-precipitation method using a similar procedure as described in the literature (Barbero et al., 2007; Habibi et al., 2003). Aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ (0.25 M) and $Mn(NO_3)_2 \cdot 4H_2O$ (0.25 M) were prepared and stirred for 5 min. The Mn/Ni atomic ratio was equal to 1. Aqueous $Na_2CO_3$ (first 1 M, then 0.25 M) was added to stirred nitrate solution, while the temperature was maintained within the range of 25-30 °C until, pH of 8.4 was achieved. The obtained precipitate was then left in this medium for 24 h. Then it was filtered, washed several times with distilled water and dried at 120 °C for 12 h obtaining the precursor. At the end, the precipitate was calcined at 250 °C (2 h) and 500 °C (3 h) to give the final catalyst. The powder material was then pressed under the pressure of $6x10^6$ Pa, gently crushed and sieved to obtain particles of 0.315-0.400 mm diameter.
The monoliths were prepared from thin foils of $Al/Al_2O_3$ (0.145 mm thickness), both sides anodized in oxalic acid at 40 °C. Anodized foils were donated from metallurgical industry Cinkarna, Slovenia. The monolithic structures were made by rolling around a spindle crimped foil. The monoliths (4 cm long and 0.6 cm of diameter) were then treated with 65 wt% $HNO_3$ in order to eliminate impurities and washed with distilled water. Then they were dried at 120 °C for 1 h and calcined at 500 °C for 2 h. Monolithic structures were dipped in a solution containing $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and citric acid for 30 minutes. Afterwards, they were dried at 120 °C for 1 h and calcined at 500 °C for 2 h. The preparation procedure is a modification of the procedure reported in the literature (Barbero et al., 2008).

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*Catalyst characterization*

Characterization of the powder catalysts included nitrogen adsorption-desorption analysis, differential scanning calorimetry (DSC), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and Fourier-transform infrared spectroscopy (FTIR).

Nitrogen adsorption and desorption isotherms were determined at -196 °C by means of ASAP-2000 analyzer (Micrometrics Inc.), from which surface area, the pore volume and pore diameter were determined, based on the Brunauer-Emmet-Teller (BET) model.

The morphology of the powder catalyst sample was examined with a SEM Tescan Vega III Easyprobe. This instrument is fully integrated with EDX microanalyser for automatic quantitative elemental analysis.

DSC analysis of the powder catalyst after the preparation and thermal treatment (drying at 120 °C) was performed on the Mettler Toledo DSC 823$^e$ instrument, based on the well proven Boersma or heat flux principle. The analysis was carried out in the temperature range from 25 to 550 °C, at the heating rate of 10 °C/min in an inert atmosphere of $N_2$ stream (50 cm$^3$/min).

FTIR spectra of the powder catalyst before and after the reaction were registered using a PerkinElmer$^®$ Spectrum One spectrometer at the room temperature in a wavelength range from 600 to 4000 1/cm.

*Catalytic tests*

Mixed Mn-Ni oxide catalysts (mass of the powder catalyst was 0.3 g; mass of the active component in the monolithic form was 0.0035 g) were evaluated in the toluene combustion under atmospheric pressure. The reactor system consisted of tubular stainless steel fixed-bed reactor (inner diameter was 8 mm), located in a vertical quartz furnace, whose temperature was regulated by a proportional-integral-derivative (PID) thermo-controller (TC208 Series). The catalyst was loaded into the reactor between two quartz wool plugs in order to achieve an uniform gas flow across the catalytic bed. The reaction temperature was recorded with a K-type thermocouple, placed in the centre of the reactor. The vapor toluene was achieved using two approaches: a) by bubbling a stream of helium (He) through a saturator containing liquid toluene and b) using a gaseous mixture of toluene in nitrogen (inlet toluene concentration in nitrogen was 243 ppm). In the first case, a stream of He saturated with toluene was further diluted with synthetic air (oxidant).

A schematic illustration of the apparatus in the system with a saturator is presented in Fig. 1. The feed mixture was controlled using the mass flow controllers (MFC) (Brooks). The gaseous mixture was analyzed before and after reaction by gas chromatography (GC) *on-line* using a GC-2014 chromatograph (Shimadzu), equipped with flame ionization detector (FID). The conditions of the chromatographic analysis are described in Table 1. The data reported at each reaction temperature and the total flow rate were the average of three measurements at the steady-state conditions. The catalyst activity for toluene oxidation was evaluated by conversion of toluene, calculated as a function of the reaction temperature from the concentration of toluene at the inlet and outlet of the reactor, i.e., ($c$(toluene$_{inlet}$) − $c$(toluene)$_{outlet}$)/$c$(toluene)$_{inlet}$). Inlet concentration of toluene in the reaction mixture was constant.

Reaction conditions used in the toluene combustion for powder and monolithic catalysts are presented in Table 2.

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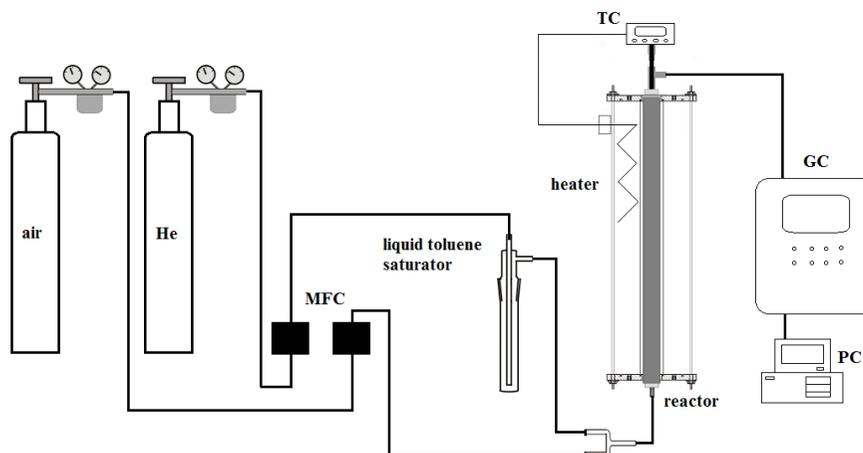


**Fig. 1.** Schematic illustration of the apparatus

**Table 1.** The conditions of the chromatographic analysis

| GC/FID | Shimadzu 2014 |
|---|---|
| Column | Carbowax 20M |
| Filler dimensions ($\mu$m) | 250/177 |
| Loop volume ($cm^3$) | 0.5 |
| Carrier gas | $N_2$ |
| Detector temperature (°C) | 250 |
| Column temperature (°C) | 120 |

**Table 2.** Reaction conditions

| Variable | Value | | |
|---|---|---|---|
| | Powder | Monolith 1 | Monolith 2 |
| Toluene concentration (ppm) | 18000 | 20000 | 48-233 |
| Pressure (Pa) | | 101325 | |
| Temperature (°C) | | 100-380 | |
| Total flow rate ($cm^3$/min) | | 23-100 | |
| Catalyst mass (g) | 0.3 | 0.0035 | 0.0025 |

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Preliminary results obtained from the combustion tests over a monolithic catalyst (monolith 1) evidenced that its activity is comparable to the activity of powder catalyst. To make further investigations, second monolithic catalyst (monolith 2) was prepared by the same procedure and tested in toluene combustion using a much lower inlet concentration of toluene. To examine the adaptability of the monolithic catalyst to the operating conditions, the toluene combustion was performed at different space times in the reactor and at different feed gas concentrations. Space time in the reactor was varied by changing total flow rates of the reaction mixture at the constant mass (or volume) of catalyst.

## Results and Discussion

Catalysts based on the mixed Mn-Ni oxides were synthesized by the co-precipitation and washcoating method and characterized using different instrumental techniques. These catalysts were evaluated for toluene combustion performed in the fixed bed reactor.

*Catalyst characterization*
The chemical composition of the catalyst sample, estimated by EDX analysis and the physicochemical properties (specific surface area $S_{BET}$, pore volume $V_{PORE}$ and pore diameter $d$), determined by $N_2$ adsorption-desorption analysis are reported in Table 3. It was shown that powder Mn-Ni catalyst possess a specific surface area of 38.4 $m^2/g$, which is similar to the value reported in the literature (Barbero et al., 2007). Based on the determined value of average pore diameter of approx. 20 nm, in terms of IUPAC standards, the catalyst can be classified in the group of mesoporous catalytic materials. The results of EDX analysis confirmed expected Mn/Ni atomic ratio. The SEM image of the prepared Mn-Ni catalyst is shown in Fig. 2. It can be seen that the surface of the catalyst consists mainly of spherical clusters with cca. 2 μm size. The FT-IR spectra of the catalyst before and after performing the reaction is shown in Fig. 3. Comparison of the spectra of the fresh catalyst and catalyst after the reaction showed the absence of changes in the catalyst structure which could arise due to a by-product adsorption to the catalyst surface during the reaction. Results of the DSC analysis (Fig. 4.) showed first endotermic peak in the temperature range from 50 to 100 °C, corresponding to water desorption, and second endotermic peak from 255 to 313 °C, which indicates a significant change in the crystal structure of the catalyst. To prevent the influence of the crystal structure change on the catalytic activity during toluene oxidation, catalyst has been calcined at 500 °C for 3 h, after which these peaks have not been found on a DSC spectra.

**Table 3.** Physicochemical properties of the prepared powder Mn-Ni catalyst

| Catalyst | $S_{BET}$[a] ($m^2/g$) | $V_{PORE}$[a] ($m^3/g$) | $d$[a] (nm) | Weight atomic ratio[b] (%) | | |
|---|---|---|---|---|---|---|
| | | | | Mn | Ni | O |
| Mn-Ni | 38.4 | 0.1956 | 20.3752 | 40 | 36.1 | 14.2 |

[a]Determined from the $N_2$ adsorption-desorption isotherms

[b]Determined from spectrometric analysis (EDX)

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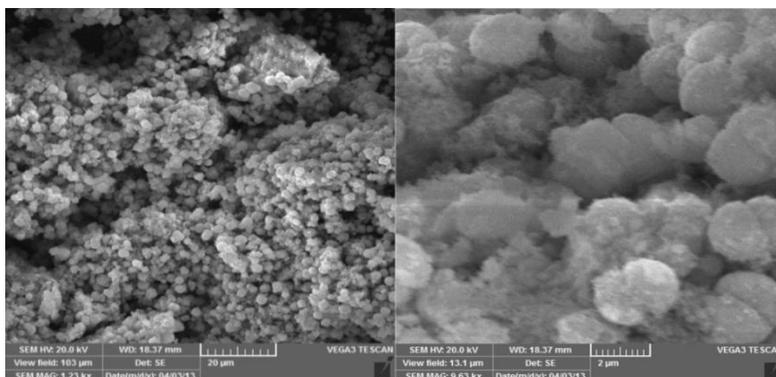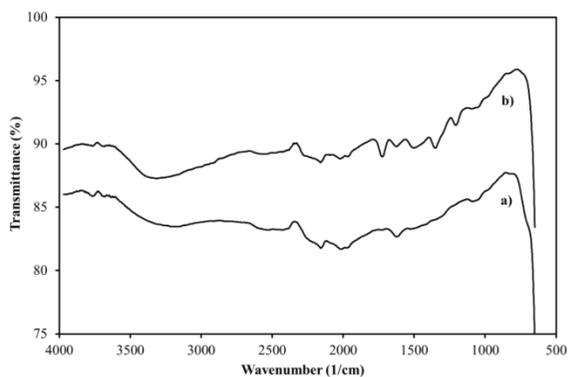


**Fig. 2.** SEM images of powder Mn-Ni catalyst



**Fig. 3.** FT-IR spectra of the sample catalyst: a) before reaction, b) after reaction


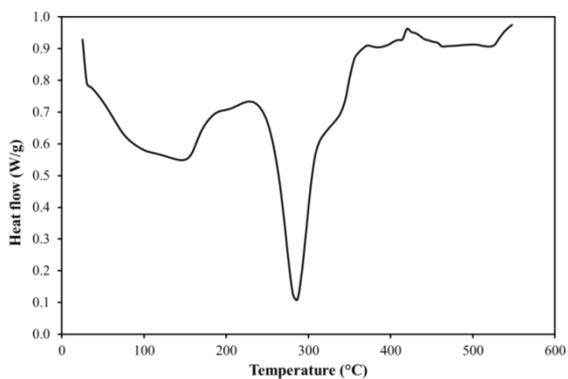
**Fig. 4.** Results of DSC analysis of the powder catalyst sample

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*Catalytic testing of the powder catalyst*

A simplified mechanism for toluene oxidation is shown in Fig. 5. It is known from earlier studies (Liu et al., 2004; Boikov et al., 2008) that possible products during partial toluene oxidation are benzaldehyde, benzoic acid, maleic anhydride and carbon oxides. While the reaction products could not be analyzed by gas chromatography, the conversion was calculated based on toluene consumption. Catalytic tests for toluene oxidation over powder Mn-Ni catalyst were performed at different total flow rates (25-100 $cm^3$/min) and in the temperature range of 150 to 350 °C. The obtained light-off curves as a function of reaction temperature are shown in Fig. 6. Contrary to the theoretical expectations, the increase of the space time at the same temperature resulted in decreasing of toluene conversion, except at a temperature of 200 °C. This can be explained by the temperature variations and incomplete saturation of He with toluene, especially when experiments were performed at the greater flow rates of toluene. Taking this into account, probably the influence of the space time on the toluene concentration before entering the reactor, and thus, toluene conversion inside the reactor, was greater in the saturator system than inside the reactor. To avoid such unexpected results all additional experiment were performed using a bottle containing a mixture of toluene in nitrogen with a known inlet toluene concentration. However, based on preliminary results it was evident that under reaction conditions employed in this study the conversion of toluene started at approximately 170 °C and was completed below 350 °C.
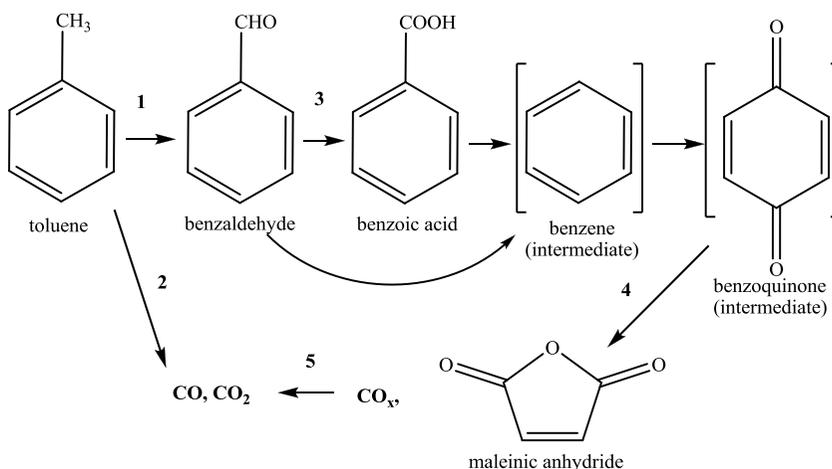


**Fig. 5.** Reaction of toluene oxidation with possible products and by-products

*Powder vs. monolithic catalyst*

The activity of powder and monolithic catalyst based on the mixed Mn-Ni oxide was compared in toluene combustion at a total flow rate of 25 $cm^3$/min and at temperatures ranging from 170 to 380 °C. In Fig. 7., it can be observed that monolithic catalyst (monolith 1) showed similar, at some temperatures even better catalytic performance in comparison to the powder one. Taking into account that the mass of the catalytically active phase deposited on a monolithic support was almost

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100 times less than the corresponding mass in the powder catalyst, a small difference in their catalytic behavior becomes very significant. The obtained results for powder Mn-Ni catalyst were comparable to similar results reported in the literature (Barbero at al., 2007). These researchers have used manganese nickel mixed oxide catalysts, $MnNi_x$ as well as NiO and $Mn_2O_3$ pure oxides in the combustion of propane, selected as model volatile organic compound. In their work complete conversion of propane was observed at a temperature of cca. 320 °C, while the temperature of 100 % toluene conversion was 370 °C. Taking into account that toluene contains an aromatic ring, which is hardly degradable, it can be concluded that the activity of Mn-Ni mixed oxide catalyst is quite similar for both volatile organic compounds. Furthermore, after performing catalytic tests at high conversions over both, powder and monolithic catalyst for a longer time, no deactivation was observed, showing the high stability of these transition-metal oxide catalysts. It is known, that in commercial applications, catalytic stability as well as activity is a very important factor.

Based on the basis presented so far, it was decided to evaluate the catalytic behavior of the second monolith sample (monolith 2) in the toluene combustion, using a much lower inlet toluene concentration and avoiding experimental problems associated with achieving the desired toluene concentration before entering the reactor. In the following experiments the influence of the space time and inlet concentration of toluene at different total flow rates and reaction temperatures on toluene conversion was examined in more details.
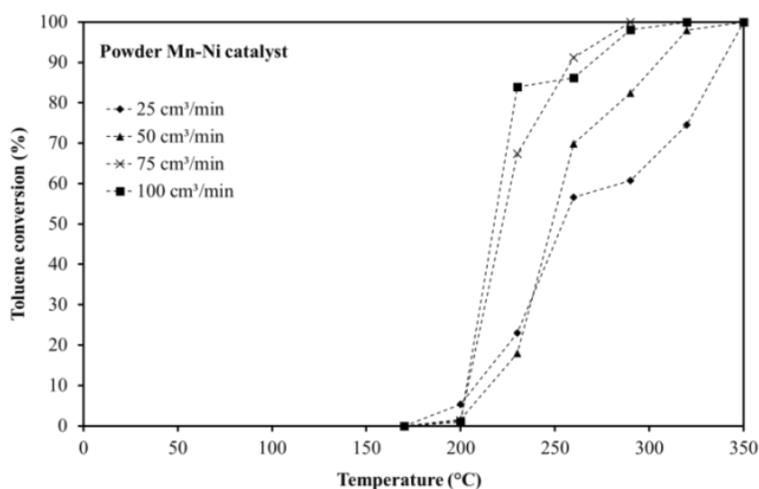


**Fig. 6.** Conversion of toluene over mixed Mn-Ni oxide powder catalyst as a function of temperature and space time inside the reactor ($m_{catalyst}$=0.3 g)

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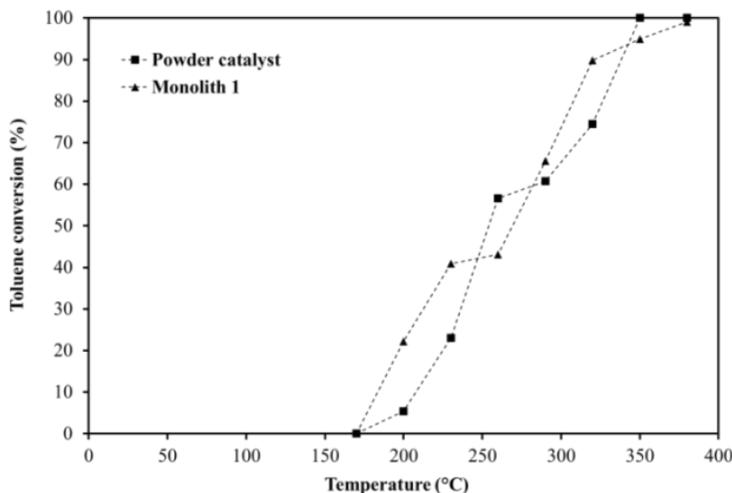


**Fig. 7.** Comparison of the results obtained for toluene combustion using the fixed bed reactor and metallic monolith reactor

*Effect of the space time*
The reaction of toluene oxidation was performed at different total flow rates, different temperatures and at constant inlet toluene concentration (210.43 ppm in $N_2$), as well as at the constant volumetric ratio of toluene/$N_2$ and air (20:3). As it can be seen in Fig. 8., an increase in the total gas flow rate results in a decrease of the toluene conversion due to a significant decrease in the contact time between the reactants and catalyst. This is particularly evident at 175 and 200 °C, while the complete oxidation of toluene is achieved at only 230 °C for a whole range of the total flow rates employed during this investigation. Similar results were reported by Li et al. (2012) in the toluene oxidation over metallic monolith catalysts based on noble metals, e.g. Pd/FeCrAl. Obviously, metallic monoliths containing Mn-Ni mixed oxide as a catalytically active component may be used as a suitable substitute for the more expensive catalysts based on noble metals.

*Effect of the inlet toluene concentration*
Further catalytic experiments have been performed at different inlet toluene concentration (48.4-193.6 ppm). The inlet toluene concentration has been changed by diluting the reaction mixture at the constant volumetric ratio of the reaction mixture and oxidant (20:3) with a stream of $N_2$ to achieve the total volumetric flow rate of 100 cm$^3$/min. Fig. 9. shows the influence of the inlet toluene concentration on toluene conversion at different temperatures and at a constant total flow rate of reaction mixture. It can be seen that the increase of the inlet toluene concentration at the same temperature results in the higher toluene conversion. This can be explained by the fact that the catalyst surface is more covered with molecules of the reactant, and thus, a greater amount of molecules is active in the oxidation reaction when higher toluene concentrations are used.

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Again, the increase in temperature at a constant toluene concentration has a significant influence on the conversion which is in line with our expectations.
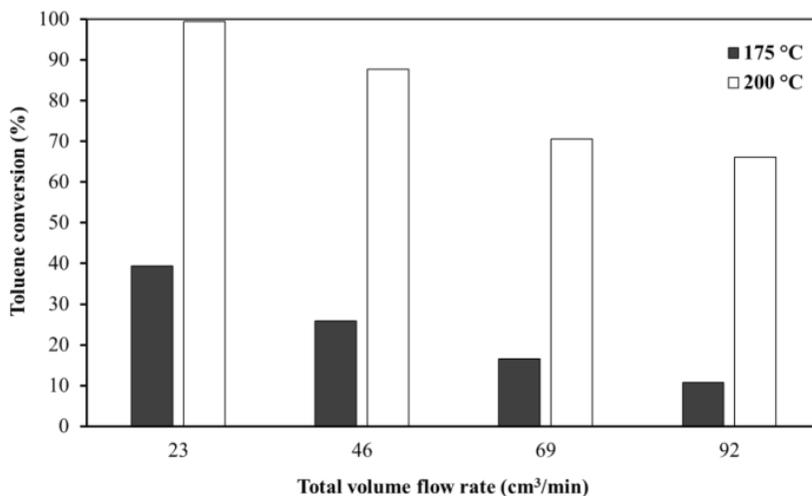
**Fig. 8.** Toluene conversion as a function of the reaction temperature and space time at constant toluene inlet concentration and catalyst weight ($\gamma$(toluene)=210.43 ppm; *m* (monolith 2)=0.0025 g)
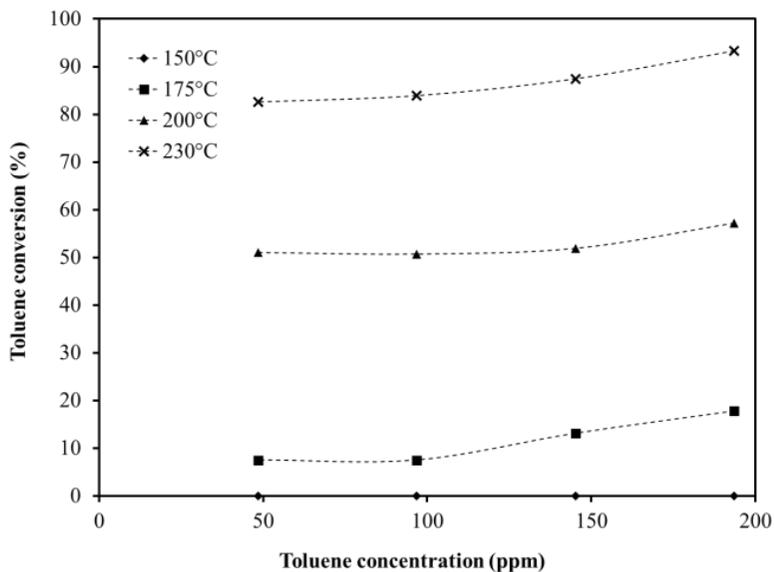
**Fig. 9.** Conversion of toluene over monolith 2 as a function of toluene inlet concentration at different reaction temperatures and constant total flow rate ($v$=100 cm$^3$/min)

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## Conclusions

This paper presents an experimental investigation of the catalytic properties of the mixed Mn-Ni based oxide catalysts in toluene combustion. The results of the catalytic tests reveal that the powder catalyst, prepared using the co-precipitation method, presents good activity in the toluene total oxidation, showing complete conversion of toluene at temperature of 350 °C. Similar results have been achieved in the testing of monolithic Mn-Ni catalyst, with much lower amounts of catalytically active phase.

The complete conversion of toluene over a monolithic catalyst in the system with much lower inlet toluene concentration was observed at much lower reaction temperatures, 230-250 °C, depending on the space time inside the reactor. Comparing the results obtained at different inlet toluene concentration, it is clear that the conversion of toluene increases at greater inlet toluene concentration. This is probably because the catalyst possesses a large specific surface area with sufficient number of catalytically active sites. Therefore, the performance of a Mn-Ni based oxide washcoated on metallic monoliths is very promising for catalytic combustion of toluene and other volatile organic compounds. Future research will include further improvement of the activities of the mixed oxides of manganese and other transition metals, with special emphasis on analysis and modelling of the metal monolith reactor using the basic methodology of chemical engineering.

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