**Design of the metal oxide catalysts for highly efficient and low temperature oxidation of VOCs**

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**Highlights**

* Low temperature oxidation of VOCs.
* Mixed manganese and copper oxide catalyst.
* Fixed bed reactor *vs.* metal monolith reactor.
* Toluene as a model VOC component.

**1. Introduction**

The quality of the air and thus the quality of life is greatly affected by excessive emissions of volatile organic compounds (VOCs) which are recognized as the major contributors to global air pollution [1]. VOCs are emitted from different industrial plants and motor vehicles. Process intensification methodology, which most often involves the integration of catalytic and adsorption processes, and the development and application of structured catalysts, in particular monolith reactors, was used to develop highly efficient monolith reactors for low temperature oxidation of VOCs. The aim was to develop a metal monolith catalyst/reactor for catalytic oxidation of toluene as a representative volatile organic compound. Toluene was chosen as a model component because it is used in various industries (such as the automotive and pharmaceutical industries), and is often emitted in the environment as a result of the production and use of organic chemicals, solvents, dyes and similar products.

**2. Methods**

Mixed manganese and copper oxide in powder form (MnCuOx) was prepared by the co-precipitation method [2]. Detailed characterization included the nitrogen adsorption-desorption analysis (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, differential scanning calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR). Catalytic properties of the prepared catalyst were tested in a fixed bed reactor for toluene oxidation at various working conditions (temperature, reaction mixture flow rate).

Preparation of metal monolith catalysts/reactors included deposition of stabile catalytically active layer of MnCuOx on the surface of the corrugated metal monolith support (Al). In order to prepare metal monolith structure for a stable catalytic layer deposition, two-sided anodization of aluminum tiles was used. Catalytically active layer composed of manganese and copper oxides was washcoated onto the metal monolith support (Al/Al2O3) [2]. The influence of working conditions, such as temperature and reaction mixture flow rate was tested.

Appropriate kinetic and reactor models for both, fixed bed and monolith reactor, were proposed and tested.

**3. Results and discussion**

The BET analysis showed textural properties of the prepared mixed oxide catalyst. With specific surface area of 23.7 m2 g-1, total pore volume of 0.10 cm3 g-1 and the average pore diameter of 16.5 nm the obtained catalyst can be classified as a mesoporous material, according to the IUPAC standards. The morphology of the MnCuOx oxide catalyst in powder form was further checked by the scanning electron microscopy (SEM) and it can be seen that the surface of the powder catalyst consists mostly of the spherical clusters with typical dimensions of about 1 micron. X-ray diffraction (XRD) of the powder MnCuOx mixed oxide identified four phases CuO, CuMnO4, MnO2 and Mn2O3. Differential scanning calorimetry over a wide range of temperatures (298-823 K) was used to investigate the thermal properties of MnCuOx mixed oxides it was found that in the temperature range from 523 K to ca. 655 K MnCuOx catalyst changes its crystalline structure which is accompanied by the release of energy of -209 J g-1. In line with these observations before testing the catalyst activity for toluene oxidation the catalyst was pre-treated (calcined) at the temperature of 523 K for 2 h and then for 3 h at the temperature of 773 K. The DCS curve after pre-treatment shows no structural changes in the observed temperature range indicating that the catalyst obtained after pre-treatment is structurally stable in this temperature range and as such suitable for catalytic experiments. FTIR analysis confirmed that during the toluene oxidation over MnCuOx oxide catalyst there was no significant adsorption of possible reaction intermediates or reactants on the surface of the catalyst. Specific T90 values (90% toluene conversion) for powder MnCuOx vary from 431 to 480 K depending on the reaction mixture flow rate and T90 values for monolith catalysts, Al/Al2O3-MnCuOx are even lower, from 432 to 468 K depending on the reaction mixture flow rate.

**4. Conclusions**

Toluene oxidation over manganese and copper mixed oxide catalyst in powder and monolith form was studied. The high specific surface area, mesoporous structure along with high catalytic activity at relatively low temperatures demonstrates that this catalyst is suitable for the catalytic oxidation of toluene at different operation conditions.

The prepared powder MnCuOx and monolith Al/Al2O3-MnCuOx catalysts show extremely high activity for the toluene oxidation. It is particularly important to point out that the observed high conversions of toluene are achieved at relatively low temperatures (< 432 K) depending on the reaction mixture flow rate, which is important for the practical application of the catalyst in real systems. Applied mathematical models give satisfactory results for the oxidation of toluene in the experimental system described in this work.

**References**

1. M. S. Kamal, S. A. Razzak, M. M. Hossain, Atmos. Environ. 140 (2016) 117–134.
2. M. Duplančić, V. Tomašić, Z. Gomzi, Environ. Technol. 39 (2018) 2004 – 2016.