



# Mechanism of complete *n*-hexane oxidation on silica supported cobalt and manganese catalysts

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## ABSTRACT

Mono- and bi-component cobalt and manganese samples were prepared by impregnation of silica with aqueous solutions of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and/or  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The bi-component samples were obtained by a common solution of Co- and Mn nitrates (CoMn-MS) or by deposition of cobalt on calcined Mn sample (Co + Mn). The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature programmed reduction (TPR), Fourier transformed infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), elemental analysis and tested in reaction of complete *n*-hexane oxidation. It was observed that the well crystalline cobalt oxide partially covers poorly crystalline manganese oxide in the Co + Mn catalysts, while finely divided oxides ( $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ) are present on the surface of the (CoMn-MS) sample. Four Langmuir–Hinshelwood and two Mars–van Krevelen models were fitted with the experimental data from the catalytic tests. According to the model calculations and results from instrumental methods, the reaction pathway over single component manganese and bi-component Co-Mn catalysts proceeds through Mars–van Krevelen mechanism (the oxidation of the catalyst surface being the rate determining step), while Langmuir–Hinshelwood mechanism is more probable for the Co sample. A considerable increase in activity for the sample obtained from a mixed solution is explained by low crystallinity, simultaneous presence of  $\text{Mn}^{4+}$ – $\text{Mn}^{3+}$  and enrichment of the surface in oxygen species.

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## 1. Introduction

Volatile organic compounds (VOCs) are known to contribute to a number of environmental problems such as formation of ground-level ozone, photochemical smog and toxic air emissions [1]. There are many different techniques for VOCs removal, such as adsorption, absorption, biofiltration, thermal and catalytic combustion [2–6]. The choice of the technique to be used depends on the VOC nature, its concentration and waste gas flow rate. The catalytic combustion is a competitive abatement technique for VOCs removal especially when the organics cannot be recycled or is present in low concentrations [5]. Compared with incineration, the catalytic oxidation occurs at lower temperatures, thus, decreasing the energy cost and  $\text{NO}_x$  emission [7,8]. Metal oxides or supported noble metals are used in catalyst preparation. The high cost of precious metals, their limited availability and sensitivity to higher temperatures and poisons has motivated the search for substitute catalysts. Among all studied metal oxides the most active single

metal oxides are those of Cu, Co, Mn and Ni [8–12]. Manganese and cobalt containing catalysts are less expensive and demonstrate high activity in VOCs combustion [13–15]. The catalytic properties of  $\text{MnO}_x$ -based catalysts are attributed to the ability of manganese to form oxides with different oxidation states and their high oxygen storage capacity (OSC) [16]. Chang and McCarty [17] reported that  $\text{MnO}_x$  has higher oxygen storage capacity and faster oxygen absorption and oxide reduction rates than the current commercial ceria-stabilized alumina-supported materials. Cobalt oxide is reported as quite promising among the metal oxides used for preparation of supported catalysts for the removal of CO [18,19] and VOCs [20–24]. There are investigations, according to which active cobalt catalysts for methane [22] and propane [23] combustion are those of high cobalt dispersion. We found in previous our investigations [25,26] that the catalysts prepared by ammonia method have better performance in the reactions of complete benzene and *n*-hexane oxidation, because the  $\text{Co}_3\text{O}_4$  particles are finely dispersed on the support. According to the data in the literature, the addition of manganese to the cobalt catalysts decreases the  $\text{Co}_3\text{O}_4$  particles size [27,28] and also facilitates their reduction [28].

In our previous study [29] we established that the combination between cobalt and manganese oxides changed significantly

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