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# Ceria based novel nanocomposites catalysts $Mn_xCe_{1-x}O_2/\alpha\text{-}Al_2O_3$ for low-temperature combustion of methanol

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ABSTRACT

A modified nanoemulsion method allowed obtaining nanoparticles (NPs) of the $MnO_x$–$CeO_2$ system within the whole range of the Mn:Ce atomic ratio. The NPs with excess of Ce consisted solely of $Mn_xCe_{1-x}O_2$ nanocrystallites (NCs) (fluorite structure) while the catalysts with excess of Mn were nanocomposite of $Mn_xCe_{1-x}O_2$ and of 3–4 times larger $Mn_3O_4$ (hausmannite) NCs. The obtained nanomaterials were mesoporous but the composite materials consisted thin slit-shaped pores of size close to the micropore range. The NPs of $Mn_3O_4$ were much more active in catalytic combustion of methanol than NPs of $CeO_2$ obtained by the same nanoemulsion method. Nevertheless, incorporation of Mn into $CeO_2$ lattice can improve these NPs to be more active than $Mn_3O_4$. The NPs of $Mn_xCe_{1-x}O_2$ deposited on $\alpha$-$Al_2O_3$ micrograins via the nanoemulsion method preserved activity of the equivalent non-supported NPs. The comparable high activity of $Mn_{0.25}Ce_{0.75}O_2$ monophasic NPs with the nanocomposite of the Mn:Ce = 3:1 ratio suggests joint catalytic action of Mn- and Ce-assembles. Complementary XPS measurements showed a surface Mn-enrichment of the monophasic NPs associated with $Mn^{4+}$ to $Mn^{2+/3+}$ reduction and increase of the $O^{2-}$ share in O 1s signal. Such active assemblies have been postulated.

## 1. Introduction

Volatile Organic Compounds (VOCs) are considered among the others as dangerous environmental pollutants. They are frequently neutralized by homogeneous combustion though such a method can evolve additional emission of $NO_x$, even more danger contaminants. Moreover, high temperature of this process demands employment of special temperature resistant materials for equipment. The catalytic combustion may be performed at much lower temperature reducing investment and operation costs. The most active in catalytic combustion are noble metal catalysts though they are expensive and sensitive for common poisons like Cl atoms [1]. There is a challenge to substitute the noble metals by other catalytic materials, e.g. transition metal oxide systems, which would show comparable catalytic activity together with better resistance against the common poisons. There are many reports on searching for such active catalysts. A part of these efforts concerns on materials contained $CeO_2$ which is known as an oxygen storage and thermal resistant material.

Mn-modified ceria materials were studied in the total catalytic oxidation or oxidative destruction of VOCs of various types. Among them were hydrocarbons like $CH_4$ [2,3], propane [4,5], n-hexane [5,6], benzene [7] and toluene [8] as well as oxygenates like ethanol [8–10], ethyl acetate and acetic acid [8] and formaldehyde [11–14]. The adsorption species of formaldehyde on (1 1 1) and (1 1 0) $CeO_2$ surfaces were studied using density functional theory (DFT) [15].

There is lack of studies on catalytic total oxidation of methanol (treated as a VOC) on the Mn-modified ceria materials though there are many reports on combustion of $CH_3OH$ on Pt-$CeO_2$ anodes in the direct methanol fuel cells, reviewed by Mori et al. [16]. In our previous paper the total oxidation of $CH_3OH$ was studied on $Cu_xCe_{1-x}O_2$ nanoparticles (NPs) [17]. The catalytic activity was related with defect structure [18] and electrical conductivity [19] of these materials. The main tasks of the present paper are extending our knowledge on catalytic combustion of methanol on $MnO_x$–$CeO_2$ NPs and undertaking attempts to support them on $\alpha$-$Al_2O_3$, without remarkable reduction of their activity.

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## 2. Experimental

The series of the $MnO_x$–$CeO_2$ nanometric precursors were obtained via a modified reverse nanoemulsion method (w/o) using cyclohexane (POCH) as the oil phase and Triton X-100 (POCH) as surfactant with n-hexanol (POCH) as co-surfactant. Details of the non-supported NPs synthesis were described in a previous paper [17]. Briefly, solutions of $Ce(NO_3)_3{\cdot}6H_2O$ (POCH) and $Mn(NO_3)_2{\cdot}4H_2O$ (POCH) salts were used in appropriate ratio to obtain the first nanoemulsion. The second nanoemulsion contained water solution of precipitation agents: TPAH (tetrapropylammonium hydroxide) or TEAH (tetraethylammonium hydroxide) or $NH_3$ (aq, 25 wt%), all purchased from Sigma–Aldrich. The series of supported catalysts were prepared in a similar method. The only difference was the addition of a commercial $\alpha$-$Al_2O_3$ support (Sigma–Aldrich) during mixing both nanoemulsions together. The obtained suspension was stirred continuously at 25 °C for 24 h. The precipitated precursors of the catalysts, supported and non-supported, were dried in air at 90 °C for 24 h, then calcined at 500 °C for 3 h. The temperature and time of calcination were chosen based on preliminary thermal analysis (TG/DTG/SDTA) of the catalysts precursors. The mass loss along the series of precursors ceased between 400 and 500 °C. The obtained oxide systems were stable up to about 850 °C then an endothermic effect began, suggesting possible phase transition or segregation.

Chemical composition of the final samples was determined with a non-destructive method XRF (ARL QUANT'X EDXRF Analyzer Thermo Scientific). Crystal structure of the catalysts was characterized by powder X-ray diffraction (XRD) with BRUKER D2 PHASER using Cu Kα radiation, 0.15418 nm. The average size ($D_{XRD}$) of the $CeO_2$ crystals was calculated using the Scherrer equation for (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections. In case of $\alpha$-$Al_2O_3$ crystals, the reflections of (0 1 2), (1 0 4), and (1 1 3) were taken into account. Surface morphology and specific surface area were evaluated from $N_2$ sorption BET isotherms measured with Micromeritics ASAP 2010. The samples were outgassed at 350 °C for 12 h under vacuum ($4 \times 10^{-3}$ Pa). $N_2$ sorption was carried out at pressure of $8 \times 10^4$ Pa. The pore size distribution was determined by the BJH method. The average size ($D_{BET}$) of the catalyst grains was estimated from the obtained specific surface area under assumption of idealized spherical shape of the grains and crystallographic density of ceria 7.2 g cm$^{-3}$. The obtained values were compared with the size of the particles ($D_{SEM}$) from the direct SEM observations. Transmission electron microscopy studies were conducted using FEI Tecnai TF-20 X-Twin (200 kV) microscope equipped with EDAX system.

The XPS measurements were performed with a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyzer using the monochrome Al Kα radiation 1486.6 eV and a low energy electron flood gun (FS40A-PS) to compensate charge on the surface during measurements. The hemisphere analyzer operated in the constant pass energy mode at 100 eV for the survey and high resolution spectra. Binding energies were referenced to the most characteristic and undisturbed Ce(IV) $3d^94f^0$ analytic peak 816.8 eV [20]. The composition and chemical surrounding of sample surface were investigated on the basis of the areas and binding energies of Mn 2p and O 1s photoelectron peaks. Fitting of the high resolution spectra was provided through the CasaXPS software.

The catalytic combustion of methanol as a probe VOC was performed in a fixed-bed flow microreactor under atmospheric pressure within the range of 100–500 °C with the linear temperature increase of 10 °C/min. Each sample (100 mg) of the catalysts was preliminary outgassed in a flow of 5.00 vol% of $O_2$ in pure helium (99.9999%) at 450 °C for 1 h. During the catalytic tests the total feed flow was controlled at $F = 20$ cm$^3$/min, corresponding to a W/F ratio of 0.30 g s cm$^{-3}$ and GHSV = 29,000 h$^{-1}$. The reactor feed contained 0.50 vol% of methanol (POCH) and 4.50 vol% of $O_2$ in pure He. Concentration of the reactants was continuously monitored with a quadruple mass-spectrometer (PREVAC) connected on-line with the microreactor. The catalysts activity was characterized by value of methanol fractional conversion ($X$) calculated from equation $X = (I_{31}{}^{in} - I_{31}{}^{out})/I_{31}{}^{in}$, using intensities of a methanol mass-line at inlet and outlet of the reactor. Among the main products, $CO_2$ and $H_2O$, only traces of formaldehyde were found at the very low methanol conversion (below 10%) and exclusively over the less active catalysts in each of the series.

## 3. Results and discussions

The results of powder X-ray diffraction of the catalysts contained from 0 to 0.20 mol% of $MnO_x$ in the prepared $MnO_x$–$CeO_2$ samples are collected in Fig. 1. The XRD patterns indicate formation of fine crystallites of only one phase ($CeO_2$) in all these samples. The mentioned patterns are fully consistent with $CeO_2$ cubic phase belonging to Fm3m space group (ICDD database, PDF-4 file #00-004-0593). To emphasize this result the formula $Mn_xCe_{1-x}O_2$ will be used suggesting formation of solid state solutions (SSS) of Mn ions in $CeO_2$ phase, at least within the range of $0 \le x \le 0.25$. Determination of the exact position of the Mn ions in the $CeO_2$ lattice demands complementary research. However, there are few papers describing the $MnO_x$–$CeO_2$ nanometric mixed oxide systems as solid state solutions up to the atomic ratio Mn:Ce = 1:1 [8,21,22] or even 3:2 [9].

The measured average sizes of the $Mn_xCe_{1-x}O_2$ crystallites ($D_{XRD}$), calculated from the Scherrer equation, are collected in Table 1. The size increases gradually from 2 to 5 nm with Mn concentration. Deposition of $Mn_xCe_{1-x}O_2$ nanocrystallites on $\alpha$-$Al_2O_3$ particles did not change the status of the solid state solution in the range of $0 \le x \le 0.25$. The XRD patterns of the supported catalysts

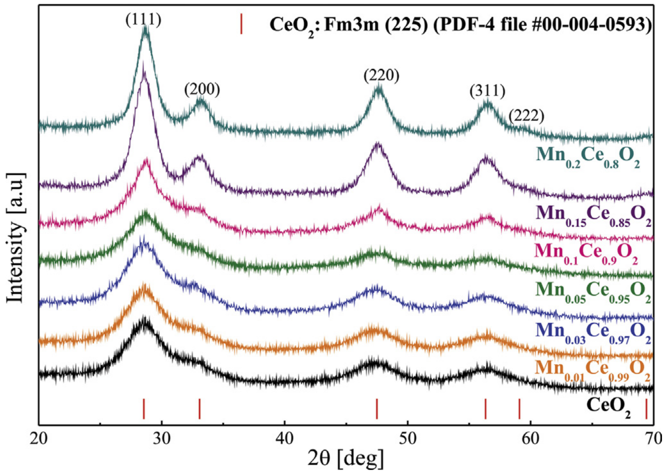

**Fig. 1.** X-ray powder diffraction patterns for $Mn_xCe_{1-x}O_2$ samples.

**Table 1**
Specific surface area and average crystallite size of the $Mn_xCe_{1-x}O_2$ catalysts.

| Sample | $S$ (m$^2$/g) | $D_{XRD}$ (nm) |
|---|---|---|
| $CeO_2$ | 100 | 2 |
| $Mn_{0.01}Ce_{0.99}O_2$ | 95 | 2 |
| $Mn_{0.03}Ce_{0.97}O_2$ | 101 | 2 |
| $Mn_{0.05}Ce_{0.95}O_2$ | 112 | 2 |
| $Mn_{0.1}Ce_{0.9}O_2$ | 87 | 4 |
| $Mn_{0.15}Ce_{0.85}O_2$ | 98 | 4 |
| $Mn_{0.2}Ce_{0.8}O_2$ | 72 | 5 |
| $Mn_{0.25}Ce_{0.75}O_2$ | 58 | – |