

NOVEL NANOSTRUCTURED MESOPOROUS MATERIALS BASED ON CeO₂: PREPARATION, CHARACTERIZATION AND APPLICATION AS CATALYSTS FOR TOTAL OXIDATION OF ETHYL ACETATE

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ABSTRACT

The current investigation is focused on the effect of the second metal oxide on the structural, redox and catalytic properties of CeO₂. For the purpose, Ce-Mn, Ce-Ti and Ce-Zr nanostructured mesoporous oxides were synthesized using template-assisted hydrothermal procedure. The obtained materials were studied by Nitrogen physisorption, X-ray diffraction, Raman and UV–Vis spectroscopies. The contribution of the metal dopant on the catalytic behaviour of the obtained catalysts in total oxidation of ethyl acetate as a representative VOC was discussed. The results demonstrate that binary materials are not a mechanical mixture of individual oxides, but complex composites in which there is interaction between the individual components.

Keywords: ethyl acetate oxidation, cerium oxide, hydrothermal procedure.

INTRODUCTION

Volatile organic compounds (VOCs) are toxic pollutants, which are emitted from the industry, transport and human activity [1]. Catalytic oxidation is promising approach for VOCs elimination, since the reaction operates at temperatures much lower than those required for the conventional thermal incineration [2]. Ceria-based materials provide excellent catalytic properties due to their high oxygen storage capacity and metal-ceria interactions [3]. Recently, efforts have been made to improve the ceria properties for diverse applications by successful synthesis of ceria nanostructured mesoporous materials doped with a second metal [4]. Here we focused our attention at the investigation on the effect of the doping with manganese oxide, titania and zirconia on the structural, morphological and redox properties of the obtained ceria-based mixed oxides. Template-assisted hydrothermal procedure was used for their synthesis and the potential application as catalysts in total oxidation of ethyl acetate was elucidated.

EXPERIMENTAL

Cerium, titanium, manganese and zirconium mono- and bi-component oxides (Ce-Ti, Ce-Mn, Ce-Zr; mol ratio=1:1) were synthesized using template-assisted precipitation technique followed by hydrothermal treatment according to a procedure reported in [5].

Powder X-ray diffraction patterns were collected on Bruker D8 Advance diffractometer equipped with Cu K α radiation and LynxEye detector. Nitrogen sorption measurements were recorded on a Quantachrome NOVA 1200e instrument and a Beckman Coulter SA 3100 apparatus at 77 K. The UV–Vis spectra were recorded on a Jasco V-650 UV-Vis spectrophotometer equipped with a diffuse reflectance unit. Raman spectra were acquired with a DXR Raman microscope (Thermo Fischer Scientific, Inc., Waltham, MA) using a 780

nm laser. The catalytic oxidation of ethyl acetate was performed in a flow type reactor (0.030 g of catalyst) with a mixture of ethyl acetate in air (1.21 mol%) and WHSV of 100 h⁻¹. Before the catalytic experiments the samples were treated in argon at 373 K for 1 h. The experimental data were obtained under temperature-programmed regime in the range of 473–773 K. Gas chromatographic analyses were done on a HP 5890 apparatus using carbon-based calibration. The products distribution was calculated as CO₂(S_{CO2}), acetaldehyde (S_{AA}), ethanol (S_{Et}) and acetic acid (S_{AcAc}) selectivity by the equation: $S_i = Y_i/X \cdot 100$, where S_i and Y_i were the selectivity and the yield of (i) product and X was the conversion.

RESULTS AND DISCUSSION

Data from X-ray diffraction technique (XRD) for pure CeO₂ shows presence of face centered fluorite type structure ICDD-PDF 34-0394 (Table 1). This is the main phase for all binary materials, but here a higher particles dispersion of cerium oxide phase is established. This effect could be the reason for the observed increase in the specific surface area of the binary oxides (Table 1). Note, that for the mixed oxide materials the unit cell parameter of Fm-3m phase differs from the one for pure CeO₂, which could be due to incorporation of foreign ions into ceria lattice and formation of solid solution.

Table 1. Structural and textural characteristics for all materials.

Sample	Phase composition (space group)	Unit cell parameters, Å	S _{BET} , m ² /g	V _p , cc/g	D _p , nm	Particles size, nm
CeO ₂	CeO ₂ (Fm-3m)	5.415	32.6	0.14	20	18
Ce-Mn	84 % CeO ₂ (Fm-3m) 12 % Mn ₅ O ₈ (C2/m) 4 % Mn ₂ O ₃ (Ia-3)	5.334	65.4	0.47	28	7
Mn _x O _y	24 % Mn ₂ O ₃ (Ia-3) 67 % Mn ₅ O ₈ (C2/m) 9% Mn ₃ O ₄ (I41/amd)	-	3.6	0.025	4	85 33 66
Ce-Ti	CeO ₂ (Fm-3m)	5.403	99	0.45	13	10
TiO ₂	Anatase (I41/amd)	3.786 9.493	85	0.29	9	17
Ce-Zr	CeO ₂ Fm-3m P42/nmc	5.407 a=3.703 c=5.341	150	0.14	4; 8	9.7 5.1
ZrO ₂	amorphous	-	296	0.42	4; 9	-

S_{BET} – BET specific surface area; V_p – total pore volume; D_p – main pore diameter

The Raman spectra of all materials contain a Raman band at 463 cm⁻¹ (E_{2g}) (Figure 1a), which is characteristic of CeO₂. The appearance of second, less prominent and broad band at about 600 cm⁻¹ is usually assigned to defects in ceria due to the formation of oxygen vacancies[6]. The observed decrease in the intensity of the main Raman band is due to improved metal oxide dispersion and formation of mixed oxide phases in binary materials and the appearance of strong interaction between them, which is also well demonstrated by the results from the powder X-ray diffraction (Table 1).

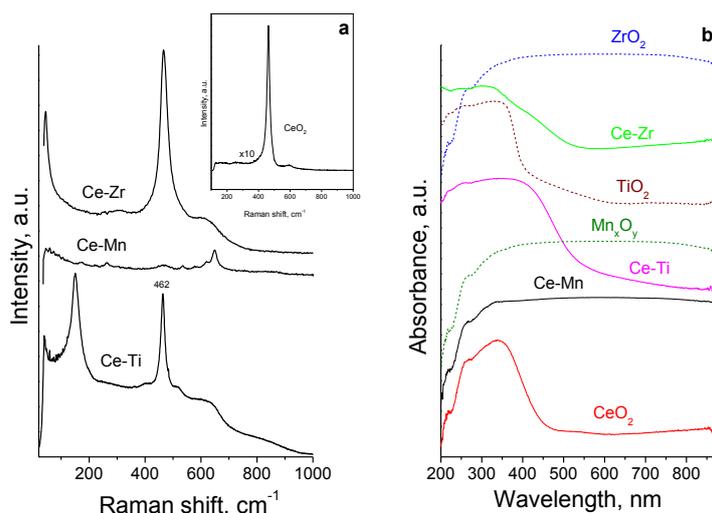


Figure 1. Raman (a) and UV-Vis (b) measurements.

The UV-Vis spectrum (Figure 1b) of pure CeO₂ represents absorption bands at about 220, 270 and 330 nm which can be attributed to O²⁻→Ce³⁺, O²⁻→Ce⁴⁺ charge transfer and inter-band transitions, respectively [6]. The latter band is related to lattice defect sites as well. When manganese oxide was added to ceria, absorption in the whole region was observed probably due to presence of manganese ions in different oxidative state. In the case of doping with titania, there is a strong shift of the absorption to the visible region. The observed features could be assigned to incorporation of titanium ions into ceria lattice with the formation of highly distorted structure and more finely dispersed oxide particles. A broad absorption band in the 350–550 nm region in the spectrum of Ce-Zr is detected. In consistence with XRD and Raman results, it could be attributed to several effects: the distortion of the fluorite structure due to incorporation of Zr in ceria lattice; segregation of a second tetragonal ZrO₂ phase substituted with Ce; formation of Ce³⁺ ions and changes in particles size as well.

Table 2. Data from the catalytic tests.

Sample	Selectivity, %				
	AA	Et	AcAc	C ₂ H ₄	CO ₂
CeO ₂	10	47	1	5	27
Ce-Zr	5	43	1	-	52
ZrO ₂	31	50	2	-	17
Ce-Ti	13	37	5	8	37
TiO ₂	25	23	1	18	33
Ce-Mn	6	1	1	-	92
Mn _x O _y	7	1	0	-	91

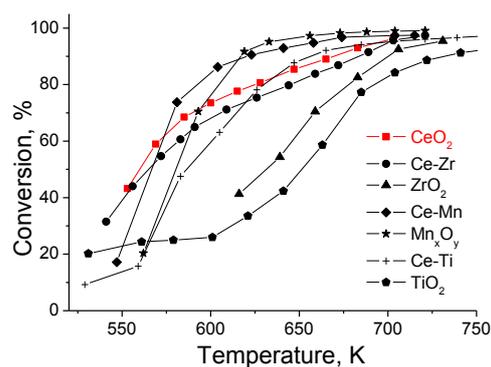


Figure 2. Temperature dependencies of conversion for various materials.

For all studied samples the ethyl acetate oxidation is initiated above 500 K and 80–90% conversion is achieved above 700 K (Figure 2). The selectivity to CO₂ and the obtained by-products acetaldehyde (AA), ethanol (EtOH), acetic acid (AcAc) and ethane are presented in Table 2. Pure ceria demonstrates relatively high catalytic activity at lower temperature but

low selectivity in total oxidation of EA due to the formation of EtOH, indicating domination of surface acidic function over the redox ones. The presence of dopants significantly improves the CO₂ selectivity, and in case of manganese oxides dopant exhibits also higher catalytic activity. In accordance with XRD and nitrogen physisorption data, the observed facilitated redox properties could be due to the improved dispersion and texture characteristics (Table 1). However, the absence of a simple relation between the catalytic activity and BET surface area (Table 1) and the data from Raman, UV-Vis and XRD study urged the authors to assume a more complex effect of the incorporated ions in the ceria lattice. It seems that the substitution of Ce⁴⁺ with smaller and more flexible polyvalent Mnⁿ⁺ ions provides the formation of oxygen vacancies and facilitates the electron transfer *via* formation of shared Ce⁴⁺-Mnⁿ⁺ redox pairs.

CONCLUSION

Nanosized and mesoporous mixed metal oxides based on CeO₂ possessing different textural and structural characteristics by using simple and not expensive preparation procedure were prepared. They have the potential to be successfully used as catalysts for total oxidation of VOCs. The results of physicochemical techniques demonstrate that binary materials are not a mechanical mixture of individual oxides, but complex composites in which there is an interaction between the individual components. They possess higher specific surface area compared to mono-component oxides. However, bi-component Ce-Mn catalyst demonstrates high catalytic activity and selectivity and this could be attributed to the increase in the dispersion of the binary oxides and their improved redox ability.

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