# Optimization of $CeO_2$-$ZrO_2$ mixed oxide catalysts for ethyl acetate combustion

M. D. Dimitrov[1]*, R. N. Ivanova[1], V. Štengl[2], J. Henych[2],
D. G. Kovacheva[3], T. S. Tsoncheva[1]

*[1] Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Sofia, Bulgaria*
*[2] Institute of Inorganic Chemistry AS CR v.v.i, Husinec-Rez, Czech Republic*
*[3] Institute of General and Inorganic Chemistry, BAS, Sofia, Bulgaria*

Nanosized ceria-zirconia mixed oxides were prepared using template-assisted co-precipitation approach followed by a hydrothermal treatment step. Some synthesis parameters (Ce/Zr ratio, presence of template and hydrothermal treatment temperature) were varied in order to get highly active mixed oxide catalysts for ethyl acetate combustion. The performed physicochemical characterization evidenced the presence of a single cubic phase for the samples with lower Ce content (Ce/Zr<5:5 mol ratio). Surprisingly, formation of separate tetragonal zirconia phase along with the cubic one was registered for the mixed oxide samples with lower Zr amount (Ce/Zr≥5:5 mol ratio). The variation of the other two synthesis parameters had an effect mostly on the textural characteristics of the final materials. The most significant effect on the catalytic properties of mixed Ce-Zr oxide samples comes from varying Ce-Zr ratio. Highest catalytic activity showed 3Ce7Zr(CTAB, HT373) sample due to the complete integration of both metal oxides into one mixed phase with a disturbed cubic lattice structure.

**Key words:** nanosized $CeO_2$-$ZrO_2$, mixed oxide phase, ethyl acetate combustion.

## INTRODUCTION

$CeO_2$ is a rare-earth metal oxide with important applications in areas of catalysis, electrochemistry, photochemistry, and materials science [1] due to both its acidity and ability to undergo a facile conversion between "+4" and "+3" formal oxidation states. That can be enhanced by decreasing ceria particle size in the nanoscale. Another possibility is the addition of zirconia which results in the formation of solid solutions of the $Ce_{1-x}Zr_xO_2$ type with improved thermal stability [2]. Besides, the fluorite-type structure of ceria, particularly the cation sublattice, could be maintained up to a high level of doping [3, 4]. The consequence is the presence of perturbations in the Me-O coordination sphere, which are responsible for the high oxygen mobility seen in ceria-zirconia mixed oxides thus enhancing the overall redox capability of the mixed oxide system [5–8]. The enhanced reducibility is likely to lead to improved catalytic properties for some reactions such as volatile organic compounds (VOC) combustion [9]. At the same time, the textural characteristics are very important features for a given porous material. Their optimization could have a significant influence on the catalytic behavior of this material with regard to active sites accessibility and the facile transportation of reactants and products to and from them. In case of nanosized mixed metal oxides usually the surface to volume ratio is high and large part of the surface is exposed, however, the presence of additional porosity coming from either the use of template or some specific treatment during synthesis could have a beneficial effect on the overall catalytic activity of the obtained materials.

The aim of the investigation is to obtain highly active nanostructured $Ce_{1-x}Zr_xO_2$ mixed oxides catalysts for VOCs elimination using template-assisted hydrothermal approach. The effect of synthesis parameters is in the focus of investigation and ethyl acetate was used as a representative VOC.

---

* To whom all correspondence should be sent:
E-mail: md2@abv.bg

## EXPERIMENTAL

### *Materials*

Mono- and bi-component oxide samples were synthesized using template-assisted precipitation technique followed by hydrothermal treatment step according to a procedure reported by Tsoncheva et al. [10]. In principle, 12.0 g N-Hexadecyl-N,N,N-trimethylammoniumbromide (CTAB) were dissolved in 100 ml distilled water. After that, a second solution of $ZrCl_4$ (6.80 g) or $CeCl_3.7H_2O$ (10.8 g) in 50 ml distilled water was added slowly and under vigorous stirring. In the case of the mixed oxide samples the second solution contains a mixture of $ZrCl_4$ and $CeCl_3.7H_2O$ according to the corresponding Ce/Zr mol ratio. Then the temperature was raised to 50 °C and stirred for 30 min before adding dropwise 40 ml $NH_3$ (12.5%). The resulting mixture was stirred overnight at 50 °C. Then it was transferred into a polypropylene container and treated at 100 °C or 140 °C for 24 h. The next step is filtration of the solution and washing with distilled water, then drying at room temperature and calcination up to 300 °C with a ramp of 1 degree per minute and dwelling time of 15 hours at the final temperature. Selected mixed oxide samples were prepared by varying certain synthesis parameters – the presence/absence of template as well as the temperature of hydrothermal treatment. The obtained samples are designated as follows: $xCeyZr(a,T)$ where $x$ and $y$ represent the mol ratio between Ce and Zr, $a$ is the organic template molecule and T is the temperature of hydrothermal treatment.

### *Methods of characterization*

Powder X-ray diffraction patterns were collected within the range of 10–80° 2θ with a constant step of 0.02° 2θ and counting time of 1 s/step on Bruker D8 Advance diffractometer equipped with Cu Kα radiation and LynxEye detector. The size of the crystalline domains in the samples was determined using Topas 4.2 software with Rietveld quantification refinement. Nitrogen sorption measurements were recorded on a Quantachrome NOVA 1200e instrument at 77 K. Before the physisorption measurements the samples were outgassed at 423 K overnight under vacuum. The UV–Vis spectra were recorded on a Jasco V-650 UV-Vis spectrophotometer equipped with a diffuse reflectance unit. The Raman spectra were recorded on a DXR Raman microscope (Thermo Fisher Scientific, Waltham, Massachussets, USA). A 532 nm laser was used at a power of 3 mW. The powdered samples were scanned at a 15 point mapping mode under a 10× objective lens with an automated autofocus at each

point to get 15 random measurements. The catalytic experiments were performed in a flow type reactor (0.030 g of catalyst) with a mixture of ethyl acetate (1.21 mol%) in air with WHSV – 335 h⁻¹. Gas chromatographic (GC) analyses were carried out on HP5850 apparatus using carbon-based calibration. The samples were pretreated in Ar at 423 °K for 1 h and then the temperature was raised with a rate of 2 K/min in the range of 423–773 °K for the temperature-programmed regime experiments.

## RESULTS AND DISCUSSION

Some physicochemical characteristics of the obtained samples are presented in Table 1. X-ray diffraction technique has been used for determination of samples crystallinity and phase composition (Fig. 1). The XRD pattern of pure zirconia (Fig. 1a) shows low degree of crystallinity due to the presence of very small zirconia particles (Table 1). The obtained broad reflections to zirconia clusters are best fitted with the parameters of tetragonal zirconia phase. This is consistent with literature data where stabilization of zirconia phase with high symmetry (tetragonal or cubic) is the preferred phase for zirconia samples with particles below 10 nm [11, 12]. At the same time, pure ceria sample shows well defined reflections of cubic fluorite-like structure with particle sizes of about 12 nm (Fig. 1a, Table 1). In case of mixed oxides samples, with the increase of Zr content up to Ce/Zr≥5:5 mol ratio, the XRD reflections became asymmetrical and a presence of separate zirconia phase is assumed while in case of the samples with higher Zr content (Ce/Zr<5:5 mol ratio) the fitting of the obtained XRD reflections shows the presence of only one cubic fluorite-like Fm-3m phase (Fig. 1). The observed significant shift of the reflections for the latter samples indicates a decrease in their unit cell parameter in comparison to the pure ceria material that could be attributed to the complete integration of both metal oxides into one single cubic lattice (Fig. 1a). On the basis of XRD results we chose the two compositions (5:5 and 3:7) that differ structurally most from the pure ceria material and prepared two more samples for each composition where we varied the synthesis conditions (Table 1). The XRD patterns for the samples prepared without template or by hydrothermal treatment at 413 °K do not differ from their analogues obtained by the main synthesis procedure (Fig. 1b). Hence, it seems that the Ce/Zr ratio is the only factor responsible for the final phase composition of the mixed oxide samples when using the present synthesis procedure.

Nitrogen physisorption measurements were conducted in order to elucidate the textural properties

of the studied samples (Fig. 2, Table 1). All isotherms are of type IV that is characteristic of mesoporous materials. Pure zirconia adsorbs nitrogen in the whole pressure interval. It is characterized with the highest specific surface area and pore volume (Table 1). The pore size distribution is bimodal due to both interparticle mesoporosity and mesoporosity due to the organic template. On the other hand,

**Table 1.** Some physicochemical characteristics of the studied samples

| Sample | Mol ratio Ce:Zr | Template | $S_{BET}$, m$^2$/g | $V_{tot}$, cm$^3$/g | Space group | Particle size, nm |
|---|---|---|---|---|---|---|
| Zr(CTAB, HT373) | – | CTAB | 296 | 0.42 | P4$_2$/nmc | 1.2 |
| 1Ce9Zr(CTAB, HT373) | 1:9 | CTAB | 196 | 0.16 | Fm$\overline{3}$m | 5.1 |
| 3Ce7Zr(CTAB, HT373) | 3:7 | CTAB | 167 | 0.14 | Fm$\overline{3}$m | 3.5 |
| 3Ce7Zr(CTAB, HT413) | 3:7 | CTAB | 180 | 0.15 | Fm$\overline{3}$m | 4.0 |
| 3Ce7Zr(HT373) | 3:7 | – | 150 | 0.10 | Fm$\overline{3}$m | 5.3 |
| 5Ce5Zr(CTAB, HT373) | 5:5 | CTAB | 150 | 0.14 | Fm$\overline{3}$m<br>P4$_2$/nmc | 9.7<br>5.7 |
| 5Ce5Zr(CTAB, HT413) | 5:5 | CTAB | 154 | 0.17 | Fm$\overline{3}$m<br>P4$_2$/nmc | 9.7<br>5.8 |
| 5Ce5Zr(HT373)573 | 5:5 | – | 131 | 0.08 | Fm$\overline{3}$m<br>P4$_2$/nmc | 13.1<br>5.4 |
| 7Ce3Zr(CTAB, HT373) | 7:3 | CTAB | 118 | 0.14 | Fm$\overline{3}$m<br>P4$_2$/nmc | 12.8<br>5.0 |
| 9Ce1Zr(CTAB, HT373) | 9:1 | CTAB | 93 | 0.20 | Fm$\overline{3}$m<br>P4$_2$/nmc | 13.6<br>4.3 |
| Ce(CTAB, HT373)573 | – | CTAB | 58 | 0.27 | Fm$\overline{3}$m | 11.7 |
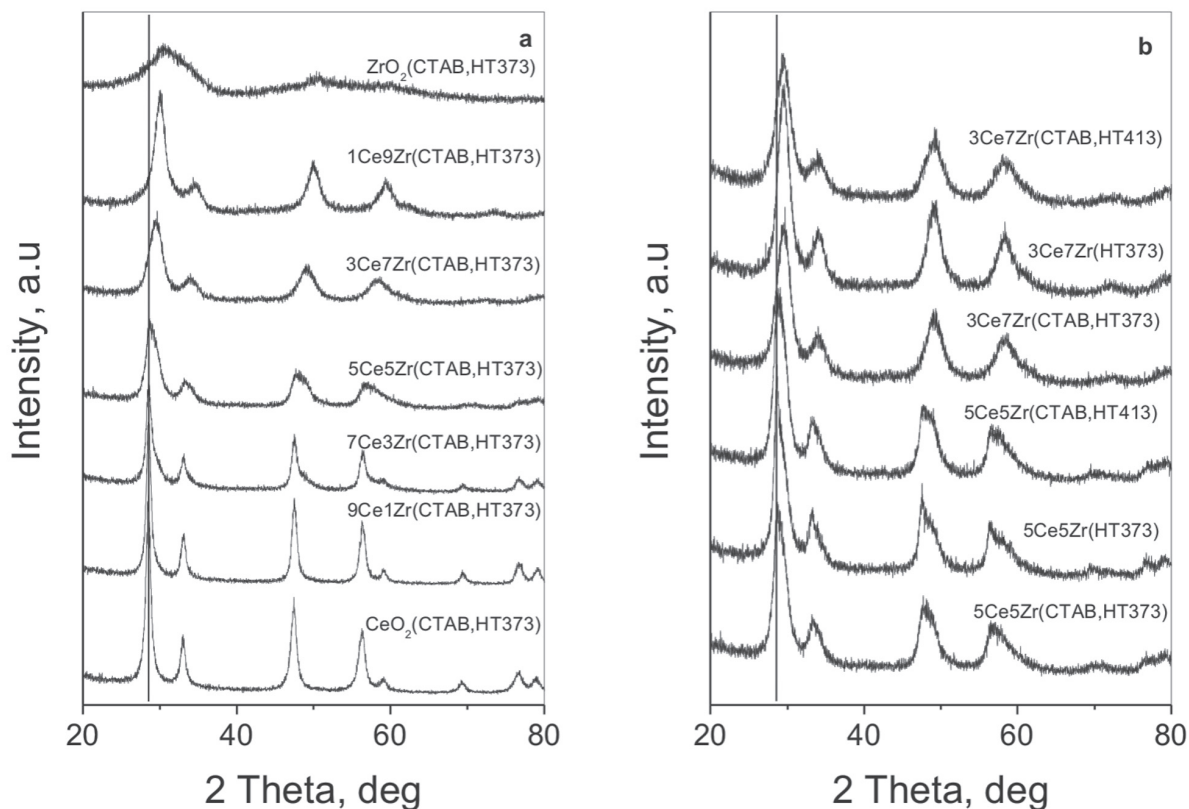


**Fig. 1.** XRD patterns of the studied samples obtained by the main synthesis procedure (a) and after varying some synthesis parameters (b)
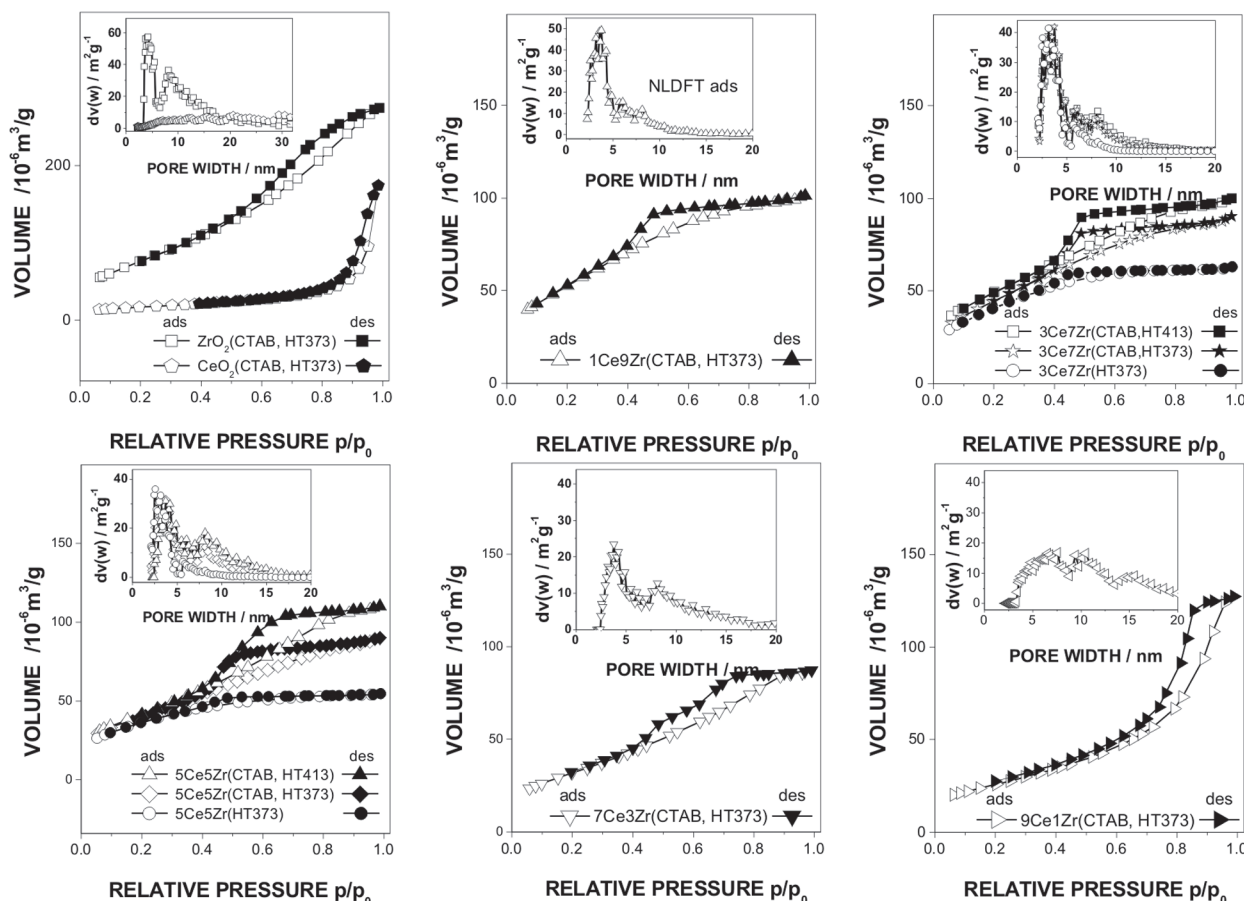
**Fig. 2.** Nitrogen physisorption isotherms with pore size distributions as insets for the studied pure and mixed metal oxide samples
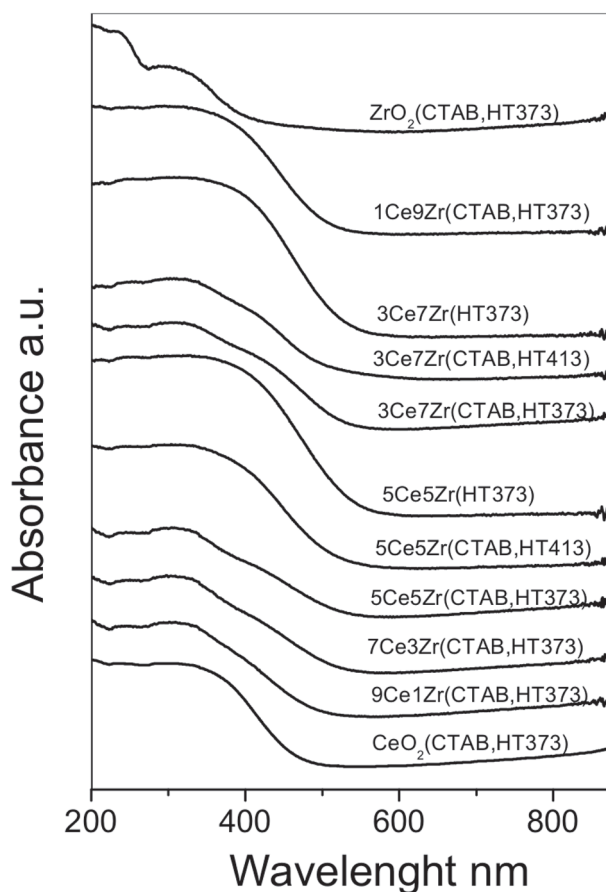
pure ceria sample show a steep step in the adsorption of nitrogen just above 0.8 relative pressure that characterizes it with very broad pore size distribution and predominant presence of large mesopores (Fig. 2). This sample has the lowest specific surface area but the presence of larger mesopores ensures relatively high pore volume (Table 1). In case of mixed oxide samples the shape of the isotherm is in-between those of the pure metal oxides (Fig. 2). With the increase of Zr content the specific surface area increases, the main pore diameter decreases, while the total pore volume goes through a minimum in case of Ce/Zr mol ratio of 5:5 (Table 1). The higher HT temperature leads to samples with slightly higher specific surface area and pore volumes. The samples prepared without template show deteriorated mesoporosity characterised with lower specific surface area and total pore volume due to the presence of slit-like pores only.

UV-vis diffuse-reflectance spectroscopy has been used to study various metal oxides to obtain information on surface coordination and different oxidation states of the metal ions. The measured UV-Vis spectra exhibit broad and poorly resolved peaks. UV–vis spectra of pure zirconia sample showed strong absorption at about 210 and 230 nm due to the band gap energy of zirconia and weaker broad absorption with maximum at about 300 nm that arises from transitions involving extrinsic states such as surface trap states and/or defect states (Fig. 3). The presence of the latter band could be attributed to the presence of very small zirconia particles [13]. For pure ceria, the strong absorption with maximum at about 315 nm is ascribed to $O^{2-} \rightarrow Ce^{4+}$ charge transfer (CT) transitions, while the one at about 250 nm – to $O^{2-} \rightarrow Ce^{3+}$ CT transitions (Fig. 3). In case of the mixed oxides samples these bands are preserved and the registered increased absorption in the 350–500 nm range could be ascribed to both particle size decrease in comparison to pure ceria sample and to disturbances in the ceria lattice and appearance of additional defects due to incorporation of Zr.

Raman spectroscopy is a good technique sensitive to both distortions of oxygen sublattice and defects in the structure. The Raman spectra of se-
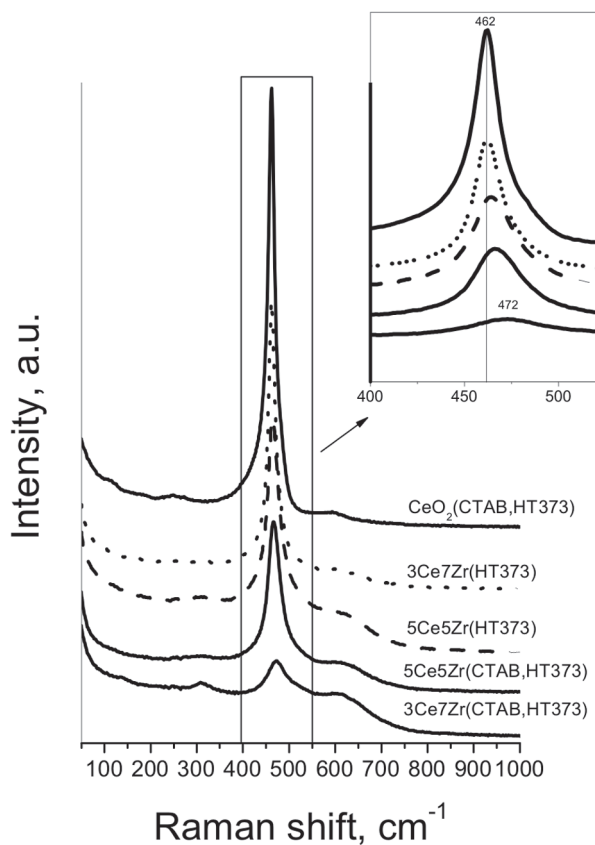
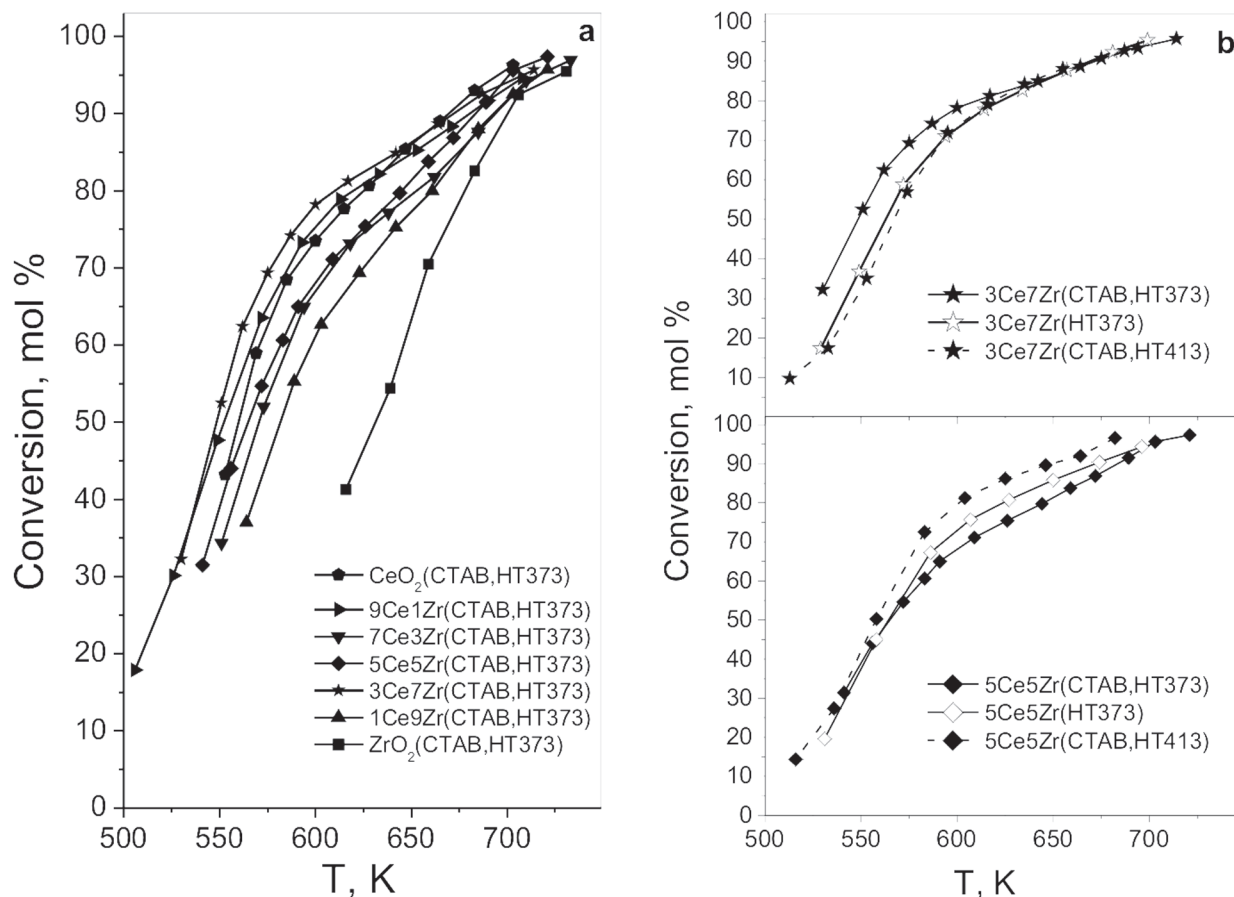**Fig. 3.** UV-Vis spectra of pure and mixed metal oxide samples

lattice. Besides, the appearance of a weak band at about 305 cm⁻¹ can be attributed to displacement of oxygen atoms from their ideal fluorite lattice positions [17]. The found effects are most evident for 3Ce7Zr(CTAB, HT373) sample and we assign this to the found complete integration of ceria and zirconia into a single cubic phase. The observed considerable broadening of the bands for this sample could be attributed to the reduction of phonon lifetime due to the observed significant decrease in the grain size (Fig. 4, Table 1).

The catalytic activity of the studied samples is presented in Figure 5. Pure zirconia starts to convert ethyl acetate just above 600 °K (Fig. 5a). At the same time pure ceria sample is much more active and the conversion of ethyl acetate starts around 550 °K due to the presence of a certain amount of $Ce^{3+}$-ions and oxygen defects within CeO₂(CTAB, HT373) sample as was shown by UV-Vis and Raman spectra. In case of the mixed oxide samples, the increase of Ce:Zr ratio leads to increase in the conversion ability in comparison with the pure zirconia sample (Fig. 5a). However, this activity increase is not linear with the increase of the Ce:Zr ratio but goes through a maximum at Ce:Zr=3:7. The observed

lected samples are presented in Figure 4. The spectrum of CeO₂ is characterized by one strong band at 462 cm⁻¹ which is due to the F2g vibration mode of the cubic fluorite structure [14]. In addition, it also exhibits two weak bands at about 250 and 600 cm⁻¹ which can be attributed to the non-degenerate transverse and longitudinal optical phonon modes of CeO₂, respectively [15]. Normally, these modes should not be observed by Raman spectroscopy but the presence of some defects, in particular oxygen vacancies in the ceria lattice, can be the reason for their appearance due to relaxation of symmetry rules [16]. At the same time, the spectrum profile of pure zirconia sample remains featureless (not shown) and we carefully could assign the lack of bands to the presence of only very small cluster-like particles in this sample. The obtained Raman spectra for selected mixed oxide samples do not possess bands due to zirconia phase (Fig. 4). The shift in the registered band positions to higher wave numbers in comparison with pure ceria sample (Fig. 4) signifies the changes in bond energies as a consequence of the substitution of zirconium into ceria



**Fig. 4.** Raman spectra of selected samples

**Fig. 5.** Temperature dependency of ethyl acetate conversion for the samples obtained (a) by the main synthesis procedure and (b) after varying some synthesis parameters

highest activity for 3Ce7Zr(CTAB, HT373) could be ascribed to the complete integration of both metal oxides into one mixed phase containing a disturbed cubic lattice structure with a lot of defects that act as active sites for the studied reaction. The change in the textural characteristics of the two selected mixed oxide sample does not lead to significant change in the catalytic activity (Fig. 5b). However, in case of Ce:Zr=3:7 series of samples, both the increase in the temperature of hydrothermal treatment or the absence of organic template during the synthesis procedure have a negative effect on the catalytic activity, while a slight positive effect of the latter synthesis parameters was registered for the Ce:Zr=5:5 series of samples (Fig. 5b).

CONCLUSION

A series of CeO$_2$-ZrO$_2$ mixed oxide nanocomposites have been prepared by template-assisted co-precipitation approach followed by hydrothermal treatment step. By varying some synthesis parameters (Ce/Zr ratio, presence/absence of organic template and temperature of hydrothermal treatment) both textural and structural properties of the obtained nanomaterials can be significantly modified. However, the Ce-Zr ratio is the key parameter that affects most the catalytic properties of mixed oxide samples. The changes in the other synthesis parameters lead to changes mainly in the textural parameters of a given sample, but have either slight or negative effect on its catalytic activity. Highest catalytic activity possesses 3Ce7Zr(CTAB, HT373) due to the found complete integration of both metal oxides into one mixed phase containing a disturbed cubic lattice structure with a lot of defects.

## REFERENCES

1. M. Boaro, M. Vicario, C. Leitenburg, G. Dolcetti, A. Trovarelli, *Catal. Today*, **77**, 407 (2003).
2. Q. Yuan, H.-H. Duan, L.-L. Li, L.-D. Sun, Y.-W. Zhang, C.-H. Yan, J. Coll. Int. Sci., **335**, 151 (2009).
3. Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science*, **301**, 935 (2003).
4. M. Fernández-García, A. Martínez-Arias, A. Guerrero-Ruiz, J. C. Conesa, J. Soria, *J. Catal.*, **211**, 326 (2002).
5. S. Arai, S. Muto, J. Murai, T. Sasaki, Y. Ukyo, K. Kuroda, H. Saka, *Mater. Trans.*, **45**, 2951 (2004).
6. P. Fang, J. Lu, X. Xiao, M. Luo, *J. Rare Earth*, **26**, 250 (2008).
7. H. Kaneko, S. Taku, Y. Tamaura, *Sol. Energy*, **85**, 2321 (2011).
8. Y. Nagai, T. Yamamoto, T. Tanaka, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda, M. Sugiura, *Catal. Today*, **74**, 225 (2002).
9. M.V. Ganduglia-Pirovano, A. Hofmann, J. Sauer, *Surf. Sci. Rep.*, **62**, 219 (2007).
10. T. Tsoncheva, L. Ivanova, D. Paneva, I. Mitov, C. Minchev, M. Fröba, *Micropor. Mesopor. Mat.*, **120**, 389 (2009).
11. N. L. Wu, T. F. Wu, I. A. Rusakova, *J. Mater. Res.*, **16**, 666 (2001).
12. V. G. Zavodinsky, A. N. Chibisov, *J. Phys.: Conf. Ser.*, **29**, 173 (2006).
13. M. R. Loghman-Estarki, R. S. Razavi, H. Edris, *Curr. Nanosci.*, **8**, 767 (2012).
14. A. Martinez-Arias, M. Fernandez-Garcia, L. N. Salamanca, R. X. Valenzuela, J. C. Conesa, J. Soria, *J. Phys. Chem. B*, **104**, 4038 (2000).
15. J. Z. Shyu, W. H. Weber, H. S. Gandhi, *J. Phys. Chem.*, **92**, 4964 (1988).
16. X.-M. Lin, L.-P. Li, G.-S. Li, W.-H. Su, *Mater. Chem. Phys.*, **69**, 236 (2001).
17. V. S. Escribano, E. F. Lopez, M. Panizza, C. Resini, J. M. G. Amores, G. Busca, *Solid State Sci.*, **5,** 1369 (2003).

# ОПТИМИЗИРАНЕ НА СМЕСЕНИ CeO$_2$-ZrO$_2$ КАТАЛИЗАТОРИ ЗА ИЗГАРЯНЕ НА ЕТИЛАЦЕТАТ

М. Д. Димитров[1], Р. Н. Иванова[1], В. Штенгъл[2], И. Хених[2], Д. Г. Ковачева[3], Т. С. Цончева[1]

[1] *Институт по органична химия с Център по фитохимия, Българска Академия на Науките, ул. „Акад. Г. Бончев", бл. 9, 1113 София, България*

[2] *Институт по неорганична химия, Академия на Науките на Чешка Република, Хузинец-Рез, Чешка Република*

[3] *Институт по обща и неорганична химия, Българска Академия на Науките, ул. „Акад. Г. Бончев", бл. 11, 1113 София, България*

(Резюме)

Получени са наноразмени церий-цирконий смесени оксиди по метода на съутаяването в присъствие на органичен темплейт и последваща хидротермална обработка. Варирани са някои от параметрите на синтеза (съотношението Ce/Zr, присъствие/отсъствие на органичен темплейт и температурата на хидротермална обработка) с цел получаване на високо-активни смесенооксидни катализатори за изгаряне на етилацетат. Проведеното физикохимично характеризиране доказа присъствието само на една кубична фаза за образците с ниско съдържание на Ce (Ce/Zr<5:5 молно съотношение). Изненадващ резултат е формирането на отделна тетрагонална циркониевооксидна фаза едновременно с кубичната за смесенооксидните образци с ниско съдържание на Zr (Ce/Zr>5:5 молно съотношение). Варирането на другите два параметъра оказва влияние основно на текстурните характеристики на получените материали. Най-значителен ефект върху каталитичните свойства на смесените Ce-Zr оксиди оказва варирането на Ce/Zr съотношението. Най-висока каталитична активност показа 3Ce7Zr(СТАВ, НТ373) образецът, поради наличието в него на пълно интегриране на двата метални оксида в една смесено оксидна фаза, при която структурата на кубичната решетка е силно деформирана.