

Influence of the hydrothermal treatment temperature on the properties of mixed ceria-zirconia catalysts for ethyl acetate combustion

R. N. Ivanova^{1*}, M. D. Dimitrov¹, D. G. Kovacheva²,
T. S. Tsoncheva¹

¹ Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Sofia, Bulgaria

² Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria

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A series of nanosized ceria-zirconia mixed oxides were prepared by an original procedure using template-assisted precipitation with urea followed by a hydrothermal treatment step at two different temperatures (373 K or 413 K). The obtained materials were characterized by X-ray diffraction, nitrogen physisorption, UV-Vis spectroscopy, temperature-programmed reduction (TPR) with hydrogen and their potential application in catalysis was tested in ethyl acetate combustion as a model reaction for total oxidation of volatile organic compounds. The results show that mixed oxide samples prepared using higher hydrothermal treatment temperature (413 K instead of 373 K) possess more finely dispersed tetragonal zirconia particles and significantly higher total pore volumes due to larger pore sizes, while the BET specific surface areas remains similar. Thus improved textural characteristics favor the higher catalytic activity found with the mixed ceria-zirconia samples synthesized by using the higher hydrothermal treatment temperature.

Keywords: CeO₂-ZrO₂ nanocomposites, precipitation with urea, ethyl acetate combustion.

INTRODUCTION

CeO₂-ZrO₂ system is one of the most studied mixed metal oxides in the literature due to its important role in the operation of automotive catalysts [1]. To enhance the redox properties and thermal stability of pure ceria, zirconia is often mixed as an additive to form solid solutions [2]. Density functional theory calculations [3] indicate that the difference in size of Ce⁴⁺ (0.97 Å) and Zr⁴⁺ (0.87 Å) is quite important for the local structure of the metal cations. Upon the addition of Zr to CeO₂, the Zr positive charge in Ce_{1-x}Zr_xO₂ is smaller than in pure ZrO₂, whereas the Ce positive charge is larger than in pure CeO₂. The perturbations in the Zr-O coordination sphere could be responsible for the high oxygen mobility seen in ceria-zirconia mixed oxides [2, 4]. The excellent ability for oxygen absorption/release observed with ceria-zirconia system leads to the enhancement in its redox-properties in comparison with pure ceria [4]. The enhanced reducibility

is likely to lead to improved catalytic properties for some reactions such as volatile organic compounds (VOC) combustion [5]. Besides, in case of nanosized mixed metal oxides 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. In the present study, a series of nanosized ceria-zirconia mixed oxides were prepared by co-precipitation of the corresponding metal chlorides with urea in the presence of hexadecyltrimethyl ammonium bromide (CTAB), followed by a hydrothermal treatment step at either 373 K or 413 K. The obtained materials were characterized by X-ray diffraction, nitrogen physisorption, UV-Vis spectroscopy, temperature-programmed reduction (TPR) with hydrogen and their potential application in catalysis was tested in ethyl acetate combustion as a model reaction for total oxidation of volatile organic compounds. Special attention was paid on the influence of the hydrothermal treatment temperature on the textural and structural characteristics of the obtained nanocomposites and their role in the studied reaction.

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

EXPERIMENTAL

Materials

Mono- and bi-component oxide samples were synthesized using precipitation technique in the presence of template followed by hydrothermal treatment (HT) step according to a procedure reported by Tsoncheva et al. [6]. Here, the difference is the use of urea as a precipitator instead of ammonia and the further overnight stirring of the solution under reflux conditions at 358 K before the following hydrothermal treatment, which has been conducted at either 373 K or 413 K for 24 h. The obtained mixed oxide samples are designated as follows: $x\text{Ce}_y\text{Zr}(\text{T})$ where x/y represents Ce/Zr mol ratio, and T is the temperature of hydrothermal treatment.

Methods of characterization

Powder X-ray diffraction patterns were collected on Bruker D8 Advance diffractometer equipped with Cu $K\alpha$ 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 TPR/TG (temperature-programmed reduction/

thermogravimetric) analyses were performed in a Setaram TG92 instrument. Typically, 40 mg of the sample were placed in a microbalance crucible and heated in a flow of 50 vol.% H_2 in Ar ($100 \text{ cm}^3 \text{ min}^{-1}$) up to 773 K at 5 K min^{-1} and a final hold-up of 1 h. 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.

RESULTS AND DISCUSSION

Some physicochemical characteristics of the obtained samples are presented in Table 1. X-ray diffraction technique (XRD) has been used for determination of samples crystallinity and phase composition (Fig. 1). Pure ceria as well as all cerium-containing samples show well defined reflections of cubic fluorite-like structure with particle sizes of about 12–14 nm (Fig. 1, Table 1). At the same time, monoclinic (P21/c) phase is registered for both pure zirconia samples. Here, an additional and more finely dispersed tetragonal (P42/nmc) phase is found only for $\text{ZrO}_2(373)$ sample (Fig. 1, Table 1). In case of mixed oxide samples, the intensity of ceria reflections decreases with zirconium content increase as expected, however, it should be noted that the unit cell parameter is smaller for the samples obtained at higher HT temperature (413 K), which could be

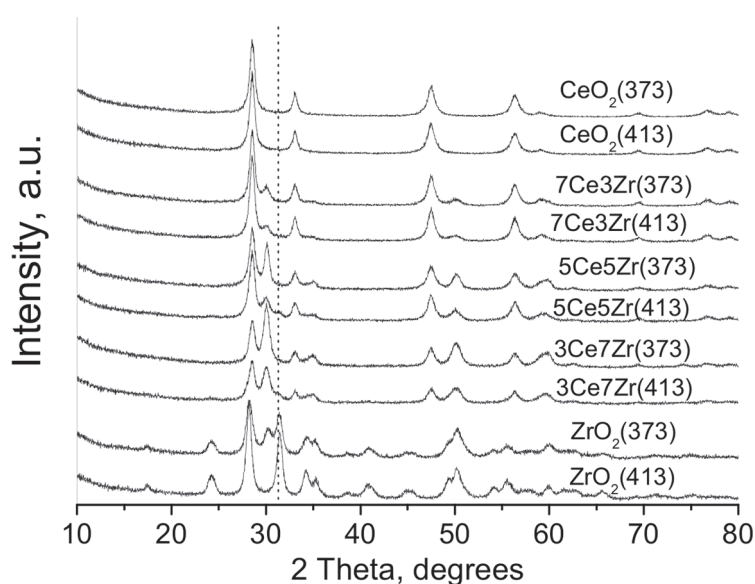


Fig. 1. XRD patterns of the studied samples.

Table 1. Texture and structure characteristics of the obtained materials

Sample	S_{BET} , m^2/g	V_{total} , cc/g	S_{micro} , m^2/g	V_{micro} , cc/g	Space Group	Unit cell, \AA	Particles size, nm
CeO ₂ (373)	70.7	0.10	64.0	0.026	Fm-3m	5.4150(7)	12
CeO ₂ (413)	92.3	0.06	76.9	0.03	Fm-3m	5.4154(7)	13
7Ce3Zr(373)	67.4	0.09	26.5	0.01	Fm-3m P4 ₂ /nmc	5.4128(8) a=3.616(1) c=5.204(4)	14 12
7Ce3Zr(413)	66.4	0.12	37.2	0.016	Fm-3m P4 ₂ /nm	5.4115(7) a=3.618(2) c=5.193(2)	14 10
5Ce5Zr(373)	67.3	0.10	17.6	0.008	Fm-3m P4 ₂ /nm	5.4118(8) a=3.618(1) c=5.208(3)	13 13
5Ce5Zr(413)	67.0	0.18	21.4	0.01	Fm-3m P4 ₂ /nm	5.409(1) a=3.614(1) c=5.194(3)	13 9
3Ce7Zr(373)	66.8	0.12	1.3	0.0004	Fm-3m P4 ₂ /nm	5.4138(9) a=3.617(1) c=5.206(2)	13 13
3Ce7Zr(413)	65.5	0.28	13.1	0.006	Fm-3m P4 ₂ /nm	5.408(1) a=3.612(2) c=5.187(3)	12 9
ZrO ₂ (373)	59.3	0.11	–	–	P2 ₁ /c P4 ₂ /nmc	a=5.150(5) b=5.202(5) c=5.303(4) β =98.85(2) a=3.592(5) c=5.19(1)	13 10
ZrO ₂ (413)	45.2	0.30	–	–	P2 ₁ /c	a=5.146(2) b=5.202(2) c=5.306(2) β =99.12(1)	15

S_{BET} – BET specific surface area; V_{total} – total pore volume; S_{micro} – micropore specific surface area defined by t-plot method; V_{micro} – micropore volume by t-plot method.

an indication of partial Zr introduction within ceria fluorite structure (Table 1). Simultaneously, a second tetragonal zirconia phase is found with all binary materials, however, its unit cell parameters are slightly expanded and we could assign this to partial cerium incorporation within the obtained tetragonal zirconia phase (Table 1). Besides, the latter phase is considerably more finely dispersed within the binary materials obtained at 413 K of HT treatment and for these samples traces of monoclinic zirconia phase is registered as well (Fig. 1, Table 1).

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 with the exception of pure ceria samples, which isotherms are combination of types I and IV with predominant presence of micropores (Fig. 2,

Table 1). On the other hand, both pure zirconia samples are exclusively mesoporous, but differ significantly in the shape of their isotherms according to the temperature of the conducted hydrothermal treatment – ZrO₂(373) is characterized with steep adsorption step within 0.6–0.8 relative pressure and H1 type hysteresis due to narrow pore size distribution (Fig. 2, Table 1), while ZrO₂(413) shows steep adsorption step just above 0.9 relative pressure due to the presence of non-uniform pores with very broad pore size distribution that gives almost three times higher total pore volume (Fig. 2, Table 1). In case of mixed oxide samples the shapes of their isotherms are similar to the ones obtained for pure zirconia samples with mesoporosity increasing with Zr content. All HT treated at 413 K binary materials are characterized with presence of non-uniform pores and broad pore size distributions, higher de-

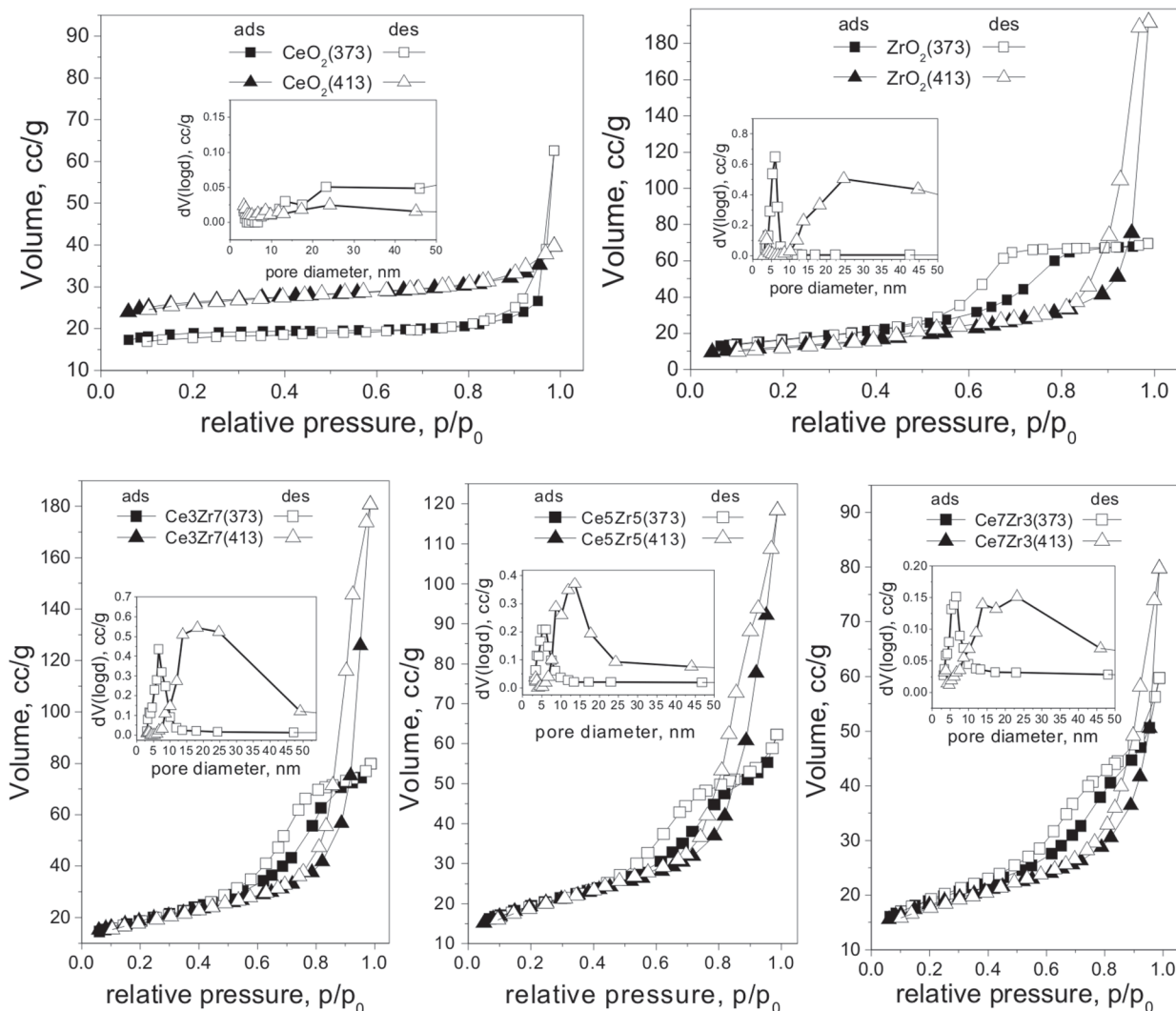


Fig. 2. Nitrogen physisorption isotherms with pore size distributions as insets for the studied pure and mixed metal oxide samples.

gree of microporosity and much higher total pore volumes in comparison to their analogues that were HT treated at 373 K, however, the BET specific surface areas remain similar (Fig. 2, Table 1).

Uv-Vis analysis has been used to obtain information for the coordination and oxidative state of metal ions. The spectra of both ZrO_2 samples show two absorption bands at around 215 and 230 nm, as expected for monoclinic ZrO_2 . The second weaker broad absorption feature in their spectra positioned at around 320 nm arises from either transitions involving extrinsic states such as surface trap states and/or defect states and could be attributed to the presence of nanosized zirconia particles [7] or reveals the co-existence of tetragonal ZrO_2 . For pure ceria samples, the strong absorption with maximum at about 250 nm is ascribed to $O^{2-} \rightarrow Ce^{3+}$ charge

transfer (CT) transitions, while that one at about 350–360 nm – to $O^{2-} \rightarrow Ce^{4+}$ CT transitions (Fig. 3). The overall absorption of the binary CeO_2 - ZrO_2 materials is significantly higher as compared to the pure ZrO_2 samples and resembles that of the pure ceria samples. An absorption increase in the 450–550 nm region is also detected, especially for the samples with high Zr content (Fig. 3) that could be ascribed to the appearance of additional defects due to partial incorporation of Ce within zirconia lattice and vice versa.

Additional information for the redox properties of the studied materials was obtained by temperature-programmed reduction (TPR) with hydrogen (Fig. 4). No significant TG effect is observed for both ZrO_2 samples, indicating weak reduction transformations due to dehydroxylation. The reduction

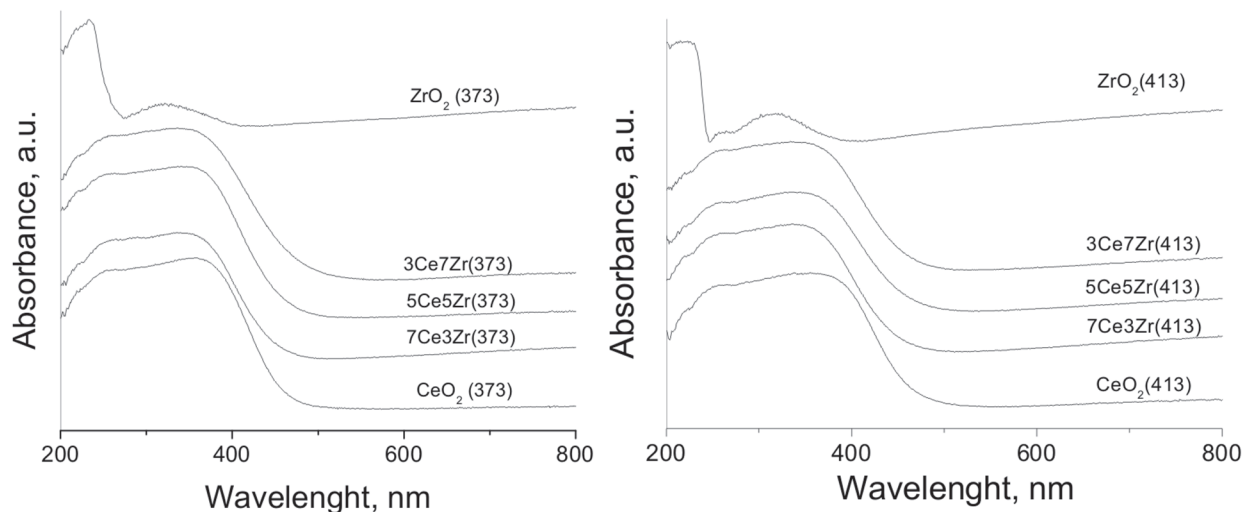


Fig. 3. UV-Vis spectra of the studied samples.

degree of Ce(IV)-Ce(III) transition for $\text{CeO}_2(373)$ is about 14%, while that for $\text{CeO}_2(413)$ is only about 9%. The reduction of all mixed oxide samples obtained at higher temperature of HT treatment (413 K) show facilitated reduction compared to $\text{CeO}_2(413)$ as well as increased reducibility (up to 25%) according to cerium content (Fig. 4). At the same time, more difficult start of reduction is observed for all samples prepared 373 K of HT treatment, but the reduction degree is significantly in-

creased, especially with Zr content above 30 mol% (Fig. 4).

The catalytic properties of the samples were studied in temperature-programmed regime within 423–773 K range (Fig. 5). Pure zirconia samples show catalytic activity just above 625–650 K with relatively low selectivity to CO_2 due to their strong acidic function and relatively low redox ability. At the same time, pure ceria samples are significantly more active and selective due to their superior re-

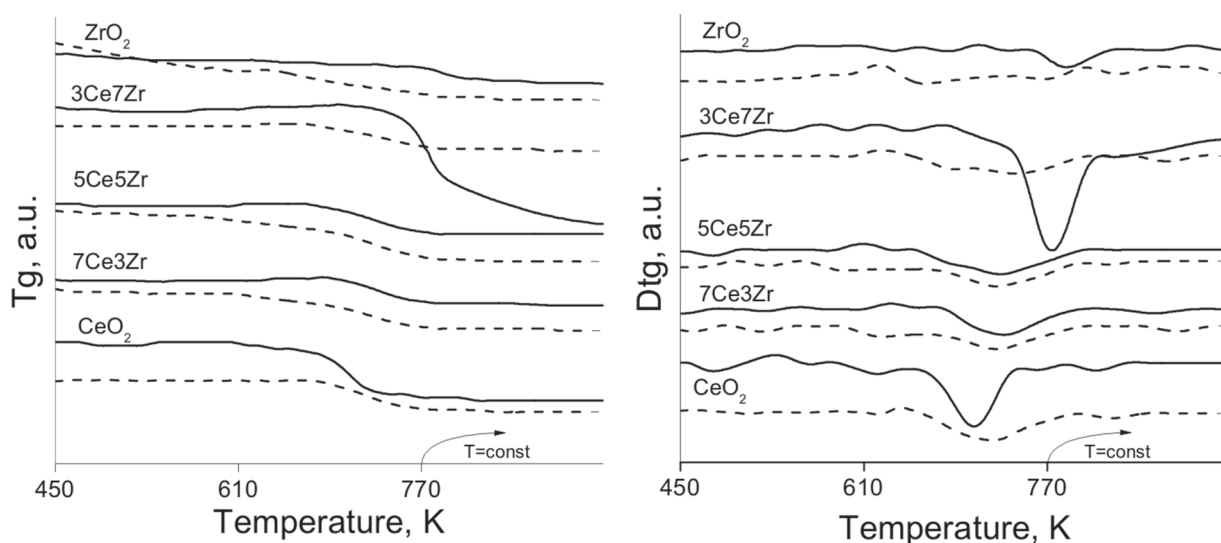


Fig. 4. TG (left) and DTG (right) data for the samples prepared at 373 K (solid lines) and 413 K (dash lines) temperature of hydrothermal treatment.

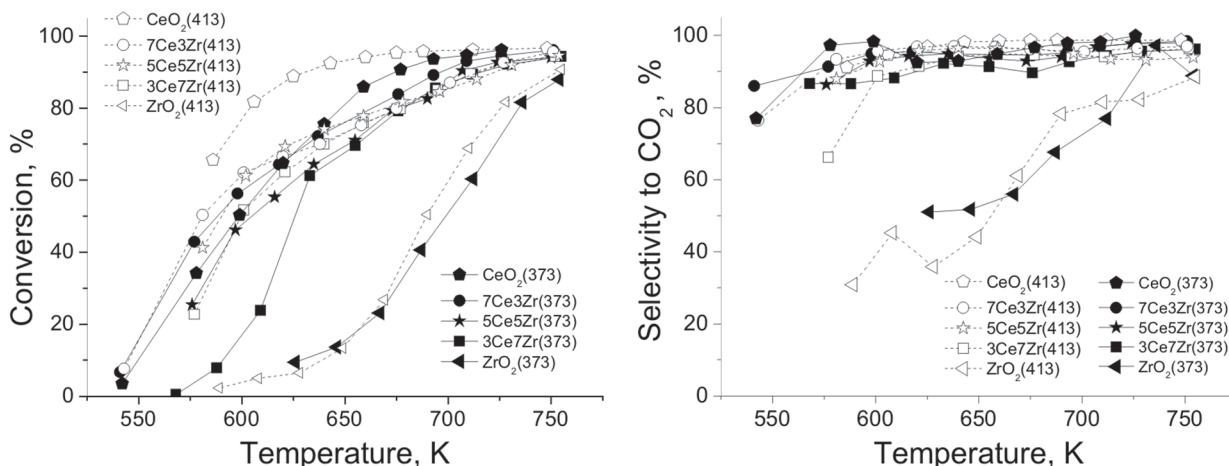


Fig. 5. Temperature dependency of ethyl acetate total oxidation for the studied samples.

dox properties (Fig. 5). The registered highest conversion ability of $\text{CeO}_2(413)$ we could assign to its much higher specific surface area compared to the other samples. All mixed oxide samples start to convert ethyl acetate at about 550 K with steeply increasing activity together with very high selectivity to CO_2 (Fig. 5). Here, the considerably higher total pore volumes and much broader pore size distributions of the HT treated at 413 K binary materials together with their improved redox properties at lower temperatures according to TPR data (Fig. 4) seems to favor their better catalytic performance.

CONCLUSION

Novel synthetic approach was applied for the synthesis of nanosized ceria-zirconia materials with micro-mesoporous structure as potential catalysts for VOCs elimination. The use of higher temperature of HT treatment (413 K instead of 373 K) during synthesis results in the development of larger and non-uniform pores which provides the higher total pore volume in the binary materials. The increased tendency for the substitution of Ce in zirconia and vice versa under the higher temperature of hydrothermal treatment facilitates the oxygen mobility in the solid. The improved textural and redox

properties for the binary materials obtained under the higher temperature of hydrothermal treatment (413 K) ensures higher catalytic activity in total oxidation of ethyl acetate.

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ВЛИЯНИЕ НА ТЕМПЕРАТУРАТА НА ХИДРОТЕРМАЛНА ОБРАБОТКА ВЪРХУ СВОЙСТВАТА НА СМЕСЕНИ CeO_2 - ZrO_2 КАТАЛИЗАТОРИ ЗА ИЗГАРЯНЕ НА ЕТИЛАЦЕТАТ

Р. Н. Иванова¹, М. Д. Димитров¹, Д. Г. Ковачева², Т. С. Цончева¹

¹ *Институт по органична химия с Център по фитохимия, БАН, 1113 София, България*

³ *Институт по обща и неорганична химия, БАН, 1113 София, България*

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(Резюме)

Бяха получени по оригинална процедура в присъствие на темплейт серия наноразмерни CeO_2 - ZrO_2 смесени оксиди, чрез използването на уреа като утаител и последваща хидротермална обработка при две различни температури (373 К или 413 К). Получените материали бяха характеризирани с помощта на прахова рентгенова дифракция, физична адсорбция на азот, UV-Vis спектроскопия, температурно-програмирана редукция (ТПР) с водород, а тяхното потенциално приложение в катализа беше изследвано в изгаряне на етилацетат, като моделна реакция за елиминиране на летливи органични съединения. Резултатите показаха, че смесените образци получени при използване на по-висока температура на хидротермална обработка съдържат по-фини ZrO_2 частици и значително по-голям общ обем на порите, дължащ се на наличието на по-големи пори, докато специфичната повърхност почти не се променя. Подобрените по този начин текстурни характеристики благоприятстват по-високата каталитична активност на смесените образци, получени при използването на по-високата температура на хидротермалната обработка.