

Influence of the presence/absence of bulky surfactant during the preparation of nanostructured ceria-zirconia materials on their catalytic performance in ethyl acetate total oxidation

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

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

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

Received October 10, 2016; Revised November 16, 2016

Novel nanostructured ceria-zirconia materials were synthesized in the presence or absence of bulky cetyltrimethylammonium bromide (CTAB) surfactant using an original approach combining the utilization of urea as a precipitator followed by hydrothermal treatment. 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 studied in ethyl acetate total oxidation as a model reaction for elimination of volatile organic compounds. The results show that the presence of the bulky CTAB molecules not only does not improve notably the textural characteristics of the obtained nanomaterials but limits Ce-Zr interactions in case of mixed oxide samples and thus provides a negative effect on their catalytic performance in the studied reaction. With increasing the amount of Zr in the mixed oxide samples both Ce-Zr interactions and textural mesoporosity are enhanced and this has beneficial effect on the catalytic activity in the total oxidation of ethyl acetate.

Keywords: CeO₂-ZrO₂ nanocomposites, precipitation with urea, CTAB, ethyl acetate total oxidation

INTRODUCTION

Ceria based systems are extensively investigated and have wide applications in materials science as they are able to easily form oxygen vacancies releasing surface and lattice oxygen [1 and references therein]. To enhance the redox properties and thermal stability of pure ceria, zirconia is often mixed as an additive to form solid solutions [2]. Actually, 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 [3]. Ce_xZr_{1-x}O₂ mixed oxides are recognised to exhibit high resistance to thermal sintering and high oxygen mobility, which improves their catalytic behaviour in some reactions, such as volatile organic compounds (VOCs) combustion [4]. In our previous study highest catalytic activity in ethyl acetate combustion was demonstrated for the binary materials, where a complete integration of both metal oxides into one mixed oxide phase is realized [5]. Here, for the first time, a series of nanosized ceria-zirconia mixed oxides were prepared by co-precipitation of the corresponding metal chlorides

with urea in the presence/absence of CTAB, followed by a hydrothermal treatment step at 373 K. We chose urea as precipitator instead of ammonia for better control of the processes of metal salt hydrolysis and metal oxide condensation. 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. Particular attention was paid to the influence of both precipitator and template on the textural and structural properties of the obtained nanocomposites and their role in the studied reaction.

EXPERIMENTAL

Materials

Mono- and bi-component oxide samples were synthesized using precipitation technique in the presence/absence of template followed by hydrothermal treatment 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

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

stirring of the solution under reflux conditions at 85 °C before the following hydrothermal treatment. The obtained mixed oxide samples are designated as follows: $x\text{Ce}_y\text{Zr}(a,T)$ where x/y represents the mol ratio between Ce and Zr, a indicates the organic template if used 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. 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. 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).

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, Å	Crystallite size, nm
CeO ₂ (CTAB, 373)	70.7	0.10	64.0	0.026	Fm-3m	5.4150(7)	12
CeO ₂ (no, 373)	71.9	0.06	59.0	0.024	Fm-3m	5.4146(6)	13
7Ce3Zr(CTAB, 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(no, 373)	90.1	0.10	46.2	0.02	Fm-3m P4 ₂ /nm	5.4139(9) a=3.616(1) c=5.191(3)	13 14
5Ce5Zr(CTAB, 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(no, 373)	55.2	0.10	20.1	0.009	Fm-3m P4 ₂ /nm	5.4139(9) a=3.616(1) c=5.194(2)	11 17
3Ce7Zr(CTAB, 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(no, 373)	80.4	0.11	5.2	0.003	Fm-3m P4 ₂ /nm	5.414(1) a=3.620(1) c=5.210(2)	11 13
ZrO ₂ (CTAB, 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 (no, 373)	44.3	0.09	-	-	P2 ₁ /c P4 ₂ /nmc	a=5.16(1) b=5.20(2) c=5.31(1) β=98.68(5) a=3.608(5) c=5.173(9)	11 13

Pure ceria as well as all cerium-containing samples show well defined reflections of cubic

fluorite-like structure with crystallite sizes of about 11-14 nm (Fig. 1, Table 1). Both monoclinic (P2₁/c)

and tetragonal ($P4_2/nmc$) phases are registered in case of pure zirconia samples (Fig. 1, Table 1).

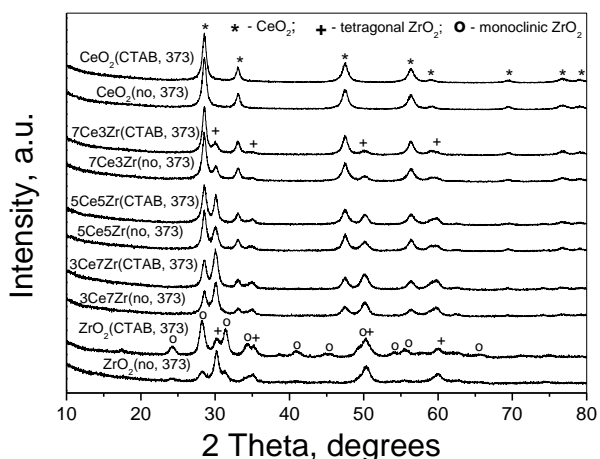


Fig. 1. XRD patterns of the studied samples.

Here, the absence of CTAB template molecules during the synthesis of $ZrO_2(\text{no}, 373)$ sample seems to provoke the formation of tetragonal phase in a higher extent at the expense of monoclinic one (Fig. 1, Table 1). In case of mixed oxide samples, the intensity of ceria reflections decreases with zirconium content increase, but the ceria phase seems to remain unchanged as its unit cell parameter is almost not influenced by zirconium addition (Fig.1, Table 1). For these materials zirconia phase with tetragonal symmetry was also detected (Table 1). Its unit cell parameters are slightly expanded in comparison with the corresponding ZrO_2 individual oxides. This indicates partial introduction of cerium within the zirconia phase, the effect being more pronounced with the zirconium content increase.

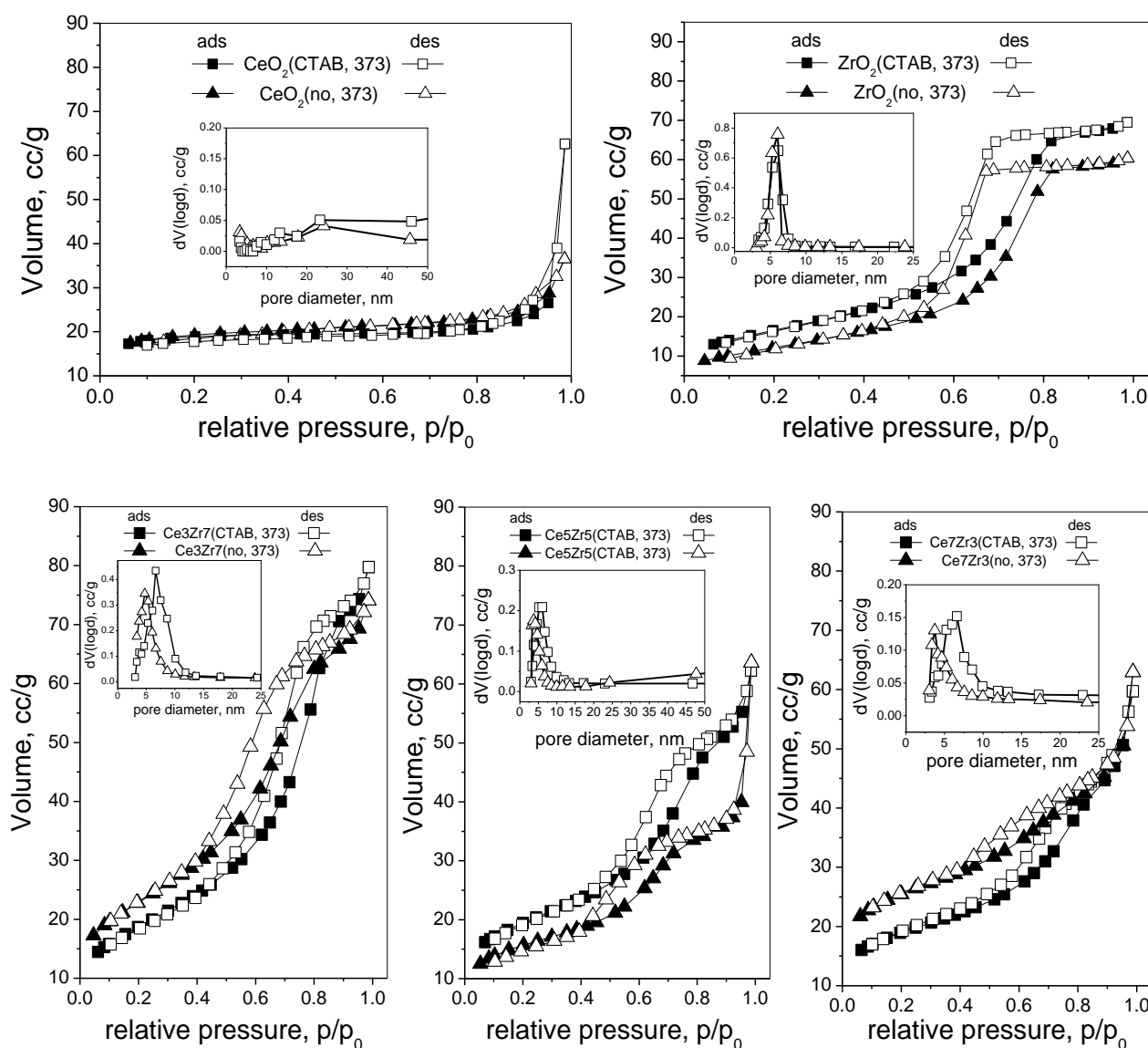


Fig. 2. Nitrogen physisorption isotherms with pore size distributions as insets for the studied pure and mixed metal oxide samples.

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). At the same time, both pure zirconia samples are exclusively mesoporous, 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). In case of mixed oxide samples the shape of their isotherms is in-between those of the pure metal oxides with mesoporosity increasing with Zr content and with comparable textural characteristics for the analogous samples, however, smaller pore sizes and narrower pore size distributions are found for the samples obtained without CTAB (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 [7]. The second broad feature in their spectra positioned at around 320 nm reveals the co-existence of tetragonal ZrO_2 [7] and it is larger for ZrO_2 (no, 373). For pure ceria (Fig. 3), the strong absorption

with maximum at about 350-360 nm is ascribed to $O^{2-} \rightarrow Ce^{4+}$ charge transfer (CT) transitions, while that one at about 250 nm – to $O^{2-} \rightarrow Ce^{3+}$ CT transitions [8]. In case of all mixed oxides samples these bands are preserved, however, the latter one is slightly red-shifted and the former – blue-shifted, which together with the slightly increased overall absorption above 500 nm could be ascribed to the appearance of additional defects due to incorporation of Ce within zirconia lattice.

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 negligible reduction transformations under studied conditions. The reduction degree of both pure ceria samples is about 14 %. The reduction of all mixed oxide samples obtained without CTAB template is facilitated as the start of the reduction is shifted to lower temperatures compared to pure ceria samples and/or the reduction degree is significantly increased, especially with Zr content above 30 mol % (Fig. 4). We could ascribe the observed effects to the partial introduction of cerium within the zirconia phase and the presence of smaller ceria crystallites within these samples (Table 1).

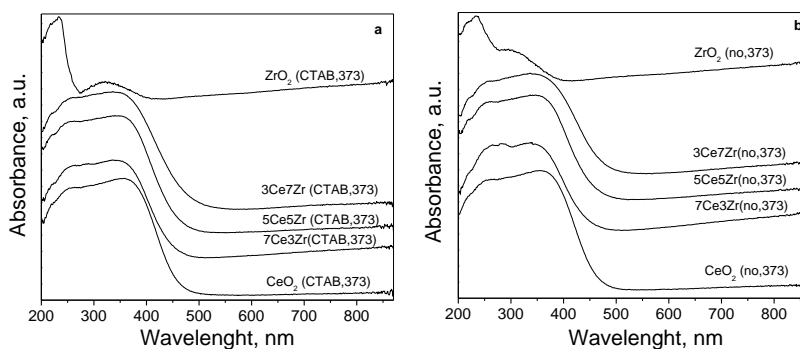


Fig. 3. UV-Vis spectra for the samples prepared with CTAB template (a) and without (b)

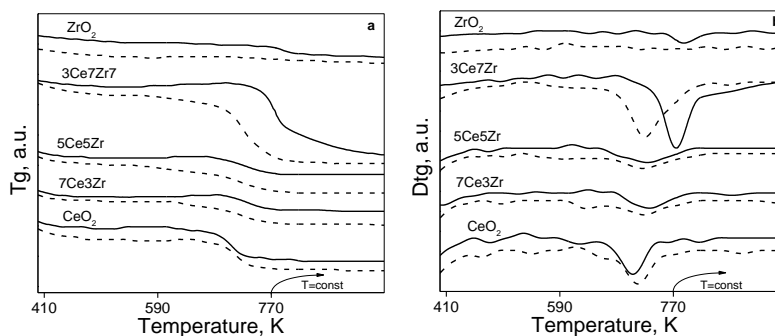


Fig. 4. TG (a) and DTG (b) data for the samples prepared with CTAB template (solid line) and without (dash line).

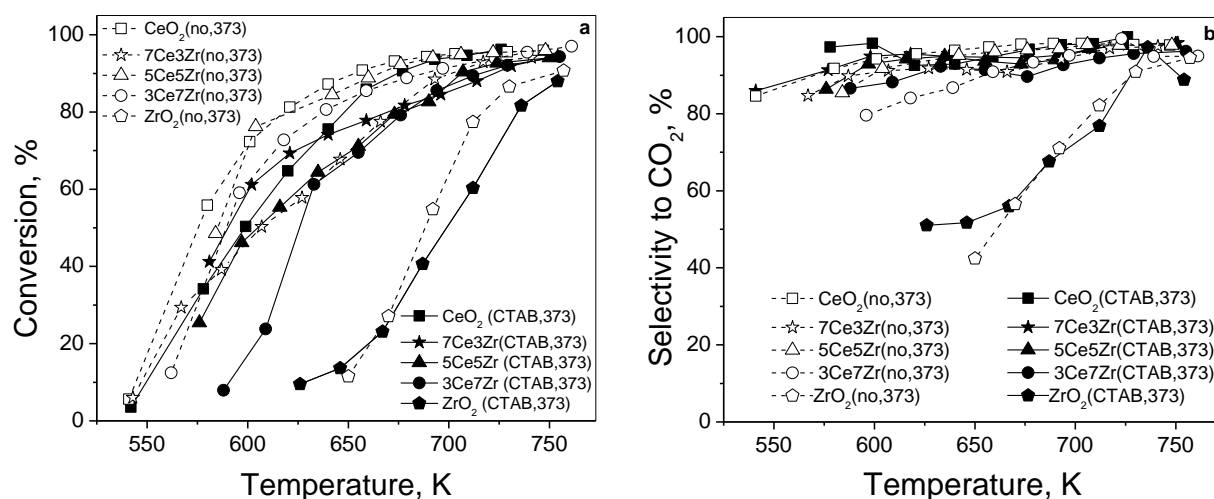


Fig. 5. Temperature dependency of ethyl acetate total oxidation for the studied samples.

The catalytic properties of the samples were studied in temperature-programmed regime within the range of 423–773 K (Fig. 5). Pure zirconia samples show catalytic activity just above 625–650 K with relatively low selectivity to CO₂ due to their significant acidic function and relatively low redox ability. At the same time, both pure ceria materials display steeply increasing conversion activity above 550 K combined with enhanced selectivity to total oxidation that could be assigned to their superior redox properties. All mixed oxide samples show improved catalytic activity, taking into consideration their cerium content, as well as very high selectivity to CO₂, and we assign this to their overall enhanced redox properties in comparison with pure ceria samples due to cerium substitution within zirconia lattice. The latter seems to be favoured by the absence of template during the synthesis (especially for the samples with Zr content above 30 mol %) and this is probably provoked by the improved intimate contact between the metal oxide particles.

CONCLUSION

By using an original synthetic approach we have prepared highly active and selective in total oxidation of ethyl acetate nanostructured ceria-zirconia materials comprised of nanosized particles arranged in a micro-mesoporous structure. The use of urea only as both precipitator and template gives optimal textural and structural characteristics of the obtained mixed oxides, especially for the samples

with Zr content above 30 mol %, while the additional presence of bulky CTAB molecules during synthesis seems to limit Ce-Zr interactions and thus has a negative effect on their catalytic performance. Further investigations with time-on-stream catalytic experiments are in progress.

Acknowledgement: Financial support by Program for career development of young scientists, BAS (project DFNP 145 /12.05.2016) is gratefully acknowledged.

REFERENCES

1. S. McIntosh, R. J. Gorte, *Chem. Rev.*, **104**, 4845 (2004).
2. S. Arai, S. Muto, J. Murai, T. Sasaki, Y. Ukyo, K. Kuroda, H. Saka, *Mater. Trans.*, **45**, 2951 (2004).
3. M. Boaro, M. Vicario, C. Leitenburg, G. Dolcetti, A. Trovarelli, *Catal. Today*, **77**, 407 (2003).
4. M. V. Ganduglia-Pirovano, A. Hofmann, J. Sauer, *Surf. Sci. Rep.*, **62**, 219 (2007).
5. M. D. Dimitrov, R. N. Ivanova, V. Štengl, J. Henych, D. G. Kovacheva, T. S. Tsoncheva, *Bulg. Chem. Commun.*, **47**, 323 (2015).
6. T. Tsoncheva, R. Ivanova, J. Henych, M. Dimitrov, M. Kormunda, D. Kovacheva, N. Scotti, V. Dal Santo, V. Štengl, *Appl. Catal., A*, **502**, 418 (2015).
7. S. Damyanova, B. Pawelec, K. Arishtirova, M.V. Martinez Huerta, J.L.G. Fierro, *Appl. Catal., A*, **337**, 86 (2008).
8. A. Kambolis, H. Matralis, A. Trovarelli, Ch. Papadopoulou, *Appl. Catal., A*, **377**, 16 (2010).

ВЛИЯНИЕ НА ПРИСЪСТВИЕТО/ОТСЪСТВИЕТО НА ОБЕМНО ПОВЪРХНОСТНО АКТИВНО ВЕЩЕСТВО ПРИ ПОЛУЧАВАНЕТО НА НАНОСТРУКТУРИРАНИ CeO₂-ZrO₂ МАТЕРИАЛИ ВЪРХУ ТЕХНИТЕ КАТАЛИТИЧНИ ОТНАСЯНИЯ В РЕАКЦИЯТА НА ПЪЛНО ОКИСЛЕНИЕ НА ЕТИЛАЦЕТАТ

Р. Иванова¹, М. Димитров¹, Д. Ковачева², Т. Цончева¹

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

²*Институт по обща и неорганична химия, БАН, 1113 София, България*

Постъпила на 10 октомври 2016 г.; коригирана на 16 ноември, 2016 г.

(Резюме)

Бяха синтезирани нови наноструктурирани материали в присъствие или отсъствие на цетилтриметиламониев бромид (СТАВ), като беше използван оригинален подход, включващ използването на уреа като утаител с последваща хидротермална обработка. Получените материали бяха характеризирани с помощта на прахова рентгенова дифракция, физична адсорбция на азот, UV-Vis спектроскопия, температурно-програмирана редукция с водород, а тяхното потенциално приложение в катализа беше изследвано в изгаряне на етилацетат, като моделна реакция за елиминиране на летливи органични съединения. Резултатите показват, че присъствието на СТАВ не само не подобрява значително текстурните характеристики на получените материали, но има негативен ефект върху техните каталитични свойства като ограничава взаимодействието Ce-Zr. С увеличаване на съдържанието на Zr в смесените образци се подобряват мезопористостта и взаимодействието Ce-Zr, което има благоприятен ефект върху каталитичната активност на образците в пълно окисление на етилацетат.