

## Unconventional ‘chemisorption-hydrolysis’ vs ‘impregnation’ technique for preparation of nanodispersed copper on mesoporous ceria and zirconia

T. S. Tsoncheva<sup>1\*</sup>, I. G. Genova<sup>1</sup>, N. Scotti<sup>2</sup>, V. Dal Santo<sup>2</sup>, N. Ravasio<sup>2</sup>

<sup>1</sup> Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

<sup>2</sup> CNR-Istituto di Scienze e Tecnologie Molecolari, Milano, Italy

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Mesoporous nanostructured zirconia and ceria were synthesized by a template-assisted hydrothermal technique and used as a host matrix of nanosized copper oxide species. A ‘chemisorption-hydrolysis’ strategy was applied for ZrO<sub>2</sub> and CeO<sub>2</sub> modification with copper. The obtained materials were characterized by XRD, nitrogen physisorption, FTIR, UV-Vis, and temperature-programmed reduction with hydrogen and compared with analogues prepared by conventional incipient wetness impregnation method. The catalytic activity was tested in methanol decomposition. Copper deposition on zirconia by the ‘chemisorption-hydrolysis’ approach ensures formation of highly active and selective catalysts for methanol decomposition to carbon monoxide and hydrogen, which is provoked by a synergistic effect between copper and zirconia components.

**Keywords:** Copper-modified mesoporous ZrO<sub>2</sub> and CeO<sub>2</sub>, ‘chemisorption-hydrolysis’ method, methanol decomposition

### INTRODUCTION

Copper-based materials are low cost and are considered effective catalysts in a number of redox processes, such as dehydrogenation of alcohols, isomerization and hydrogenation of hydrocarbons, hydrogenation of carbonyl compounds, hydrogenolysis of carbon-carbon and carbon-silicon bonds, *etc.* [1 and refs. therein]. A strong control on dispersion and oxidation state of the copper species is needed, which could be achieved by copper deposition on various porous supports with tunable surface and texture characteristics as well as by the preparation procedure used [2]. Recently, mesoporous silicas revealed good prospects for a host matrix of nanoscale metal/metal oxide particles due to their unequal pore structure characteristics [3, 4]. Advantages of zirconia as a catalyst support originate from its strong interaction with the active phase, a high thermal stability, and a unique combination of acidic, basic, and redox ability [5]. It has been established that ZrO<sub>2</sub> surface properties depend strongly on zirconia polymorphs, which could easily be controlled by particle size [6]. Effects on the interaction between copper and zirconia are concerned about and a higher dispersion and catalytic activity were reported for copper supported on a tetragonal rather than amorphous or monoclinic ZrO<sub>2</sub> support. Alternatively, ceria also possesses promising properties. Due to high oxygen storage/ transport capacity,

ceria alone, or combined with other elements, is recognized as an efficient catalyst for various environmental processes, namely NO reduction and CO oxidation, light hydrocarbons combustion, removal of diesel soot, water-gas shift reaction, and VOCs oxidation. A superior catalytic activity of the copper-ceria binary system in different reactions has been a subject of intense investigation and controversial discussion. Generally, a synergistic coupling of the redox properties of both metal oxides is assumed and it is assigned to a strong interaction between CuO and CeO<sub>2</sub>, which facilitates CuO introduction into the ceria lattice to form a solid solution and to disperse over the surface [7 and refs. therein].

Nowadays, advanced technologies, such as sol-gel, chemical vapour synthesis, and combustion and precipitation procedures have been developed to produce nanopowder metal oxides, which can be used for catalyst supports. Among them, a hydrothermal process is reported to be a soft chemical route to prepare phase-pure products at a low temperature and enable easy control of crystal size by altering process conditions [8]. Much attention is paid to the synthesis of nanostructured mesoporous oxides of high surface area and uniform pore size distribution using a surfactant-assisted route [9, 10 and refs therein]. It has been established that direct synthesis for modification of mesoporous silica supports typically results in deposition of a relatively low copper loading, while the traditional impregna-

\* To whom all correspondence should be sent  
E-mail: tsoncheva@orgchm.bas.bg

tion method [11] provides an undesirable agglomeration of copper species. A common grafting method causes the formation of  $\text{Cu}^+$  ions [12]. A predominant formation of oligomeric Cu-O-Cu species has been found using a molecular design method [13], while isolated  $\text{Cu}^{2+}$  ions dominate when an impregnation method is applied [13]. In a previous study [14] we reported that copper oxide species deposited by a ‘chemisorption-hydrolysis’ (CH) procedure is finely divided and interact strongly with the silica support. It was further demonstrated that this method, if applied to ordered mesoporous silicas, essentially improves the catalytic activity and stability of copper materials for methanol decomposition.

In the present study we report our attempts to apply the ‘chemisorption-hydrolysis’ strategy to deposition of copper oxide nanoparticles on mesoporous  $\text{ZrO}_2$  and  $\text{CeO}_2$  supports and to compare their properties with similar composites obtained by a conventional incipient wetness impregnation technique. The catalytic behaviour of the prepared materials was tested in methanol decomposition. Recently, fossil fuel depletion and large  $\text{CO}_2$  emissions focused the attention on biomass as renewable environmentally friendly feedstock, the latter resulting in no net increase in atmospheric carbon dioxide. Methanol, which can be produced from biomass, is regarded as an attractive alternative fuel and hydrogen release from methanol can be obtained through various techniques, such as simple decomposition, steam reforming, partial oxidation, and oxidative steam reforming [15].

## EXPERIMENTAL

### Materials

Mesoporous zirconia and ceria were prepared by a hydrothermal procedure using  $\text{ZrCl}_4$  or  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  as a precursor and CTAB as a structure-directing agent as described in Ref. 14. Zirconia and ceria samples were calcined at 573 K in air for 15 h. Samples denoted as Cu/ $\text{CeO}_2$ \_CH and Cu/ $\text{ZrO}_2$ \_CH were prepared by a ‘chemisorption-hydrolysis’ method which included: (i) impregnation of the supports with an aqueous solution of a tetramine copper complex ( $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , pH = 9) at room temperature for 20 min; (ii) hydrolysis of the obtained product with water at 273 K; (iii) filtration and drying at 373 K overnight. Alternatively, samples denoted as Cu/ $\text{CeO}_2$ \_WI and Cu/ $\text{ZrO}_2$ \_WI were prepared by conventional incipient wet impregnation with an aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . The obtained CH and WI samples were calcined in air at 623 K for 4 and 2 h, respectively. Copper content in the studied materials,

determined by atomic absorption spectroscopy, is given in table 1.

### Methods of investigation

Atomic absorption analyses were performed on a Pye Unicam SP 192 instrument. The porous structure of selected modifications was studied by nitrogen physisorption at 77 K, which was carried out in an ASAP 2020 Micromeritics automatic volumetric apparatus. The isotherms were used to calculate specific surface area,  $S_{\text{BET}}$ , and pore volumes of the obtained materials. Powder X-ray diffraction patterns were collected within the range of  $5.3$  to  $80^\circ$   $2\theta$  on a Bruker D8 advance diffractometer with  $\text{Cu K}\alpha$  radiation and a LynxEye detector. Scherrer equation was used to evaluate average crystallite size. UV-Vis spectra of powder samples were recorded on a Jasco V-650 apparatus. FTIR spectra in the region of skeletal vibrations were recorded on a Bruker Vector 22 spectrometer at a resolution of  $1$ – $2$   $\text{cm}^{-1}$  by accumulating 64–128 scans and using the KBr pellet technique. TPR/TG (temperature-programmed reduction/thermogravimetric) analyses were performed on a Setaram TG92 instrument in a flow of 50 vol.%  $\text{H}_2$  in Ar ( $100$   $\text{cm}^3 \cdot \text{min}^{-1}$ ) at a heating rate of  $5$   $\text{grad} \cdot \text{min}^{-1}$ .

Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst) using argon as a carrier gas ( $50$   $\text{cm}^3 \cdot \text{min}^{-1}$ ). Methanol partial pressure was 1.57 kPa. The catalysts were tested under conditions of a temperature-programmed regime within the range of 350–770 K at a heating rate of  $1$   $\text{grad} \cdot \text{min}^{-1}$ . Online gas chromatographic analyses were performed by means of an HP apparatus equipped with flame ionization and thermal conductivity detectors and a PLOT Q column using an absolute calibration method and carbon-based material balance.

## RESULTS AND DISCUSSION

Nitrogen physisorption isotherms of  $\text{ZrO}_2$  and  $\text{CeO}_2$  supports (Fig. 1, Table 1) exhibit a sharp jump in the relative pressure region of 0.6–0.8 and above 0.8, respectively, which, according to IUPAC classification, is typical of mesoporous materials. The specific surface area was about 5 times higher for zirconia as compared to ceria support (Table 1). Hysteresis loop shape reveals presence of nearly cylindrical mesopores for  $\text{ZrO}_2$  with an average pore diameter ( $D_{\text{av}}$ ) of 6 nm, while slit-like mesopores of much broader pore size distribution ( $D_{\text{av}}$  about 26 nm) dominate with  $\text{CeO}_2$ . In general, after modification with copper a decrease in BET surface area, total pore volume, and average pore diameter was

observed without substantial changes of the isotherms. This effect was more significant with the WI-obtained materials and could be assigned to pore blocking due to deposition of copper phase into the mesopores without considerable textural collapse. However, an extremely strong decrease in BET surface area and pore volume combined with a shift of the maximum of pore size distribution to higher values was observed for Cu/ZrO<sub>2</sub>\_WI and for that reason, structure changes of zirconia due to high temperature treatment during modification are not excluded.

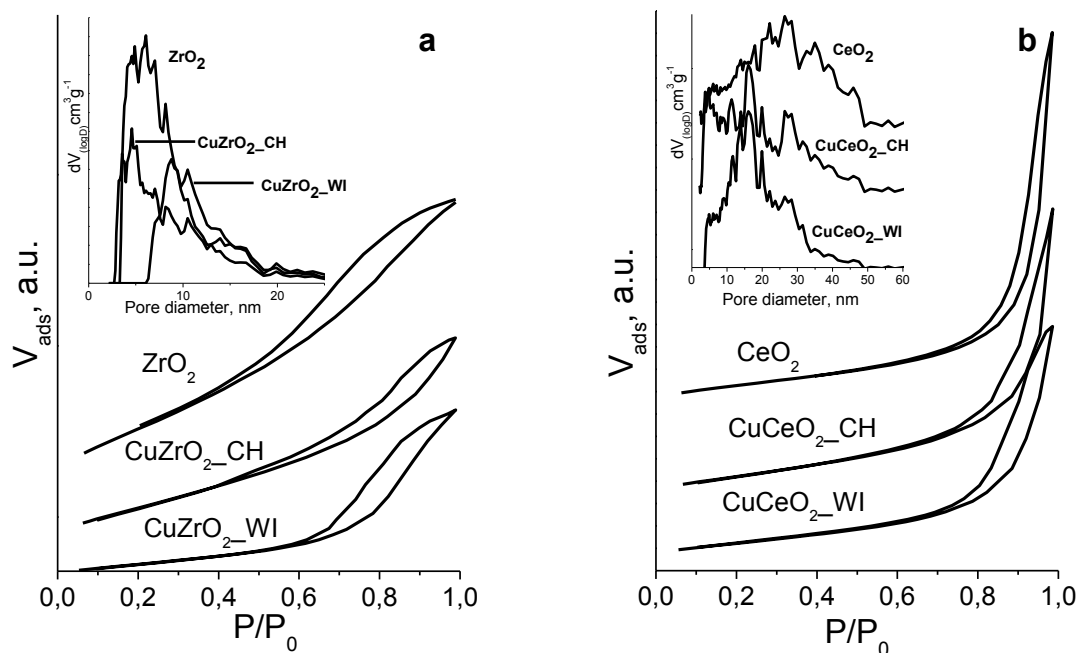
**Table 1.** Copper content, specific surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_{\text{tot}}$ ), and average pore diameter ( $D_{\text{av}}$ ) of studied samples.

Sample	Cu %??	$S_{\text{BET}}$ , $\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{tot}}$ , $\text{cm}^3\cdot\text{g}^{-1}$	$D_{\text{av}}$ , nm
ZrO <sub>2</sub>	-	300	0.42	6.0
Cu/ZrO <sub>2</sub> _CH	9.83	200	0.31	4.5
Cu/ZrO <sub>2</sub> _WI	9.83	80	0.23	8.8
CeO <sub>2</sub>	-	58	0.27	26.4
Cu/CeO <sub>2</sub> _CH	9.65	62	0.21	16.0
Cu/CeO <sub>2</sub> _WI	9.65	44	0.17	16.0

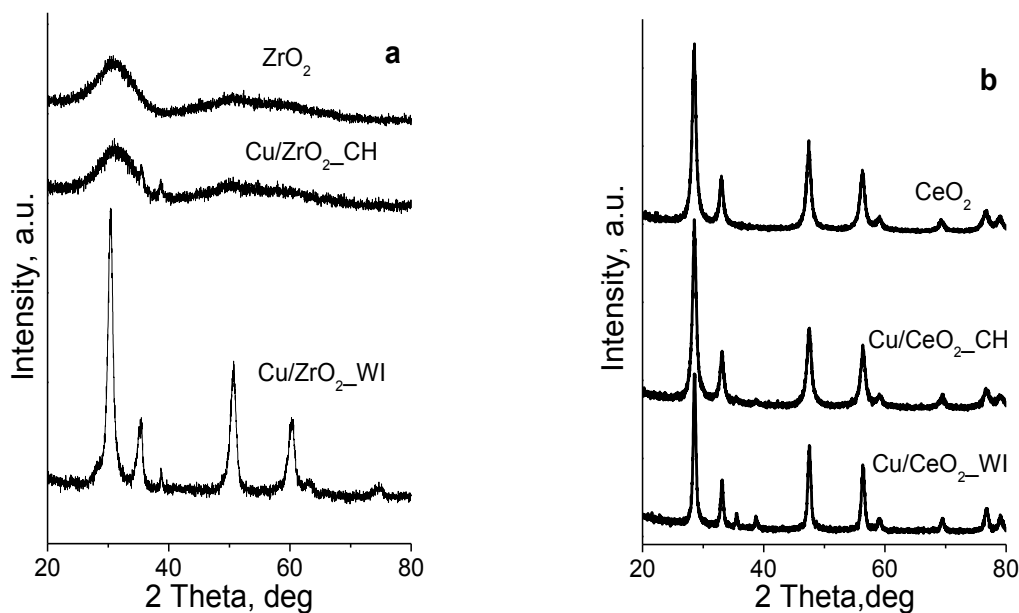
The XRD pattern of pure ZrO<sub>2</sub> represents a broad hump typical of amorphous materials (Fig. 2a). Bands at around 750, 650, and 550  $\text{cm}^{-1}$  in the FTIR spectrum of ZrO<sub>2</sub> (not shown) reveal coexistence of monoclinic and tetragonal phases. This phase compo-

sition of the support was preserved after modification by the CH procedure (Fig. 2a), while the WI method resulted in the formation of a well-crystallized tetragonal zirconia phase with average crystallite size of 9 nm. XRD patterns of pure and copper-modified ceria (Fig. 2b) represent typical reflections of a fluorite type structure with average particle size of 12 nm. No additional reflections of a copper containing phase could be distinguished for Cu/CeO<sub>2</sub>\_CH, while small reflections at 35.6 and 38.5° 2 $\theta$ , characteristic of CuO tenorite phase with average crystallite size of 3–5 nm, were registered for all other modifications of ceria and zirconia.

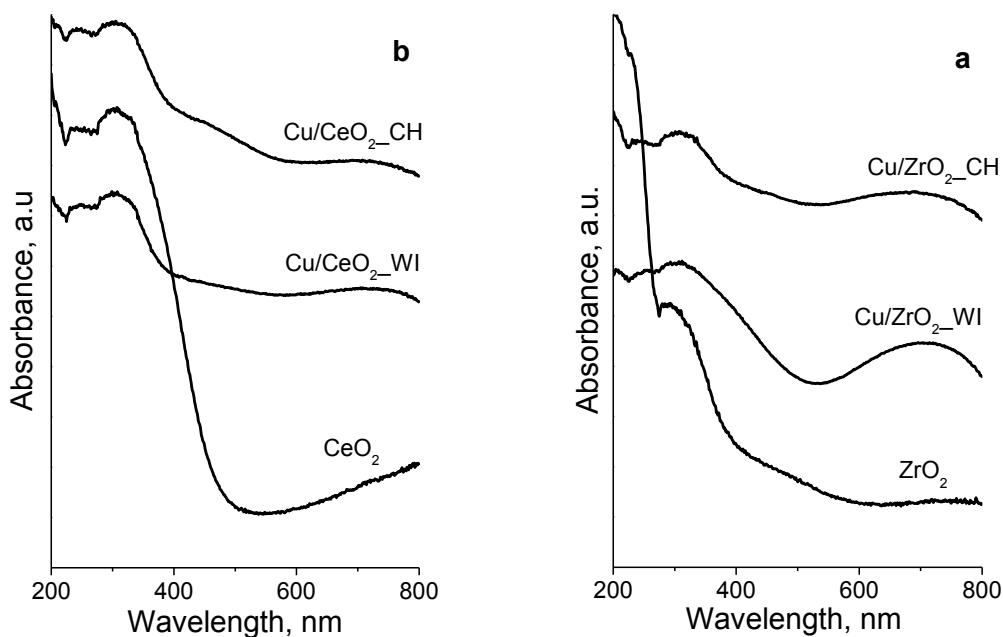
Fig. 3 displays UV-Vis spectra of parent and copper-modified ZrO<sub>2</sub> and CeO<sub>2</sub>. The electronic spectra of ceria and zirconia are very sensitive to cation coordination environment [17]. A blue shift observed in the UV-Vis spectrum of ceria (Fig. 3b) and a red shift in the spectrum of zirconia (Fig. 3a) as compared to the bulk materials (400 and 275 nm, respectively) disclose a decrease in coordination number of the Ce and Zr ions incorporated in highly defective finely dispersed crystallites. Absorption in the region of 300–500 nm and above 720 nm for all copper modifications is associated with the presence of oligomeric Cu-O-Cu species and well-crystallized CuO particles, the highest amount of the former being in Cu/CeO<sub>2</sub>\_CH in agreement with XRD data.



**Fig. 1.** Nitrogen physisorption isotherms and pore size distribution (inset) for parent and copper-modified ZrO<sub>2</sub> (a) and CeO<sub>2</sub> (b).



**Fig. 2.** XRD patterns of parent and copper-modified ZrO<sub>2</sub> (a) and CeO<sub>2</sub> (b) materials.



**Fig. 3.** UV-Vis spectra of parent and copper-modified ZrO<sub>2</sub> (a) and CeO<sub>2</sub> (b) materials.

Further information about the state of the copper species was gained by temperature-programmed reduction (TPR) experiments with hydrogen (Fig. 4). In principle, this method could provide useful data on metal ion oxidation state and environment, but usually interpretation of the results is rather complicated due to superposition of various effects. TPR profiles of pure CeO<sub>2</sub> show a slight weight loss above 650 K which corresponds to about 80% reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> ions at the surface [18]. In accordance with our previous study [14], the observed weight loss for pure ZrO<sub>2</sub> in the completely

studied temperature range could be related to a release of surface hydroxyl groups. Two reduction effects with maxima at 430 and 516 K appeared in the TPR profile of Cu/ZrO<sub>2</sub>-WI. According to Liu *et al.* [19] they can be assigned to stepwise reduction (Cu<sup>2+</sup> → Cu<sup>1+</sup> → Cu<sup>0</sup>) of bulk CuO particles. However, taking into account XRD and FTIR data (see above), reduction of CuO particles, which are in intimate contact with different zirconia phases (amorphous, monoclinic, and tetragonal) cannot be fully disregarded, as reported in Refs. 20 and 21. Calculations based on these two reduction effects gave a

reduction degree of about 95%. Only one reduction effect in the 350–430 K range with a maximum at about 400 K was observed with Cu/ZrO<sub>2</sub>\_CH. It is related to a complete Cu<sup>2+</sup>→Cu<sup>0</sup> transition of more finely divided particles as compared with Cu/ZrO<sub>2</sub>\_WI. It should be noted that weight losses observed in the whole temperature interval exceeded theoretical values of Cu<sup>2+</sup> total reduction to metallic copper and the effect was much more pronounced for Cu/ZrO<sub>2</sub>\_CH. We assign this phenomenon to a release of OH groups from the ZrO<sub>2</sub> surface, which are continually restored *via* spillover of hydrogen from finely divided copper particles to the zirconia surface [22].

TPR-TG profiles of both ceria modifications consist of only one TPR effect. It is narrower and centred at a lower temperature as compared to their ZrO<sub>2</sub> analogues, and is consistent with a 90–100% reduction degree of Cu<sup>2+</sup> to Cu<sup>0</sup>. This indicates that CuO species on CeO<sub>2</sub> is more finely and uniformly dispersed as compared to that on the ZrO<sub>2</sub> support. This effect was more pronounced for Cu/CeO<sub>2</sub>\_CH indicating that the CH procedure ensures formation of a finely dispersed CuO phase.

Fig. 5a shows temperature dependencies of methanol conversion over various materials. Selectivity to CO, its formation being closely related to the production of hydrogen from methanol, is presented in Fig. 5b. Methane, dimethyl ether (DME), and carbon dioxide are also registered as by-products. Both CeO<sub>2</sub> and ZrO<sub>2</sub> supports exhibit own catalytic activity above 650 K, which exceeds about 50% at 725 K. CO selectivity for both supports

is below 40% due to formation of DME, the latter being provoked by the presence of Lewis and Brønsted acidic sites. Modification of both supports with copper increased not only their catalytic activity in methanol decomposition (Fig. 5a), but also improved the selectivity to CO formation (Fig. 5b). These effects were more pronounced if the CH procedure was used. ZrO<sub>2</sub>-supported copper modifications manifested a higher catalytic activity as compared to their ceria-based analogues. Bearing in mind XRD, UV-Vis, and TPR data, we assume a synergistic effect between ZrO<sub>2</sub> support and deposited copper species. Formation of methoxy intermediates seems to be promoted by interaction between methanol and hydroxyl groups from the zirconia surface, while hydrogen transfer assists further transformation of the latter to and from the copper species. It seems that this mechanism is facilitated by higher dispersion of the copper entities, which is achieved during the ‘chemisorption-hydrolysis’ procedure. According to TPR data, they not only promote recovery of a ‘OH group reservoir’ on the zirconia surface but also demonstrate a high redox activity. The conversion curve of Cu/ZrO<sub>2</sub>\_WI shows a complicated behaviour that can be due to agglomeration of reduced copper species by the influence of reaction medium. Obviously, on increasing copper dispersion this effect is suppressed to a higher extent. This could be achieved using a ‘chemisorption-hydrolysis’ procedure or by copper deposition on ceria, where formation of an interface layer between CeO<sub>2</sub> and CuO prevents copper particles from agglomeration [23].

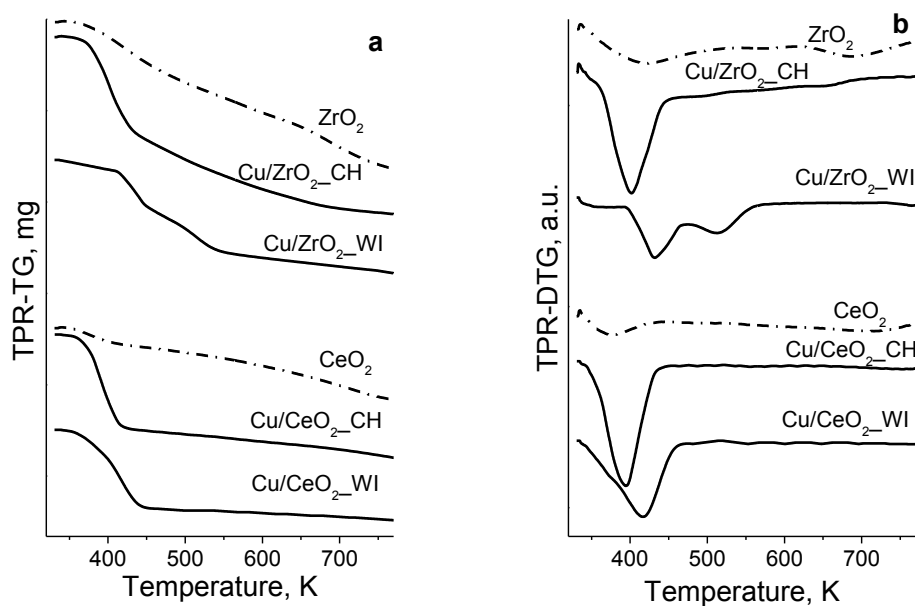


Fig. 4. TPR-TG (a) and TPR-DTG (b) profiles of copper modifications of ZrO<sub>2</sub> and CeO<sub>2</sub>.

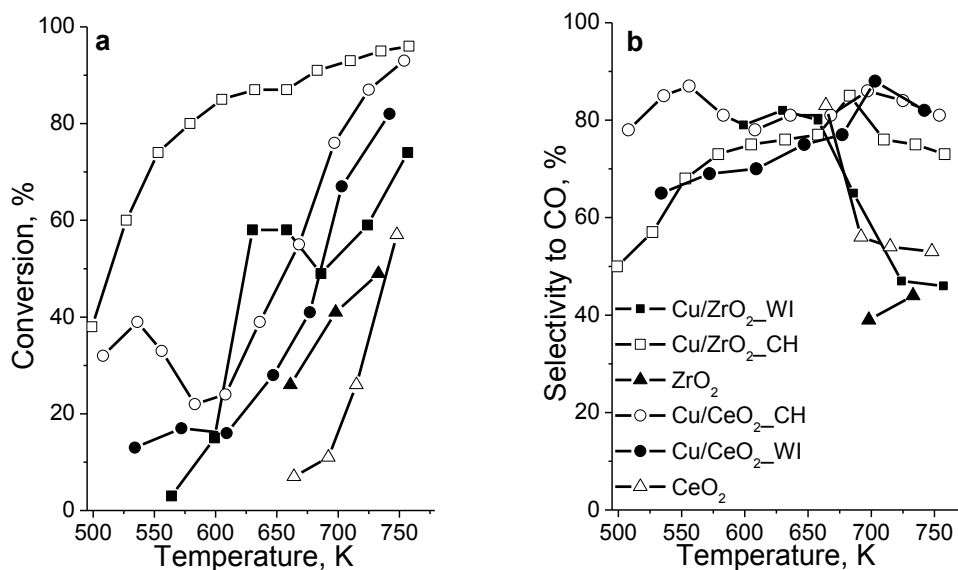


Fig. 5. Temperature profiles of methanol conversion (a) and CO selectivity (b) for various materials.

## CONCLUSIONS

A ‘chemisorption-hydrolysis’ method was applied to prepare nanosize copper oxide supported on nanostructured mesoporous  $\text{CeO}_2$  and  $\text{ZrO}_2$ . In comparison with conventional incipient wetness impregnation technique, this method provided deposition of readily reducible and highly active copper species in methanol decomposition. A higher catalytic activity achieved with zirconia-supported copper catalyst prepared by ‘chemisorption-hydrolysis’ procedure is assigned to a synergism between copper species and  $\text{ZrO}_2$ .

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НЕСТАНДАРТЕН МЕТОД НА „ХЕМИСОРБЦИЯ-ХИДРОЛИЗА“ И МЕТОД НА  
„ИМПРЕГНИРАНЕ“ ЗА ПОЛУЧАВАНЕ НА НАНОДИСПЕРСНА МЕД ВЪРХУ МЕЗОПОРЕСТИ  
ЦЕРИЕВ ДИОКСИД И ЦИРКОНИЕВ ДИОКСИД

Т. С. Цончева<sup>1\*</sup>, Из. Г. Генова<sup>1</sup>, Н. Скоти<sup>2</sup>, В. Дал Санто<sup>2</sup>, Н. Равазио<sup>2</sup>

<sup>1</sup> *Институт по органична химия с Център по фитохимия, Българска академия на науките, 1113 София, България*

<sup>2</sup> *CNR-Институт по молекулярна наука и технология, Милано, Италия*

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(Резюме)

Синтезирани са мезопорести наноразмерни циркониев диоксид и цериев диоксид чрез темплейтен хидротермален синтез, които са използвани като матрица за нанасяне и стабилизиране на наноразмерни меднооксидни частици. Приложен е метод на „хемисорбция-хидролиза“ за получаване на медни модификации на  $ZrO_2$  и  $CeO_2$ . Получените материали са охарактеризирани с прахова рентгенова дифракция, азотна физисорбция, ИЧ и УВ спектроскопии и температурно програмирана редукция с водород и са сравнени с техни аналози, получени чрез традиционен метод на „импрегниране“. Каталитичната активност на така получените материали е изследвана в разлагането на метанол. Показано е, че чрез прилагане на метода на „хемисорбция-хидролиза“ за отлагане на медни частици върху  $ZrO_2$  се получават високо активни и селективни катализатори за разлагане на метанол до въглероден оксид и водород, което се дължи на синергичен ефект между медния и циркониевооксидния компоненти.