

MESOPOROUS NANOSTRUCTURED COPPER-ZIRCONIUM-TITANIUM MIXED OXIDES AS CATALYSTS FOR HYDROGEN PRODUCTION: EFFECT OF PHASE COMPOSITION

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ABSTRACT

In present study mesoporous nanostructured zirconium-titanium oxide materials with different composition were prepared by template assisted hydrothermal technique. All zirconia-titania materials were modified with copper using wetness impregnation method. The obtained samples were characterized by nitrogen physisorption, XRD, Raman and TPR with H₂. Their catalytic properties were tested in methanol decomposition as hydrogen carrier. All copper modifications of the binary ZrO₂-TiO₂ oxides demonstrated higher dispersion and improved textural characteristics in comparison with their mono-component analogues. The catalytic activity of the samples in methanol decomposition was in a complex relation to their structure and texture characteristics and could be controlled with the variation of the Zr/Ti ratio. The domination of amorphous Zr_xTi_{1-x}O₂ solid solution in the equimolar material provides stronger interaction with the supported copper species. Resulting, highest catalytic activity was observed for this material.

Keywords: copper-zirconium-titania composites, phase composition study, hydrogen production from methanol.

INTRODUCTION

Hydrogen is assumed as the most efficient and environmental energy carrier. Due to the limitations in H₂ storage technologies, fuel processors which can convert liquid fuel into H₂ have attracted great interest. Among them, methanol has been commonly studied due to its many advantages like high H/C ratio, biodegradability and possibility to be produced from renewable sources. Nowadays, the catalytic decomposition of methanol is reported as the simplest process for hydrogen release [1]. Up to now, significant efforts have been devoted to find active, stable and low cost catalysts for methanol decomposition. Recently, titanium oxide provoked a great interest in many technological areas due to its unique electronic, optic and catalytic properties [2]. The application of titania as catalyst or catalyst support is related to its crystalline structure, specific surface area, porosity, particle size, etc. [3]. Doping titania with different metal oxides is well known procedure to improve its dispersion and redox properties due to the specific interaction and/or synergism between the components [4]. This investigation is focussed on the potential of mesoporous copper-zirconium-titanium mixed oxides as catalysts in methanol decomposition. The effect of Zr/Ti ratio was studied by complex characterization of the samples with different physicochemical techniques.

EXPERIMENTAL

The zirconia-titania mixed oxides with different composition were synthesized by template-assisted technique according to procedure described in [5]. The samples were modified by incipient wetness impregnation with aqueous solution of Cu(NO₃)₂·9H₂O and further calcination in air at 773 K for 2 h. The samples were denoted as Cu/xZr_yTi, where x:y was the metal mol ratio, which in the bi-component samples was 2:8, 5:5 or 8:2. The Cu content was 8 %. The textural characteristics were collected from nitrogen adsorption-

desorption isotherms at 77 K on a Quantachrome NOVA 1200 apparatus. Powder X-ray diffraction patterns were obtained on a Bruker D8 Advance diffractometer with Cu K α radiation using a LynxEye detector. Raman spectra were acquired with a DXR Raman microscope using a 780 nm laser. The TPR/TG analyses were performed on a Setaram TG92 instrument in a flow of 50 vol.% H₂ in Ar. Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst), argon being used as a carrier gas and methanol partial pressure of 1.57 kPa. On-line gas chromatographic analyses were performed using absolute calibration method and carbon based material balance.

RESULTS AND DISCUSSION

The nitrogen physisorption isotherms of all samples are of IV type according to IUPAC classification, which is typical of materials with mesoporous structure (not shown). The ternary CuO-ZrO₂-TiO₂ oxides exhibit higher BET surface area and total pore volume (Table 1). Their BET surface area overcomes the expected one if the samples were considered as a mechanical mixtures of the individual oxides, which suggests interaction between them.

Table 1. XRD and Nitrogen physisorption data of Cu/Zr-Ti materials.

Sample	Space Group	Crystallite size, nm	BET m ² g ⁻¹	Pore Volume ml/g
Cu/TiO ₂	Anatase, syn	21	40	0.24
	Tenorite	36		
Cu/2Zr 8Ti	Anatase, syn amorphous (47 %)	18	119	0.37
Cu/5Zr 5Ti	Amorphous		187	0.60
Cu/8Zr 2Ti	Tetragonal ZrO ₂ amorphous (86 %)	20	122	0.44
	Tenorite	30		
Cu/ZrO ₂	ZrO ₂ -tetragonal	13	61	0.31
	ZrO ₂ -monoclinic	14		
	Tenorite	57		

Co-existence of anatase and tenorite phase is detected in the XRD pattern of Cu/TiO₂ (Table 1) [6,7]. Larger crystallites of CuO as well as monoclinic and tetragonal ZrO₂ are found for Cu/ZrO₂ [7,8]. The appearance of amorphous phase in the XRD patterns of all ternary modifications, which is most pronounced for Cu/5Zr5Ti, indicates increase in the dispersion, which well correlates with the increase in the BET surface area (Table 1). Besides, here monoclinic ZrO₂ phase is not observed. Thus, interaction between the individual oxides, which is probably accompanied with the formation of solid solution, could be assumed.

Raman spectroscopy is applied for better understanding of the microstructure of the obtained nanocrystalline materials (Figure 1). The Raman spectrum of Cu/TiO₂ consists of well-defined Raman shifts which are typical of pure anatase structure [9]. Raman shifts of monoclinic and tetragonal ZrO₂ are observed in the Cu/ZrO₂ spectrum and this is in accordance with the XRD data (Table 1). The slight blue shift of the Raman E_{1g} mode of anatase for Cu/TiO₂ and Cu/2Zr8 Ti could be due to the changes in the environment of titanium ions probably due to the incorporation of Cu²⁺ in anatase lattice. The disappearance of Raman shifts in the spectra of Cu/5Zr5Ti and Cu/8Zr2Ti indicates increase in the dispersion of the samples, probably due to the formation of solid solution. For all copper modifications no Raman shifts typical of any copper containing phase are observed. This suggests that most of CuO species are in highly dispersed state.

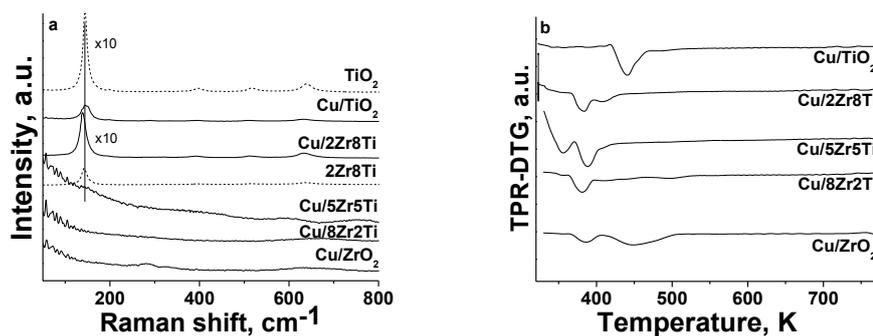


Figure. 1 Raman spectra (a) and TPR-DTG (b) of Cu/ZrTi materials.

In Figure 1 data from TPR analyses are presented. The reduction of Cu/TiO₂ is initiated above 430 K with a maximum at about 470 K. This temperature is much lower than the reported one for the reduction of bulk CuO (523 K), which confirms the facile effect of TiO₂ support. In case of Cu/ZrO₂ two reduction peaks centered at 387 K and 450 K, are observed. The low temperature effect could be attributed to the reduction of copper species in close contact with ZrO₂, while the high temperature one probably originates with the reduction of bulk CuO crystallites. We could not fully exclude the contribution of different monoclinic and tetragonal ZrO₂ phases, as was demonstrated by XRD (Table 1) and Raman (Figure 1) data. All effects in the TPR profiles of Cu-Zr-Ti ternary materials appear below 400 K. In accordance with the XRD data, the facile effect of the formation of ZrO₂-TiO₂ solid solution on the reducibility of the loaded copper species could be assumed. Taking into account the nitrogen physisorption data (Table 1) this could be related to the increase in the BET surface area. However facile electron transfer between CuO and Zr-Ti oxides could be assumed as well.

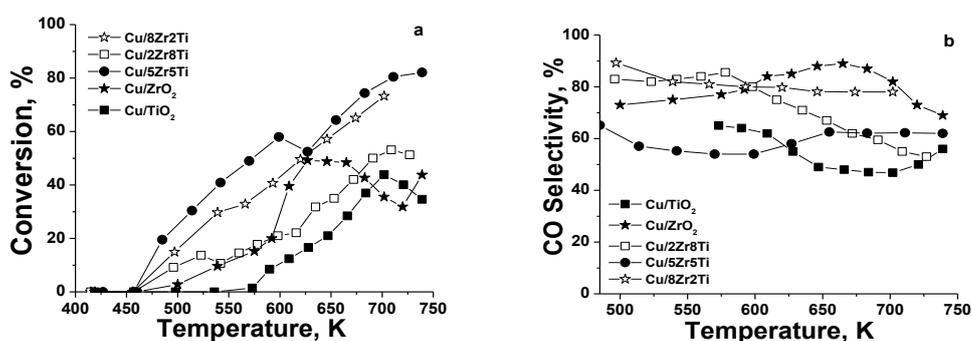


Figure 2. Methanol conversion (a) and selectivity to CO (b) of Cu/Zr-Ti materials

The temperature dependencies of methanol conversion and selectivity to CO are presented in Figure 2. Mainly CO₂, CH₄ and negligible amounts of dimethyl ether, methyl formate and C₂-C₃ hydrocarbons are registered as by-products as well. The highest catalytic activity is registered for Cu/5Zr5Ti, followed by Cu/8Zr2Ti. This could be attributed to the improved BET surface area of the composites (Table 1). However, the catalytic activity of Cu/2Zr8Ti is lower than Cu/8Zr2Ti despite the similarity in their texture characteristics (Table 1). The lowest catalytic activity is demonstrated for Cu/TiO₂. The absence of strong relation between the texture and catalytic behaviour of the samples confirms our assumption (see above) for the specific interaction between in the ternary Cu-Zr-Ti materials. We can

speculate on the formation of complex highly active Cu-Zr-Ti „interface layer“ where the electron transfer is facilitated and this is controlled by the Zr/Ti ratio. Note the appearance of maximum in most of the conversion curves which indicates significant changes with the catalysts during the catalytic test. According to the TPR data this could be due to the reduction transformations by the influence of the reaction medium and this could be also regulated by the samples composition.

CONCLUSION

Nanosized CuO-ZrO₂-TiO₂ ternary materials with high dispersion, high surface area and mesoporosity and improved reducibility are successfully prepared using combined template assisted/impregnation techniques. Their catalytic behaviour in methanol decomposition could be easily controlled by the variation in the samples composition and it is facilitated with the increase of ZrO₂ content in the samples. The equimolar Zr/Ti ratio promotes the catalytic activity in the reaction in a highest extent.

ACKNOWLEDGEMENT

This work was supported by Bulgarian National Scientific Fund (Grant Number KII-06-H29/2). Project BG05M2OP001-1.002-0019: „Clean technologies for sustainable environment – water, waste, energy for circular economy“ (Clean&Circle), for development of a Centre of Competence is also acknowledged.

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