



Nanostructured copper-zirconia composites as catalysts for methanol decomposition



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ABSTRACT

Nanostructured mesoporous ZrO₂ was obtained by hydrothermal synthesis using surfactant assisted approach. Copper modifications of thus obtained ZrO₂ (4–25 wt.% copper) were prepared by incipient wetness impregnation with the corresponding nitrate or acetyl acetonate precursors and further treatment in oxidative or reduction atmosphere. The obtained materials were characterized by N₂ physisorption, XRD, UV–vis, FTIR, XPS and temperature programmed reduction with hydrogen and tested as catalysts in methanol decomposition to hydrogen and CO. Selected samples were investigated after partial coverage of the surface with ¹¹C-labeled methanol and ¹¹C-labeled methyl formate. The formation of monolayer of finely dispersed copper oxide species on zirconia at about 4 wt.% copper loading and bulk copper nanoparticles at higher one is observed. It was assumed that zirconia support provides the formation of two types of catalytic sites: the first ones strongly adsorb methanol and exhibit predominantly dehydrogenation activity, while the others, possess acidic function. The modification of zirconia with copper significantly improves the catalytic activity and selectivity in methanol decomposition via (i) creation of additional surface acidic sites which contribute to generation of methoxy intermediates; (ii) stabilization of Cu²⁺–Cu⁺ and Cu⁺–Cu⁰ redox pairs where the electron transfer is facilitated by zirconia support and (iii) assisting the recombination and release of hydrogen during the transformation of produced on zirconia surface intermediates.

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1. Introduction

The properties of zirconia, namely, high strength and hardness, good elastic modulus, corrosion resistance, biocompatibility, and high melting temperature make the material interesting for applications as advanced ceramics in bio-sensors, piezoelectric devices, oxygen sensors, abrasives, as well as catalysts, catalyst support or promoters [1–9 and refs. therein]. Meanwhile, zirconia doped with copper oxides receive great attention as anode materials for solid oxide fuel cells [10] and catalysts for methanol synthesis [11–13], carbon monoxide oxidation [14], NO reduction with hydrocarbons or CO [15], water–gas-shift reaction [16,17], methanol reforming [18], CO and CO₂ hydrogenation [19]. The advantages of using zirconia as a catalyst support originates from its strong interaction with

the active phase, high thermal stability, and unique combination of acidic, basic, and redox ability [20]. Brønsted acidic and basic hydroxyl groups and co-ordinatively unsaturated Lewis acid–base Zr⁴⁺–O²⁻ pairs [19 and refs. therein] were simultaneously detected on zirconia surface. The surface properties of zirconia strongly depend on zirconia polymorphs. Hertl [21] suggested that tetragonal zirconia possessed high basicity, while monoclinic zirconia had relatively high Lewis and Brønsted acidity. It was established [19] that during the catalysts preparation, surface properties of zirconia polymorphs impacted the interaction between copper and zirconia leading to higher dispersion of copper on tetragonal ZrO₂ support. The authors [19] observed also higher catalytic activity in methanol synthesis for copper modified tetragonal ZrO₂ than the amorphous and monoclinic modifications. ZrO₂ polymorphs could be tuned with addition of certain divalent or trivalent cations or by decreasing the crystallite size below a critical value [22,23]. Nowadays, advanced technologies, such as sol–gel, chemical vapor synthesis, combustion and precipitation procedures have been

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developed to produce nanopowder zirconia [24–26]. Among them, hydrothermal process is reported to be a soft chemical route to prepare phase pure products at low temperature and easy control of crystal size by altering the process conditions [7 and refs therein]. Recently, much attention was paid to the synthesis of nanostructured mesoporous oxides with high surface area and uniform pore size distribution using a surfactant-assisted route [27,28 and refs therein].

Hydrogen production is one of the most important technologies for the chemical industry, power generation and fuel cell application [29]. Instead of handling H_2 under high-pressure or cryogenic conditions, hydrogen can be produced on board by catalytic steam reforming of natural gas and oil-derived naphtha, and partial oxidation of heavy oils. Nevertheless, these technologies are developed enough into market value, the depletion of fossil fuels and the large quantity of CO_2 emissions focused recently the attention on biomass as renewable, environmentally friendly feedstock with no contribution to a net increase in atmospheric carbon dioxide [30]. Methanol, which can be produced from biomass, is regarded as an attractive alternative fuel, also for portable power systems, due to the low temperature of hydrogen release and higher specific energy than either lithium batteries or stored hydrogen [31–33]. Hydrogen can be obtained from methanol through various techniques such as simple decomposition, steam-reforming, partial oxidation and oxidative steam reforming [34–36]. Number of recent studies assumed that copper and zirconia behaved in a bi-functional manner during the methanol decomposition or methanol synthesis, with Cu serving as a site for the dissociation or removal of hydrogen molecules, and zirconia as an adsorption site for carbon containing intermediates [17,37–39 and refs therein]. However, in spite of such bi-functional roles of copper and ZrO_2 , the influence of the intrinsic nature of each component on the beneficial synergy between them is not yet well understood. The aim of current paper is to highlight the effect of composition and preparation procedure of nanosized copper-zirconia composites on their catalytic behavior in methanol decomposition. The elucidation of mechanism of the reaction and the role of different catalytic sites is also in the scope of the study using original catalytic ^{11}C -radiolabeling approach. Nanodispersed mesoporous ZrO_2 was obtained by surfactant-assisted procedure and used as a catalyst support. The copper loading was varied in a wide range by incipient wetness impregnation of ZrO_2 with aqueous solutions of copper nitrate. Alternatively, selected samples were obtained by molecular design dispersion method (MDD) by anchoring of copper acetyl acetonate to the zirconia surface hydroxyl groups [40,41]. In order to study the specific role of copper and zirconia as well as the synergy between them thus obtained materials were compared with some copper modifications of ordered mesoporous SBA-15 silica. A complex of conventional physicochemical techniques, such as N_2 physisorption, XRD, UV-vis, FTIR, XPS and TPR was applied for catalysts characterization.

2. Experimental

2.1. Materials

The synthesis of the nanostructured zirconia was achieved by template-assisted approach according to the procedure reported in [42]. In principle, 6.0 g N-hexadecyl-N,N,N-trimethylammoniumbromide (CTAB) were dissolved in 50 ml distilled water. To this solution was added slowly and under vigorous stirring a solution of $ZrCl_4$ (3.40 g) in 25 ml distilled water. Then, the temperature was raised to 323 K and the reaction mixture was stirred for 30 min before adding drop-wise 20 ml NH_4OH (12.5%). The resulting mixture was stirred overnight at

323 K. Then it was transferred into a polypropylene container and heated at 373 K for 24 h. The so-prepared particles were then filtrated, washed with distilled water, then dried at room temperature and extraction of the organic template in absolute ethanol (100 ml per 1 g carrier) was conducted at 343 K for 24 h under reflux conditions. Then, the sample was filtrated and dried at room temperature before calcination in air with a ramp of 1 K/min and dwelling time of 6 h at 473, 573 and 673 K. The mesoporous SBA-15 silica was prepared according to the procedure described in [43] using Pluronic 123 as a structure directing agent. The template was released by calcination for 6 h at 773 K. The zirconia modifications with nominal copper content of 4, 8, 12 and 25 wt.%, were prepared by wet impregnation of ZrO_2 support with aqueous solution of copper nitrate. After drying, the samples were calcined in air at 673 K for 2 h and denoted as $nCu/ZrO_2(N,o)$ where n was the nominal copper loading in wt.%. Selected samples were additionally reduced in hydrogen at 523 K for 2 h and denoted as $nCu/ZrO_2(N,r)$. The reference SBA-15 silica based materials, treated in air, $nCu/SBA-15(N,o)$, or in air and hydrogen, $nCu/SBA-15(N,r)$, were prepared following the same procedure. The copper content of the samples, determined by Atomic Absorption Spectroscopy was presented in Table 1. Alternatively, the samples denoted as $4Cu/ZrO_2(A,o)$ and $8Cu/ZrO_2(A,o)$ were prepared by impregnation of ZrO_2 with toluene solution of copper acetyl acetonate. After the decomposition of acetyl acetonate precursor in air at 673 K (1 K/min) for 2 h, materials containing 4.3 and 7.8 wt.% Cu were obtained.

2.2. Methods of investigation

Copper content in the samples was determined by Atomic Absorption Spectroscopy on an Atomic Absorption Spectrometer 3100 – Perkin-Elmer; flame: acetylene/air. Specific surface area and pore size distribution were measured through nitrogen adsorption-desorption isotherms at 77 K using a Quantachrome NOVA 1200 apparatus. S_{BET} was calculated applying the Brunauer, Emmet and Teller (BET) equation for N_2 relative pressure in range of $0.05 < P/P_0 < 0.30$. Pore size distribution was determined by DFT method from the desorption branch of the isotherm. Powder X-ray diffraction patterns were on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and using a LynxEye detector. The average crystallite size was evaluated according to Scherrer equation. The UV-vis spectra were recorded on a Jasco V-650 UV-vis spectrophotometer equipped with a diffuse reflectance unit. FTIR spectra in the region of skeletal vibrations were recorded on a Bruker Vector 22 spectrometer at a resolution of $1-2\text{ cm}^{-1}$, accumulating 64–128 scans and KBr pellets technique. The pyridine desorption spectra were carried out with a BioRad FTS-60 spectrophotometer equipped with mid-IR MCT detector. The experiments were performed on sample disk (15–20 mg) after a pre-treatment (dehydration under vacuum at 383 K for 1 h or reduction at 523 K under H_2 for 2 h). One spectrum was collected before probe molecule adsorption as a blank experiment, then pyridine (Py) vapors were adsorbed on the disk at room temperature and following desorption steps (30 min, vacuum, every 50 K) were performed from RT to 523 K. The spectra were collected after each desorption step after cooling the sample. The X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatised Al $K\alpha$ source (1253.6 eV) run at 14 kV and 15 mA. The analyzer operated in the constant analyzer energy (CAE) mode. Survey spectra were measured at 50 eV pass energy. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. The sample powders were mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range

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