



# Catalytic combustion of toluene over copper oxide deposited on two types of yttria-stabilized zirconia



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## ABSTRACT

Yttria-stabilized zirconia (YSZ) was obtained by the coprecipitation at pH 9.0 and by the sol–gel method. These oxide systems crystallized in the tetragonal phase which was revealed by powder X-ray diffraction (XRD). The YSZ supports were mesoporous solids with different kinds of porosity and various BET specific surface areas determined by low-temperature sorption of nitrogen. The incipient wetness technique was used to modify these materials with different amounts of Cu (2.5, 5.0 and 7.5 wt%). The changes in structural and textural properties of the YSZ supports after the CuO introduction were discussed, and the surface composition of the Cu-loaded samples was studied by X-ray photoelectron spectroscopy (XPS). It was found that the intra- and interparticle porosity influences the dispersion of CuO active phase, which is the parameter determining the catalytic activity in the toluene combustion. The material based on coprecipitated YSZ containing 5 wt% of Cu turned out to be the most active catalyst with  $T_{50} = 264^\circ\text{C}$  and the total conversion of toluene observed at  $350^\circ\text{C}$ .

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## 1. Introduction

Volatile organic compounds (VOCs) emitted during processes involving organic chemicals are harmful to organisms and the environment. Various kinds of organic substances belong to this group, e.g. paraffins, olefins, aromatics, ketones, aldehydes, carboxylic acids or chlorinated hydrocarbons [1]. Among the widely encountered VOCs, toluene, emitted during fuel usage and industrial processes, can be listed. This aromatic compound is dangerous for the human nervous system at concentration as low as 100 ppm [2].

If the VOCs' concentration is low, they can be simply removed by the non-catalytic or catalytic total oxidation [3]. Supported noble metals—particularly platinum or palladium—are the most efficient systems in the VOC's abatement. On the other hand, such catalysts can be easily poisoned by contaminants and are expensive, and therefore transition metal oxides have been often examined as components of catalysts for the purification of VOCs containing gases [1]. Among them, supported copper and manganese oxides turned out to be the most active materials [4–7]. It was postulated [8] that the adsorption of the toluene molecule is the initial step of toluene oxidation over a CuO–CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. Subsequently, abstraction of hydrogen from the methyl and the phenyl

group, abstraction of the carbon atom of the methyl group, and finally, destruction of the aromatic ring, occur. Both lattice and adsorbed oxygen are involved in (i) reoxidation of mildly reduced copper species and (ii) abstraction of hydrogen atoms and scission of C–C bonds.

It should be noticed that better catalytic performance in the total oxidation of toluene was observed for metal oxides deposited on zirconia than on γ-alumina [9,10]. This effect was attributed to the formation of active phases exhibiting higher reducibility, because zirconia limits the dispersion of an active phase. Lower reducibility, typical of alumina-supported catalysts, results from strong interactions between an active phase and the support. Larger active phase crystallites facilitate oxygen adsorption on noble metals, which is the rate-determining step in the toluene oxidation occurring according to the Mars van Krevelen or Eley-Rideal mechanisms. Moreover, the presence of oxygen surface vacancies in ZrO<sub>2</sub> enables the chemisorption of reactants [9]. Zirconia is also characterized by good mechanical and thermal stability [10,11].

ZrO<sub>2</sub> is often more effective in the so-called stabilized form, which contains an addition of another metal oxide (e.g. SiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, CaO, Y<sub>2</sub>O<sub>3</sub> or Ce<sub>2</sub>O<sub>3</sub>) appearing in the fluorite structure and forming a solid solution with zirconia. The presence of additives causes that zirconia crystallizes in the tetragonal phase, exhibiting higher specific surface area than more stable monoclinic ZrO<sub>2</sub>. Yttrium was recognized as the best dopant of zirconia in the case of the catalysts for oxidation processes, because it increases the number of available oxygen vacancies, helping to store oxygen and return it at low

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temperatures. The content of 1–10 mol.% of yttria in ZrO<sub>2</sub> ensures the highest ion conductivity [11].

The aim of the presented work was the synthesis of zirconia stabilized by 5 mol.% of yttria using two various methods: coprecipitation (at controlled pH of 9.0) and sol–gel. The obtained yttria-stabilized zirconia materials with different structural and textural properties were used as supports for a copper oxide phase. The catalytic activity of the obtained CuO/YSZ materials was studied in the total oxidation of toluene. The influence of the support properties as well as dispersion and content of CuO on the catalytic performance was discussed.

## 2. Experimental

### 2.1. Synthesis of catalysts

To obtain yttria-stabilized zirconia (5 mol.% of Y<sub>2</sub>O<sub>3</sub>), two methods were applied: coprecipitation (c) and sol–gel (s). In the coprecipitation procedure, zirconyl chloride octahydrate (23.85 g) and yttrium(III) nitrate hexahydrate (2.99 g) (both supplied by Sigma-Aldrich) were dissolved together in deionised water (50 mL). This solution was added dropwise to another solution (370 mL) containing 1.2 wt% of ammonia (Lach-ner) under stirring till achieving pH 9.0. The obtained precipitation was stirred for 30 min, then filtered and washed a few times with deionised water to remove chloride and ammonium ions.

In the sol–gel synthesis, the two separate solutions containing (I) 2.99 g of yttrium(III) nitrate hexahydrate in 1-propanol (50.0 mL, Sigma-Aldrich) and (II) 24.26 g of zirconium(IV) propoxide in 1-propanol (100.4 mL, Sigma-Aldrich) were simultaneously added drop by drop (for 30 min) into the mixture of 1-propanol (240 mL) and deionised water (3 mL) under stirring. The obtained sol was heated to 70 °C and kept at this temperature for 6 h. The final suspension was stirred for further 16 h at room temperature. Subsequently, the precipitation was filtered and washed a few times with deionised water.

Both obtained materials (cZrY and sZrY) were dried overnight and then calcined at 600 °C for 6 h. The calcination temperature was achieved at a rate of 5 °C/min.

Such synthesized supports were subsequently modified with an aqueous solution of copper(II) nitrate using the incipient wetness technique to obtain catalysts containing 2.5, 5.0 and 7.5 wt% of Cu after calcination at 500 °C (achieved at a heating rate of 5 °C/min) for 3 h. The synthesized samples are denoted as xCu/cZrY or xCu/sZrY, where x expresses the intended copper loading.

### 2.2. Characterization

The crystallographic structure of the samples was determined with powder X-ray diffraction by means of a Philips X'pert APD diffractometer with a Cu radiation ( $\lambda = 1.540560 \text{ \AA}$ ). The XRD patterns were recorded in the  $2\theta$  range of 2–64° with a step of 0.02°. Textural properties of the supports and catalysts were determined with low-temperature sorption of nitrogen using an ASAP 2020 sorptometer (Micromeritics). Before the measurements, the samples were outgassed at 350 °C under vacuum for 5 h.

The X-ray photoelectron spectra were recorded on a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyser. The spectra were measured using a monochromatised aluminum Al K $\alpha$  source ( $E = 1486.6 \text{ eV}$ ) and a low-energy electron flood gun (FS40A-PS) to compensate the charge on the surface of nonconductive samples. The base pressure in the analysis chamber during the measurements was  $5 \times 10^{-9}$  mbar. Spectra were recorded with a constant pass energy of 100 eV. The binding energies were referenced to C 1s core level

( $E_b = 285.0 \text{ eV}$ ). The composition and chemical surrounding of the sample surface were investigated on the basis of the areas and binding energies of Cu 2p, Zr 3d, Y 3d, O 1s and C 1s photoelectron peaks. The fitting of high-resolution spectra was provided through the CasaXPS software.

### 2.3. Catalytic tests

The synthesized materials were tested as catalysts in the total oxidation of toluene. 0.1 g of a catalyst (with particle size between 160 and 315  $\mu\text{m}$ ) was placed on quartz wool in a quartz flow microreactor. The reaction temperature was maintained by a thermoregulator connected with a thermocouple placed in a catalyst bed. Prior to a catalytic test, the catalyst was outgassed at 500 °C in flowing air (82 mL/min) for 30 min. Then the reactor was cooled down to 200 °C and toluene dosing from a saturator (kept at 0 °C) began with an additional stream of air (18 mL/min), connected to the main airstream in front of the reactor, giving the total air flow of 100 mL/min. Toluene concentration in the reaction mixture passing by the catalyst bed was equal to 1000 ppm. The catalytic tests were carried out at 200, 250, 275, 300, 325, 350, 400, 450 and 500 °C. These temperatures were attained at a rate of 10 °C/min and kept for 65 min. At each temperature, three analyses of reaction products were conducted using a Bruker 450-GC gas chromatograph equipped with three columns (Molecular Sieve 5A for separation of O<sub>2</sub>, N<sub>2</sub> and CO, Porapak S for separation of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O, and Chromosorb WAW-DMCS for separation of aromatic compounds), a thermal conductivity detector, two flame ionization detectors as well as a methaniser. Toluene conversion ( $X_T$ ) was calculated from the following formula:

$$X_T = \frac{n_{T,0} - n_T}{n_{T,0}} \times 100\%$$

where  $n_{T,0}$  and  $n_T$  are numbers of moles of toluene present in the inlet and outlet stream.

## 3. Results and discussion

To check the crystallographic structure of yttrium-doped zirconia supports, their powder X-ray diffraction patterns were recorded (Fig. 1). For the coprecipitated sample, the reflections at  $2\theta$  equal to 30.26°, 35.14°, 50.39°, 59.92°, 62.86° and 74.07°, whereas for the sol–gel support at 30.34°, 35.12°, 50.52°, 60.01°, 62.96° and 74.19° are observed. These reflections are ascribed to (1 0 1), (1 1 0), (1 1 2), (2 1 1), (2 0 2) and (2 2 0) planes, respectively, of ZrO<sub>2</sub> in the tetragonal form [JCPDS 79-1764]. In the XRD patterns, no reflections characteristic of yttrium oxide are visible. It can be caused by the low concentration of added yttrium, or as described in the literature yttrium is a structural dopant forming a solid solution with zirconia and enforcing tetragonal structure of YSZ [11,12]. Depending on the yttrium content, YSZ can form tetragonal phase (t) (for an oxide system containing 0–3.0 mol.% Y<sub>2</sub>O<sub>3</sub>), which is transformable into the monoclinic structure, or the metastable tetragonal phase (t') (at a higher yttrium concentration—3.0–6.5 mol.% Y<sub>2</sub>O<sub>3</sub>) which is non-transformable. These two phases can be distinguished by calculating the  $c/a \cdot \sqrt{2}$  parameter. For the pure zirconia tetragonal phase [JCPDS 79-1764], the  $c/a \cdot \sqrt{2}$  value is 1.020, considered to be the low-stabilized t phase. The  $a$  and  $c$  lattice parameters determined for the cZrY (3.600 and 5.142) and sZrY (3.611 and 5.110) samples indicate that in the case of these supports the  $c/a \cdot \sqrt{2}$  values are equal to 1.010 and 1.001, respectively, which confirm the incorporation of yttrium into the ZrO<sub>2</sub> structure forming the highly stabilized t' phase [13].

The impregnation of the yttria-stabilized zirconia supports with various amounts of copper nitrates and their subsequent calcination resulted in the appearance of a new phase beside the

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