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Titanium and zirconium-based mixed oxides prepared by using pressurized and supercritical fluids: On novel preparation, microstructure and photocatalytic properties in the photocatalytic reduction of CO_2

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The $Zr_xTi_{1-x}O_n$ mixed oxides with various Ti:Zr molar ratios and parent TiO_2 and ZrO_2 were prepared unconventionally, combining the reverse micelles-controlled sol-gel method with high-pressure processing by pressurized and supercritical fluids. The mixed oxides were characterized using several complementary characterization methods and investigated in the photocatalytic reduction of CO_2. Applied novel unconventional processing affected significantly the (micro)structure of mixed oxides, which was further reflected to their optical and thus electronic properties. The $Zr_{0.1}Ti_{0.9}O_n$ mixed oxide showed the best photocatalytic behavior in a consequence of the optimal crystallinity and the lowest band gap energy from all mixed oxides. The $Zr_{0.1}Ti_{0.9}O_n$ mixed oxide was of bicrystalline TiO_2 anatase-brookite structure (67:33 wt.%) showing small crystallite-sizes, which allowed the optimal surface phase junction.

1. Introduction

According to the International Panel on Climate Change (IPCC) most of the warming observed over the past 50 years is attributable to human activities. Human influences are expected to continue to change the atmospheric composition throughout the 21st century. Greenhouse gases (GHGs) such as CO_2, CH_4, N_2O, HFCs, PFCs, and SF_6 are the primary cause of global warming [1,2].

Carbon dioxide contributes largely to the global climate change because it is one of the main greenhouse gases that are present in the atmosphere. CO_2 takes part in raising the global temperature through absorption of infrared light and re-emitting it. International Panel on Climate Change predicted that atmospheric CO_2 level could reach up to 590 ppm by 2100 and the global mean temperature would rise by 1.9 °C [1].

The reduction of CO_2 by photocatalysts is one of the most promising methods since CO_2 can be reduced to useful compounds by irradiating it with UV light at room temperature and ambient pressure. The reaction scheme is following:

$$CO_2 + H_2O \overset{h\nu,\, catalyst}{\rightarrow} Carbonaceous\ products + O_2 \qquad (1)$$

Titania (TiO_2) has been considered to be the most suitable photocatalyst for these environmental applications owing to its nontoxicity, biological and chemical inertness, strong oxidizing power and the long-term stability against corrosion. Therefore, a great effort has been spent on revealing and improving its photocatalytic activity for practical applications. It is well known that the photocatalytic activity of titania depends on its crystal structure, doping, surface area, surface hydroxylation etc. [3].

Nowadays a lot of studies dealing with modification and/or tuning of TiO_2 characteristics by doping of a second metal oxide or

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metal (non-metal) element have occurred. In the first instance, incorporating TiO_2 into another metal oxide with large band gap energy, such as SnO_2, SiO_2, and ZrO_2 has been investigated to improve the thermal stability and photocatalytic activity of TiO_2 [4]. The mixed oxide of TiO_2 and ZrO_2 has widely been examined in the photocatalysis field, since TiO_2–ZrO_2 mixed oxide photocatalysts with suitable TiO_2 and ZrO_2 composition are more effective than pure TiO_2 photocatalysts for many photocatalytic reactions [4–13].

The aim of this work is to investigate the effect of ZrO_2 doping on microstructure, physico-chemical properties and photocatalytic properties of formed $Zr_xTi_{1-x}O_n$ mixed oxides. The $Zr_xTi_{1-x}O_n$ mixed oxides with different Ti:Zr molar ratios were prepared combining the sol-gel method with unconventional processing by pressurized hot water and supercritical methanol. Advantages of utilization of processing by pressurized hot water and supercritical methanol consist in crystallization of $Zr_xTi_{1-x}O_n$ mixed oxides at significantly lower temperatures than by using common thermal treatment (calcination), moreover, the (micro)structure can be tuned on the nano-size level, reaching material with higher surface area and high purity [14–17]. Since the preparation method plays the key role in affecting the microstructure and physico-chemical properties of materials, the attention was focused on precise determination of all material properties. The photocatalytic properties of prepared $Zr_xTi_{1-x}O_n$ mixed oxides were examined for the photocatalytic reduction of CO_2.

2. Experimental

2.1. Preparation of $Zr_xTi_{1-x}O_n$ mixed oxides

The preparation of $Zr_xTi_{1-x}O_n$ mixed oxides was realized via sol-gel synthesis controlled in reverse micelles environment using titanium (IV) isopropoxide as a Ti source and zirconium (IV) propoxide in propan-2-ol as Zr source, and using unconventional processing by pressurized hot water and supercritical methanol at 250 °C and 10 MPa, using 1.5 l of deionized water and 0.25 l of methanol. The solvent flow rate during the processing was kept 3.5–4.5 ml/min. The 5 various molar mixtures of Ti:Zr were prepared; 0.9:0.1, 0.7:0.3, 0.5:0.5, 0.3:0.7, 0.1:0.9. Parent TiO_2 and ZrO_2 under the same high-pressure processing conditions as $Zr_xTi_{1-x}O_n$ mixed oxides were prepared as well. The preparation was realized on a home-made high-pressure set-up operating up to 40 MPa with a heating up to 400 °C [16].

2.2. Characterization of $Zr_xTi_{1-x}O_n$ mixed oxides

The purity (present elementary C in wt.%) of the mixed oxides was determined using a Vario EL III apparatus from Elementar. The detection limit of the apparatus was 0.1 abs.%. Each test was duplicated.

Determination of the chemical composition of the mixed oxides was performed on an ARL9400 XP sequential WD-XRF spectrometer. All spectra were collected under vacuum conditions; the data analysis was performed with the use of WinXRF software.

Nitrogen physisorption measurements were performed at 77 K on an automated volumetric apparatus Nova2000 (Qunatachrome, USA) after degassing of materials at 110 °C overnight under vacuum less than 1 Torr. The specific surface area, S_{BET}, was calculated according to the classical Brunauer–Emmett–Teller (BET) theory for the p/p_0 range = 0.05–0.30. Net pore volume, V_{net}, was evaluated at relative pressure p/p0 ~ 0.990.

X-ray diffraction patterns were measured on a Panalytical X'Pert MPD Pro diffractometer using CuKα radiation in Bragg-Brentano geometry. Primary radiation was conditioned using slits and Soller slits (0.04 rad divergence). Diffracted radiation was collected by using position sensitive detector PiXCel in the range of diffraction angle $2\theta = 10 - 140°$ with a step of 0.026 deg. Each diffraction pattern was measured for 24 h. Powder materials were placed into plexiglass holder. During measurements the constant irradiated area (approx. $5 \times 3\,mm^2$) was hold. Diffraction patterns were analysed with the aid of MStruct [18], the powder diffraction software which is based on the Rietveld method with several extensions for nanocrystalline materials [19]. Mainly quantitative phase analysis and real structure parameters (size of diffracting particles) were determined. XRD quantitative phase analysis was done using the Rietveld method and assuming following phases: anatase, brookite and rutile TiO_2, tetragonal and monoclinic ZrO_2 and in addition the monoclinic Titanium Zirconium Oxide phase with composition of $Zr_{0.19}Ti_{0.81}O_2$ (PDF database record no. 04-013-6879, [20]). Peaks significantly shifted from pure monoclinic ZrO_2 were found in two $Zr_xTi_{1-x}O_n$ mixed oxides and they were well-fitted by this phase.

Raman spectra were measured with a smart Raman microscopy system XploRATM (HORIBA Jobin Yvon, France). Spectra were acquired in the range of 100–1100 cm^{-1} with 25% of the initial laser beam, objective with 50x magnification, and 1200 grooves/mm grating.

UV–vis diffuse reflectance spectra of hydrated and granulated mixed oxides were measured in quartz cuvettes by using a GBS CINTRA 303 spectrometer (GBC Scientific Equipment, Australia). The reflectances were recalculated to the absorption using the Kubelka–Munk (KM) equation:

$$F(R_\infty) = (1-R_\infty)^2/2 \times R_\infty, \tag{2}$$

where R_∞ is the diffuse reflectance from a semi-infinite layer.

2.3. Experimental apparatus for the CO_2 photocatalytic reduction

The photocatalytic reduction of carbon dioxide was realized in a home-made stirred batch reactor (volume of 355 ml) with a suspended $Zr_xTi_{1-x}O_n$ mixed oxides illuminated by the UV 8 W Hg lamp (peak light intensity at 254 nm wavelength) situated on the top of the quartz glass visor (diameter = 75 mm) (Fig. 1). The shell of reactor was made of stainless steel and magnetic stirrer at the bottom provided ideal mixing. The investigated powder mixed oxide (0.12 g) was suspended in 120 ml of 0.2 mol/l NaOH solution. A supercritical fluid-grade CO2 with a certified maximum of hydrocarbons less than 1 ppm was used as the reactant to avoid any hydrocarbon contamination from reaction gas. The initial pH of the solution dropped from 12.5 to 7. The pressure probe was placed at the top and pressure was measured by a digital manometer (Greisinger, GMH 3110).

The gaseous samples were measured before switching on the UV lamp and during the irradiation in the interval of 0–12 h, samples were taken discontinuously through a septum gastight syringe. The gaseous reaction products (CH_4, CO and H_2) were analyzed using a gas chromatograph (Tracera GC – 2010 plus, Shimadzu) equipped with a barrier discharge ionization detector.

The accuracy of measurements was verified by series of reproduced tests and the relative error of products yields of 10% was determined. Blank tests were also made to guarantee that the CH_4 and CO production was due to the photoreduction of CO_2 [21]. The first blank test was UV-illuminated without the photocatalyst, the second one was in the dark with the catalyst and CO_2 under the same experimental conditions and the third one was over the illuminated photocatalyst in the absence of CO_2. CH_4 and CO were not detected in any blank tests.

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