



# Hydrothermal synthesis and characterization of zirconia based catalysts



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## ABSTRACT

In this work, three equimolar mixed oxides  $\text{ZrO}_2/\text{CeO}_2$ ,  $\text{ZrO}_2/\text{TiO}_2$ ,  $\text{ZrO}_2/\text{La}_2\text{O}_3$  and a reference  $\text{ZrO}_2$  have been synthesized by hydrothermal method. The structural and surface properties of these materials have been fully characterized by X-ray diffraction, transmission electron microscopy, surface area measurement, chemical analysis, XPS, infrared spectroscopy after adsorption of pyridine and adsorption microcalorimetry of  $\text{NH}_3$  and  $\text{SO}_2$  probe molecules. All investigated mixed oxides are amphoteric and possess redox centers on their surface. Moreover, hydrothermal synthesis leads to catalysts with higher surface area and with better acid–base properties than classical coprecipitation method. Both Lewis and Brønsted acid sites are present on the surface of the mixed oxides. Compared to the other samples, the  $\text{ZrO}_2/\text{TiO}_2$  material appears to be the best candidate for further application in acid–base catalysis.

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## 1. Introduction

Zirconia, due to its high mechanical and thermal stability, presents considerable interest in catalysis. Indeed, it is an important catalytic material with high Lewis acidity, significant basicity and weak Brønsted acidity used in many catalytic reactions in different research areas as for instance petrochemical industry [1,2], fuel cells [3], air remediation [4,5] or glycerol valorization [6]. Zirconia can be used directly as support or can be associated with other oxides which are active under reductive atmosphere [7–9]. For example, its association with ceria can lead to highly selective catalysts for the reaction of Knoevenagel [10], its association with titanium oxide can yield a mesoporous catalyst more active than classic  $\text{TiO}_2$  catalyst for the combustion of volatile organic compounds [11] and its association with lanthanum oxide can improve the yields of isomerization reactions used in the production of biodiesel [12]. The usual preparative procedures are based on precipitation with ammonia from a solution containing chloride (or oxychloride) precursors followed by a high temperature heat treatment. However, these oxide mixtures exhibit generally a too low surface area (often due to high temperature heat treatment) to obtain satisfactory catalytic conversions. The aim of this work is to develop a protocol to obtain these catalysts with the highest surface area possible. Among the wet chemical preparation methods, hydrothermal route has been recognized as energy and time saver with faster kinetics of crystallization than classic co-precipitation or sol–gel methods. Moreover, it is often used to synthesize nanoparticles of oxides [13–15]. This method has been applied to prepare zirconia based catalysts associated to ceria, zirconia and lanthanum

oxide respectively. The physico-chemical properties, redox properties and the surface acidity and basicity of the catalysts were characterized with regard to the effect of the compound added to zirconia.

## 2. Experimental procedure

### 2.1. Sample preparation

All the chemical reactants,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (Aldrich 98%),  $\text{TiCl}_4$  (Aldrich 99.9%),  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$  (Aldrich 99.9%),  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  (Prolabo 99.9%) and ammonium hydroxide ( $\text{NH}_4\text{OH}$ , Prolabo, Normapur, 28%) were reagent grade, and thus, used without further purification. To promote the germination stage, the solution containing the precursors was added dropwise to an ammonium hydroxide solution ( $\text{pH}=10$ ) under stirring. The pH of the solution was maintained at 10 using a second burette containing ammonium hydroxide. Then, the mixture was transferred to a stainless-steel autoclave equipped with a teflon liner and heated with two electrical resistances. The temperature and the pressure were controlled continuously with a thermocouple and a manometer, respectively. Thermal treatment was applied during 4 h at 220 °C and 25 bars under stirring. After several washes in distilled water in order to eliminate chloride ions, samples were dried in an oven at 120 °C and calcined at 500 °C in air for 10 h. The calcination temperature was chosen on the basis of thermogravimetric measurements.

### 2.2. Characterization methods

After the preparation, the fresh samples were calcined with the aim of removing the chloride ions, water from the bulk and any

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carbonaceous species present at the surface of the fresh catalysts. Thermogravimetry (TG–dTG, performed on a “Labsys-TG” instrument from Setaram) was used in order to determine the lowest temperature needed for calcination of fresh samples, at which no significant loss of mass occurred with further increase of temperature. The fresh samples (~50 mg) were heated from 30 to 900 °C with a heating rate of 5 °C min<sup>-1</sup> in a flow of air, which was chosen as a soft oxidizing agent for calcination.

The chemical composition of the catalysts was determined using inductively coupled plasma–optical emission spectroscopy (ICP–OES) with an ACTIVA spectrometer from Horiba Jobin Yvon after they were digested in a mixture of inorganic acids (sulfuric and nitric acids).

The surface areas, pore volumes and pore sizes were measured by low temperature nitrogen adsorption at 77 K on a Micromeritics ASAP 2020 apparatus after heat pretreatment under vacuum for 2 h at a temperature of 350 °C. The Brunauer–Emmet–Teller (BET) method was used to derive surface areas from the resulting isotherms.

XRD measurements were performed at room temperature using a Bruker (Siemens) D5005 powder diffractometer using Cu-K $\alpha$  radiation source (0.15,418 nm) to determine the crystalline phases present on the samples. Diffractograms were recorded from 5 to 70° in 0.02° steps with 1 s per step. The applied voltage and current were respectively 50 kV and 35 mA.

Transmission electron microscopy (TEM) experiments were performed in a JEOL JEM 2010 microscope operated at 200 kV. This microscope is equipped with LaB<sub>6</sub> thermoionic electron gun, an ultra high resolution (UHR) pole-piece and an energy dispersive X-ray (EDX) spectrometer (Pentafet Link-Isis from Oxford Instruments). The point resolution is 0.196 nm and the information limit is 0.140 nm. Prior to the observation, the samples were diluted in ethanol and ultrasound-dispersed; a drop of the solution was then deposited onto an electron microscopy Cu grid ( $\phi$ =3.05 mm, 300 mesh) coated with a holey-carbon film. The morphology of the samples was characterized by conventional TEM [16–18] whereas local structural information was obtained by high resolution TEM (HRTEM) [18–20]; finally, the global (with de-condensed probes) and local (with condensed 5–25 nm probes providing sufficient current to make EDX analysis within acceptable times) composition was determined by EDX [21–24].

Surface composition was determined by XPS experiments which were performed using a KRATOS Axis Ultra DLD spectrometer equipped with an hemispherical electron analyzer and a monochromatic Al X-ray source ( $K\alpha$ =1486.6 eV) powered at 150 W. The spot size aperture was 300 × 700  $\mu$ m. The base pressure in the analysis chamber was better than 5 × 10<sup>-8</sup> Pa. XPS spectra were measured at a pass energy of 20 eV and a charge neutralizer was used to control charge effects on powder samples. The peaks were referenced to the C–(C, H) components of the C 1s band at 284.6 eV. Shirley background subtraction and peak fitting to theoretical Gaussian–Lorentzian functions were performed using an XPS processing program (Vision 2.2.6 KRATOS).

Temperature programmed reductions (TPR) were performed using a TPD/R/O-1100 instrument (ThermoFisher) to determine the samples redox properties. Prior to the TPR run, the fresh sample was treated in a O<sub>2</sub>/He stream (0.998% flowing at 20 mL min<sup>-1</sup>); the temperature ramp was set at 10 °C min<sup>-1</sup> from 40 to 350 °C and maintained at the latter temperature for 60 min. Subsequently, samples were cooled down to 40 °C. The TPR measurements were carried out using H<sub>2</sub>/Ar (4.98%) as a reducing gas mixture, flowing at 20 mL min<sup>-1</sup>. The heating rate was 10 °C min<sup>-1</sup> from 40 to 1000 °C.

The acid–base properties were studied by adsorption microcalorimetry of NH<sub>3</sub> and SO<sub>2</sub>, respectively. Experiments were performed at 80 °C in a heat flow calorimeter (C80 from Setaram)

linked to a conventional volumetric apparatus equipped with a Barocel capacitance manometer for pressure measurements. The samples (about 100 mg) were pretreated in a quartz cell by heating overnight under vacuum at 350 °C and then evacuated at the same temperature for 1 h prior to the measurements. This temperature was reached using a heating rate of 1 °C min<sup>-1</sup>. The differential heats of adsorption were measured as a function of coverage by repeatedly sending small doses of respective gas on to the sample until an equilibrium pressure of around 67 Pa was reached. The sample was then outgassed for 30 min at the same temperature, and a second adsorption run was performed at 80 °C until an equilibrium pressure of about 27 Pa was attained. The difference between the amounts adsorbed in the first and second adsorptions at 27 Pa represents the irreversibly adsorbed amount ( $V_{\text{irr}}$ ) which provides an estimation of the number of strong acidic/basic sites.

FTIR spectra after pyridine adsorption were recorded at room temperature with a Bruker Vector 22 FTIR spectrophotometer (DTGS detector) operating in the 4000–400 cm<sup>-1</sup> range, with a resolution of 2 cm<sup>-1</sup> and 100 acquisition scans. In each pyridine adsorption FTIR measurement, the self-supporting wafer (about 50 mg, 18 mm diameter) was first activated in situ at 400 °C in oxygen flow for 14 h, then evacuated at the same temperature for 2 h and then exposed to pyridine (Air Liquide, 99.8%, vapor pressure 3.3 kPa) at room temperature for 5 min. The desorption was carried out by evacuation for 30 min each at room temperature, 100, 200 and 300 °C, respectively. The spectra were recorded at room temperature after adsorption and desorption at each temperature.

### 3. Results and discussion

Thermogravimetric analyses were carried out to provide information about any decomposition of the sample and also to help in determining the more accurate calcination temperature of the uncalcined samples. TG and dTG curves of the catalysts before calcination are shown in Fig. 1. All samples showed a first mass loss at 100 °C which can be attributed to the releasing of water molecules adsorbed on the catalysts. Between 100 and 500 °C, one large or two separate mass losses were observed for all samples. These mass losses correspond to desorption of physisorbed and, at for the contribution at higher temperature, chemisorbed hydroxyl groups. After 500 °C, no more weight losses were observed except for ZrO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub>. For this sample, a peak at 800 °C is observed and corresponds to a structural change of the solid at high temperature; as evidenced hereafter by XRD and HRTEM/EDX chlorine remains within the sample after calcination at 500 °C leading to the formation of an oxychloride that only decomposes at around 800 °C yielding a mass loss at this temperature (due to the elimination of chlorine). Despite this result, in order to compare our samples after calcination and since the catalysts will not be used at very high temperature, 500 °C was chosen as standard calcination temperature.

The values of the chemical analysis and the surface areas of catalysts are presented in Table 1 whereas chemical composition of the surface of catalyst (obtained by XPS) is given by Table 2. Chemical compositions are in agreement with the expected values at the exception of the ZrO<sub>2</sub>/TiO<sub>2</sub> mixture in which a deficit in titanium oxide is observed. This deficit is probably due to the difficulty to manipulate the titanium chloride precursor which is very hygroscopic and decomposes instantaneously in air. Table 2 indicates that all samples are contaminated on their surface by fluorine (between 1 and 2%). This contamination is most certainly due to the Teflon liner of the autoclave [25]. The binding energy of the F<sub>1s</sub> peak (684.4 eV) is rather representative of a metal fluoride

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