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Thermal analysis and temperature-programmed reduction studies of copper–zirconium and copper–zirconium–yttrium compounds

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Abstract

Differential thermal analysis evidenced that introduction of copper or yttrium into zirconia matrix delays its crystallization temperature. This result was connected to the stabilization of the zirconia tetragonal phase observed by X-ray diffraction. In addition, it was observed a decomposition delay of supported copper nitrate with yttrium content in a zirconia support. Temperature-programmed reduction revealed the existence of different copper species: isolated copper ions, copper clusters, small particles of copper oxide and bulk copper oxide. The reduction temperature of these species was strongly influenced by the preparation method of Cu–Zr systems and by the presence of yttrium in ZrO_2. But in all the samples, isolated copper ions and clusters were postulated to be reduced at the same temperature since these species have the same electron paramagnetic resonance parameters and then occupy the same sites. A correlation was done between the reducibility of these copper species and their activity in propene and toluene oxidation reactions. In the absence of yttrium, the best activity measured was correlated to an easier reduction but also to a higher quantity of isolated copper ions and clusters. Addition of yttrium to the support modified the copper interaction. At low copper/zirconium atomic ratio (0.01), the reduction temperature of small CuO particles increased with the yttrium content in the support. At high copper content ($Cu/Zr = 0.1$), the easier copper species reduction was obtained for Y_2O_3 content of 5 wt.%, the corresponding solid providing the best activity in the propene oxidation.

Keywords: DTA-TG; H_2-TPR; Copper–zirconium; Copper–zirconium–yttrium

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1. Introduction

The problem to diminish the amount of harmful industrial and automotive emissions (such as VOCs, diesel soot, NO_x, etc.) is one of the most actual problems. Different methods could be used for this aim. The catalytic oxidation was proposed because of the controlled selectivities that might be obtained, the low cost of the necessary materials and low energy consumption. The choice of oxide catalysts was claimed for catalytic oxidation, since a mechanism was proposed where the oxygen of the oxide is involved in the oxidation and is substituted by the oxygen of the phase gas [1–3]. Zirconium dioxide or zirconia (ZrO_2) is an interesting material used in oxidation catalysis. Lability and easiness to exchange oxygen atoms of the tetragonal or cubic ZrO_2 phase make them suitable for redox catalysis [4,5]. In our previous study [6], different samples zirconia modified by copper synthesized according to different preparation modes were characterized and tested in propene complete oxidation reaction. In another article from our group [7], different zirconia–yttria supports were characterized and tested towards propene and toluene deep oxidation reactions before and after copper impregnation. A difference in the catalytic behaviour was measured between these different studied samples. The present paper will focus on the thermal behaviour of these different samples under oxidizing and reducing atmosphere. Indeed the stability of the support zirconia and the interaction of the cop-

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per species with the support can be followed by differential thermal analysis (DTA) combined to a simultaneous thermogravimetric analysis (TG). Since the activity of oxide catalysts towards total oxidation reactions is mainly correlated to the reducibility of the active species [8–12], temperature-programmed reduction (TPR) of the copper samples has been investigated. Copper could be present in different forms on the support surface depending on the amount of deposited copper and on the support properties:

- isolated copper species Cu^{2+} with strong interaction with the support [5,11,13];
- Cu^{2+} clusters dispersed on the solid surface [11,13,14];
- highly dispersed CuO particles also designated by small particles of CuO [15];
- big aggregates of CuO also known as bulk CuO [5,13,15–18].

TPR allows a fine analysis of the different copper species present in the solids since, in this technique, each copper species has its own reduction peak. However, the interpretation of the TPR peaks is not always evident and the peaks assignments remain a subject of debate.

Therefore, the goal of the present work is to make clear DTA-TG and TPR results with the help of our previous studies [6,7]. The work will be divided into two parts: the first one will consist on the influence of the preparation mode of the copper–zirconium samples studied in the Ref. [6] and the second one will report the influence of the support type in the samples of copper supported zirconia–yttria studied in the Ref. [7]. In each part, two copper atomic ratios with Cu/Zr = 0.01 and 0.1 are investigated.

2. Experimental

2.1. Samples preparation

Copper–ZrO_2 samples were synthesized by three different methods: coprecipitation of copper and zirconium, impregnation of copper over zirconium oxyhydroxide and impregnation of copper over zirconium oxyhydroxide previously calcined at 600 °C (zirconium dioxide). For the coprecipitated samples, appropriate amounts of copper nitrate trihydrate $Cu(NO_3)_2 \cdot 3H_2O$ (PROLABO, purity ≥99.9%) and zirconium oxychloride octahydrate $ZrOCl_2 \cdot 8H_2O$ were dissolved in deionized water. This solution was added to an excess of ammonia solution $NH_3 \cdot H_2O$ 0.7 M. The resultant coprecipitate was filtered, washed, dried overnight at 100 °C and finally crushed. The impregnated samples were prepared by wet impregnation of appropriate amounts of copper nitrate trihydrate $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solution on $ZrO(OH)_2$ or ZrO_2 (previously calcined at 600 °C). Preparation details are described elsewhere [6].

All the samples were calcined at 600 °C (4 h) and designated by Cu_x–Zr600 for the coprecipitates (specific area of 80 and 40 $m^2\,g^{-1}$ for respectively $x = 0.01$ and $x = 0.1$), $Cu_x/ZrO(OH)_2600$ for the samples copper impregnated over zirconium oxyhydroxide (100 $m^2\,g^{-1}$) and by Cu_x/Zr600/600 for the samples copper impregnated over zirconium dioxide (70 $m^2\,g^{-1}$), where x = Cu/Zr designates the atomic ratio in the sample ($x = 0.01$ and 0.1).

Yttrium was introduced into zirconia matrix as a stabilizer of zirconia tetragonal phase, zirconia crystalline phase known to be catalytically active in oxidation reactions [4,19]. Tetragonal solid solutions of ZrO_2–Y_2O_3 calcined at 600 °C were impregnated by copper cations (using copper nitrate solution) with the subsequent drying at 100 °C (24 h) and calcination at 450 °C (4 h). Synthesis details are reported elsewhere [7]. The solids were denoted by Cu_x/Zr-aY600, where x represents the Cu/Zr atomic ratios of 0.01 and 0.1 and a the molar percentage of yttrium in the support (a = 1, 5 and 10).

2.2. Characterization methods

Differential thermal analysis and thermo-gravimetric analysis (DTA-TG) experiments of the samples before calcination were carried out in air (75 mL/min) at a heating rate of 5 °C/min till 700 °C with a Netzsch STA 409 C instrument equipped with a microbalance and a gas flow system. About 45 mg of sample were used for each analysis.

Temperature-programmed reduction (TPR) of the calcined solids was carried out in a conventional laboratory apparatus (Zeton Altamira AMI 200) consisting of a gas supply system with mass-flow controllers, a quartz U-reactor, a water vapour trap and a thermal conductivity detector (TCD). The sample bed temperature was monitored with a thermocouple protected by a quartz tube inserted in the centre of the sample bed with its tip located a few millimetres above the sample bed. In order to minimize the contribution of adsorbed species to the TPR profiles, prior to the TPR experiments all samples were pretreated in argon at 150 °C for 1 h. The samples were heated from ambient to 600 °C under H_2 (5 vol.% in argon) flow (30 mL/min) at a heating rate of 5 °C/min.

3. Results and discussion

3.1. Influence of the preparation mode

DTA experiments (Fig. 1) of the different copper–zirconium samples show the existence of one exothermic peak. This peak is not accompanied by any significant mass loss (TG curves not shown) and is attributed to the crystallization into the tetragonal phase of ZrO_2 containing copper. This crystallization phenomenon occurring at 420 °C for pure zirconium oxide [20] is delayed when copper was present in the solid.

For the same type of preparation, the crystallization delay is enhanced with increasing copper content. Furthermore, for the same copper content in different preparations, the crystallization is more delayed in the following order: