

Active and recyclable sulphated zirconia catalysts for the acylation of aromatic compounds

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Abstract

Mesoporous sulphated zirconia catalysts have been prepared by precipitation of $Zr(OH)_4$ at constant basic pH and tested for the acylation of anisole with benzoic anhydride. All samples have been characterized by N_2 physisorption, ion chromatography and thermal analysis coupled with MS analysis of evolved gases (EGA). The samples possessed high specific surface areas and mean pore size in the mesopore range. TG/DSC/EGA analysis allowed us to observe all phenomena related to the calcination process and to better understand the catalyst behavior. Observed phenomena are physisorbed water elimination, dehydroxylation, sulphating agent decomposition, phase transitions and sulphate species removal. Catalytic tests were carried out at different temperatures (30–50 °C) after a thermal treatment. The effects of the precipitation pH, calcination temperature and activation temperature on the catalytic performances were studied. Reuse of the catalyst was also appraised.

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1. Introduction

Liquid-phase reactions, such as Friedel–Crafts acylation [1], are important unit processes for the preparation of many industrially valuable chemicals. Traditionally, these reactions have been conducted using stoichiometric amount of liquid Brønsted acids (such as H_2SO_4) or Lewis acids (such as $AlCl_3$ or BF_3). Nowadays, the restrictions imposed by the waste minimization laws and economic considerations drive to the development of a new catalytic technology. Modern processes are, in fact, based on solid acids. In particular, sulphated zirconia (SZ) has been shown to be active for a number of reactions [2,3] including isomerization [4–7], cracking [8], alkylation [9–12] and also Friedel–Crafts acylation [13–23]. This work deals with the preparation of sulphated zirconia catalysts which are active and selective towards the acylation of aromatic compounds. Thermal techniques coupled with the analysis of the evolved gas (EGA) helped us to understand the phenomena which occurred

during the calcination process and to better explain the catalytic behavior of our samples.

2. Experimental

2.1. Catalysts synthesis

Catalysts were prepared via a conventional precipitation method [24–26]. $ZrOCl_2 \cdot 8H_2O$ (99%, FLUKA) was dissolved in distilled water and added with a peristaltic pump under vigorous stirring to an ammonia (30%, AnalaR) solution. During the entire course of the precipitation, the pH value was kept constant at 8.0 ± 0.1 or 10.0 ± 0.1 by the continuous addition of a 5N ammonia solution. In both cases, after the complete addition of the salt solution, the hydroxide suspension was aged for 20 h at room temperature. The aged hydroxides were filtered and washed with warm distilled water until they were free from chloride ions ($AgNO_3$ test).

The samples were dried at 110 °C and then impregnated with $(NH_4)_2SO_4$ by an incipient wetness method. The nominal sulphates loading was 8 wt% SO_4^{2-} by weight. The samples were then calcined at different temperatures (550, 600 or 650 °C) for 3 h in flowing air.

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The samples have been labeled as follows: SZ[pH]c[TTT], where [pH] stays for the precipitation pH and assumes the value of 8 or 10 and [TTT] is the calcination temperature. As an example, the sample prepared by hydroxide precipitation at pH 8 and calcined at 600 °C has been labeled SZ8c600.

2.2. Catalysts characterization

Surface areas and pore size distributions were obtained from N₂ adsorption/desorption isotherms at –196 °C (Micromeritics ASAP 2000 Analyser). Samples were pre-treated at 300 °C for 2 h under vacuum. Surface area was calculated from the N₂ adsorption isotherm by the BET equation, whereas the pore size distribution was determined by the BJH method also applied on the adsorption branch [27]. Total pore volume was taken at $p/p_0 = 0.99$.

Thermal analyses (TG/DSC) were performed on a NETZSCH STA 409C instrument in flowing air (40 ml/min) with temperature rate set at 10 °C/min in the 25–1000 °C temperature range.

Evolved Gas Analysis (EGA) [28] was performed to determine the substances released during the TG/DSC thermal treatment. About 100 mg of uncalcined samples were put in a U-shaped quartz reactor. A 10 °C/min temperature ramp was applied while 40 ml/min of air passed through the sample. The reactor outlet was connected to a Genesys 422 quadrupole mass analyzer (QMS) by a heated capillary. The signals for masses 15 (NH₃⁺), 18 (H₂O⁺), 30 (NO⁺), 44 (CO₂⁺), 46 (NO₂⁺), 48 (SO⁺), 64 (SO₂⁺) and 80 (SO₃⁺) were recorded.

Sulphate content was determined by a previously described ion chromatographic method [29].

In situ FTIR spectra were obtained on a BRUKER 113v spectrophotometer (2 cm⁻¹ resolution, MCT detector). Used SZ10c650 sample was inspected in the form of thin layer deposition (~10 mg cm⁻²) on Si wafers, starting from aqueous solutions. The sample was activated in controlled atmosphere either at 100, 250 and 400 °C in order to simulate the activation conditions. Quartz cells (equipped with KBr windows) connected to a gas vacuum line equipped with rotary and turbomolecular pumps (residual pressure $p < 10^{-5}$ Torr) were used.

2.3. Catalytic tests

The liquid-phase reaction (acylation of anisole with benzoic anhydride) was carried out in a thermostated batch reactor, using benzoic anhydride (1.3 mmol), anisole (10 ml) and *n*-tetradecane (employed as internal standard for GC). Before introducing into the reaction medium, the catalyst was activated at 450 °C, if not otherwise indicated, in flowing air for 90 min and kept dry.

Reactivity tests have been carried out at 40 °C for 3 h employing 250 mg of catalyst, if not otherwise indicated.

During the kinetic measurements, a small amount of the reaction medium was sampled at fixed time, filtered to remove the catalyst particles and analyzed on a HP-6890 gas chromatograph equipped with an HP-5 column and a FID detector.

After 3 h, the reaction mixture was quickly cooled down. The catalyst was separated, washed with anisole and kept for reusability tests.

Conversion and methoxybenzophenone yields (*para* + *ortho* isomers) were calculated with respect to benzoic anhydride (AN₀ – AN):

$$\text{conversion (\%)} = \frac{C_{AN_0} - C_{AN}}{C_{AN_0}} \times 100,$$

$$\text{yield (\%)} = \frac{C_{MBP}}{C_{AN_0}} \times 100.$$

3. Results and discussion

3.1. Surface features

Physisorption measurements results are summarized in Table 1. All isotherms relative to calcined samples belong to type IV IUPAC classification, with hysteresis loop of type H2–H3. As it is well known, the specific surface area decreased as the calcination temperature increased and the mean pore size followed the opposite trend. This is because of the crystallite growth and pore wall thickening, as reported by other authors [30,31]. It is instead interesting to notice that the total pore volume increased with the calcination temperature. This is an quite unusual behavior which is clearly shown in Fig. 1. The physisorption isotherm slope in the p/p_0 range 0.0–0.4 decreases as the calcination temperature increased and this means that the specific surface area decreases. However, the

Table 1
N₂ physisorption data for all calcined samples

Sample label	Surface area BET (m ² /g)	Pore volume (cm ³ /g)	Mean pore diameter (nm)
SZ8c550	122	0.086	3.7
SZ8c600	114	0.087	3.6
SZ8c650	94	0.094	4.2
SZ10c650	84	0.104	5.0

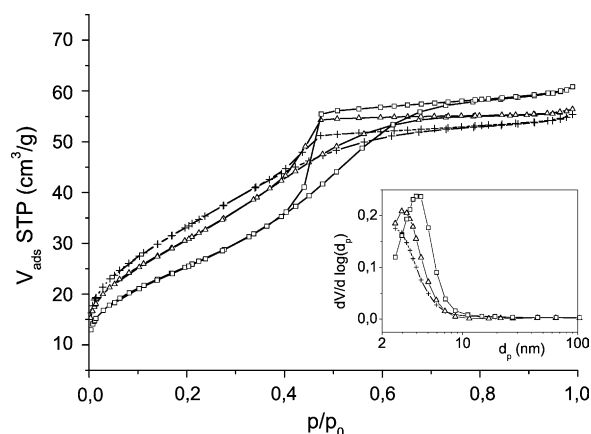


Fig. 1. N₂ physisorption isotherms and BJH pore size distributions for the SZ8 samples. (Cross signs) SZ8C550, (triangle) SZ8C600 and (square) SZ8C650.

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