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Microwave-assisted polyol synthesis of Pt/H-ZSM5 catalysts

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ABSTRACT

Three H-ZSM5 solids with Si/Al atomic ratios of 22, 71 and 96 were synthesized and characterized by X-ray diffraction (XRD), ICP-AES chemical analysis and nitrogen physisorption at $-196\,^{\circ}\mathrm{C}$. These were employed as supports in the synthesis of Pt/H-ZSM5 catalysts with platinum contents around 1 wt.%, by means of the microwave-assisted polyol method: platinum salt solutions in ethylene glycol were irradiated at powers of 184 and 461 W for time periods of 30 and 60 s in order to obtain Pt nanoparticles suspensions which were mixed with the supports and ultrasonically irradiated for 30 min to obtain the catalysts. This methodology allowed the synthesis of the catalysts efficiently and in relatively short times. Characterization of the catalysts by XRD showed that the ultrasonic irradiation did not affect the support structure. X-ray photoelectron spectroscopy revealed the presence of Pt(0) species on the solids surfaces. Temperature-programmed reduction studies suggested an effect of the time and power of microwave irradiation on the reducibility of the catalysts, *i.e.*, at the shorter times and lower irradiation powers, the reducibility of the platinum species decreases. Catalytic testing through the hydrogenation of toluene indicated that there is an effect of time and power of microwave irradiation on the initial hydrogenation activity of the Pt/H-ZSM5 catalysts. The catalyst prepared from suspensions irradiated at 461 W for 60 s showed the highest activity, which seems to be related to the lower particle size and better dispersion of Pt.

1. Introduction

Platinum-based catalysts supported in different types of solids have been extensively employed in a large variety of chemical reactions, such as hydrogenation [1,2], oxidation [3], hydrodeclorination [4], and hydrodesulfurization [5]. Different preparation methods for these kinds of solids have been proposed, including radiolytic synthesis [6], incipient impregnation [7], exchange-impregnation [8], sonochemical synthesis [9] and microemulsion synthesis [10], among others. Nevertheless, the microwave-assisted-polyol method is under development as an alternative route for preparing this type of catalysts [11,12], given that it is a soft chemical procedure, simple, energetically efficient, fast, and rendering uniform particle sizes.

Studies using the polyol method for the synthesis of transition metal-based catalysts have been reported by several workers. For example, Lu et al. [13] prepared transition metal catalysts using the polyol method, using conventional convective heating, and evaluated them in the volatile organic compounds (VOCs) catalytic combustion. Activated carbon (AC) was selected as support to deposit well-dispersed active phases such as copper, nickel, iron and cobalt. The activity order respect to the metal was: Cu > Co > Fe > Ni, while the order respect to the aromatic feed molecules for Cu/AC was: xilenes > toluene > benzene. The obtained results suggest that the polyol process can be effectively employed in the preparation of nanocatalysts to be employed in VOCs elimination. Zhao et al. [14] reported the one-pot synthesis of Pt–CeO_2/C employing the microwave-assisted polyol process, and compared these catalysts with solids prepared by a two-step route: conventional impregnation of Ce precursor on Pt/C catalyst, so called Pt/C (E-TEK). Electrochemical activity in methanol oxidation using cyclic voltammetry and chronoamperometry was measured. Cerium addition was found to inhibit CO poisoning of Pt, due to its ability to switch between Ce^{4+} and Ce^{3+} oxidation states, thus promoting CO oxidation to CO_2. The results showed that Pt-Ce/C exhibited better electrocatalytic activity and stability than Pt/C (E-TEK).

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In the present work it is reported the preparation of Pt/H-ZSM5 catalysts using the microwave-assisted polyol process. The synthesized solids were tested in the toluene hydrogenation model reaction under standard conditions [15]. To our best knowledge, this is the first publication reporting studies related to the preparation of Pt/H-ZSM5 catalysts by the proposed methodology.

2. Experimental

2.1. Preparation of suspensions of platinum particles

Suspensions with platinum contents around 17 mg, were prepared by mixing the appropriate amount of $Pt(NH_3)_4Cl_2$, employed as precursor salt, with 15 mL of ethylene glycol (EG) and regulating the pH by dropwise addition of 0.5 mL of a 1 M NaOH aqueous solution. This mixture was irradiated in a Samsung MW1050 microwave oven with powers of 184 and 461 W for periods of time of 30 and 60 s. The power output of the oven was calibrated as described elsewhere [16].

2.2. Synthesis and characterization of H-ZSM5 zeolites

The methodology proposed by Guth and Caullet [17] was employed to synthesize three H-ZSM5 zeolites of nominal Si/Al atomic ratios of 20, 70, and 100. The crystalline structure of the solids was verified by X-ray diffraction (XRD) using a Siemens D-5005 instrument and Cu Kα source. Specific surface area (SSA) of the samples was measured by nitrogen physisorption at −196 °C employing the BET method, by means of a Micromeritics ASAP 2010 equipment. Chemical analysis (ICP-AES) was carried out with a Jobin Yvon JY-24 spectrometer, to measure the Si/Al ratios of the solids. Synthesized support samples will be labelled as "H-ZSM5 (B)", where B is the experimentally determined Si/Al atomic ratio.

2.3. Synthesis and characterization of supported Pt/H-ZSM5 catalysts

The synthesized solids were employed as supports in the preparation of Pt/H-ZSM5 catalysts with Pt contents of approximately 1 wt.%. After microwave treatment of the metal suspension (containing ~17 mg of platinum), it was mixed with 1 g of the selected support and submitted to ultrasound irradiation for 30 min. Afterwards, the solvent was evaporated by heating to 90 °C under stirring. The resulting solid was dried and reduced under H_2 current at 500 °C for 6 h. The obtained catalysts were characterized by XRD to verify the effects (if any) of the incorporation of metal on the crystalline structure of the supports. The SSA of the solids was measured as described above. Chemical analysis of Pt content and Si/Al ratios was done by ICP-AES. The oxidation state of the species present at the surfaces of the samples was determined, as reported previously [18], by X-ray photoelectron spectroscopy (XPS) with a VG Scientific ESCALAB 220i-XL spectrometer. Peak position was referenced to the C 1s signal at a B.E. of 284.6 eV. Temperature-programmed reduction (TPR) measurements were carried out with a home made apparatus, consisting of continuos-flow gas lines attached to a thermal conductivity detector (TCD) with signal output to a digital register; a fixed-bed quartz reactor followed by a cold trap for condensing reduction products (mostly water) before measurement of the TCD signal; and mass-flow controllers for regulating the gas flows. Measurements were carried out on 100 mg samples pre-dried for 1 h at 150 °C under N_2 flow of 30 mL/min. After cooling to room temperature, a 10 °C/min heating program up to 600 °C was applied while measuring the H_2 consumption from a 5% H_2/Ar current, flowing at 30 mL/min. Transmission electron microscopy (TEM) of the catalysts and of solids obtained from the metal suspensions was performed with a Philips CM-10 electron microscope operated at 120 kV. After microwave and ultrasonic irradiation, a drop of the metal suspensions in EG was deposited on appropriate support grids. For the case of the supported catalysts, aqueous suspensions were previously sonicated; a drop was deposited and allowed to dry. Catalyst samples will be labelled as: "A%Pt/H-ZSM5 (B)", where *A* is the measured concentration (wt.%) of Pt and B is the Si/Al atomic ratio.

2.4. Catalytic evaluation

Toluene hydrogenation was carried out in a fixed-bed, continuous-flow reactor at 110 °C, under 1 atm pressure, molar ratio H_2/toluene of 4, and space velocity (WHSV) of 21.5 h^{-1}. The only observed product was methylcyclohexane. The analysis of the reaction effluent was performed with a HP 6890 gas chromatograph with flame-ionization detector and a 5% phenylmethylsiloxane column.

3. Results and discussion

3.1. Physicochemical characterization of the supports

X-ray diffraction patterns of the H-ZSM5 solids with various Si/Al atomic ratios are shown in Fig. 1 It can be seen that the three solids show intense and sharp lines for 2θ values between 7–10 and 22–25. These signals are characteristic of ZSM5-type zeolites [19]. It can also be appreciated that signals within the first region increase their intensity with an increment in the Si/Al ratio. This phenomenon is in line with a higher structural order due to the increasing number of equal Si–O–Si linkages in tetrahedral positions, thus decreasing the average T–O–T bond length [20].

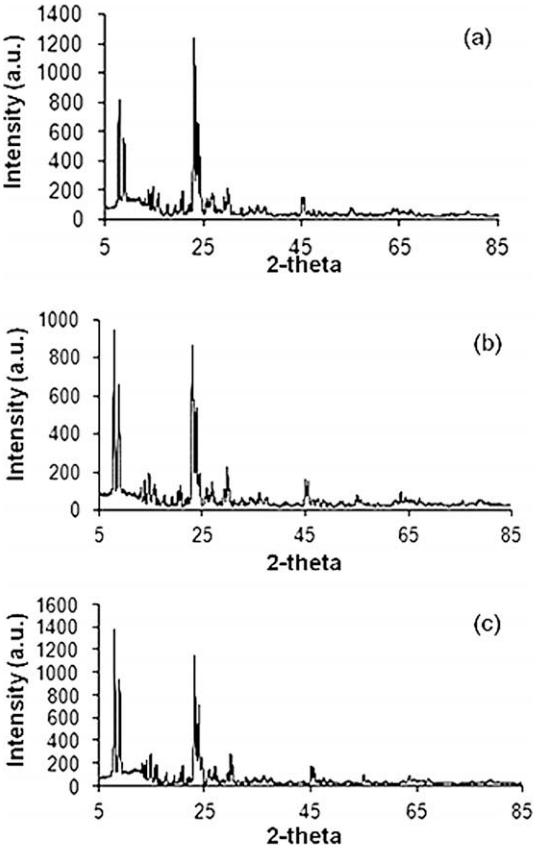

Fig. 1. X-ray diffractograms of: (a) H-ZSM5(22); (b) H-ZSM5(71); (c) H-ZSM5(96).