Zeolitized-pumice as a new support for hydrogenation catalysts

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ARTICLE INFO

ABSTRACT

A zeolitized-pumice (Z-PM), obtained from a pumice mine waste by extraction of most of the silica contained, has been proposed as a new catalyst support. The as prepared Z-PM material was characterized by surface area and porosity measurements, XRD, SEM and TEM-EDX, showing a high content of crystalline zeolite Pc (about 60%) and a higher (33 m^2/g) surface area compared to starting pumice.

Pt and Pt–Sn supported on Z-PM were prepared by impregnation and their catalytic properties in the selective hydrogenation of campholenic aldehyde to naturanol investigated in detail. Results highlighted the better performance of Pt and Pt–Sn/Z-PM catalysts in the selective reduction of –C=O group in comparison to corresponding silica-supported catalysts.

1. Introduction

Pumice is a porous, natural glass formed from volcanic activity. It is largely used in place of sand in light concrete, as a filtering agent for water clarifying, as a softly abrasive material in the textile industry (jeans stone-washing) and in a number of other industrial applications [1,2]. Pumice has also been used as a support for metal catalysts [3–9]. Among various reactions, the hydrogenation of the unsaturated carbon-carbon bonds was the most investigated on pumice supported catalysts. Deganello and coworkers investigated in details the preparation, characterization and behaviour of these catalysts. They exhibited good activity and selectivity in the liquid phase hydrogenation of 1,3-cyclooctadiene [5,6] and phenylacetylene [7,8] and in the gas phase hydrogenation of acetylene in ethylene rich feedstocks [9].

At our knowledge, no pumice supported catalysts were investigated in the selective hydrogenation of unsaturated aldehydes, despite of the significant attention received by the synthesis of unsaturated alcohols from these substrates in the last years, owing to the importance of these compounds in the cosmetic, food and flavors industry [10–13].

The untreated pumice materials so far used as catalyst support have the disadvantage of a low surface area [3–9]. It is well known that a wide surface area is an important requisite for this application. Therefore, we are here proposing as catalyst support in place

of untreated pumice a new pumice material (Z-PM) where a suitable treatment caused a plentiful crystallization to zeolite Pc and an increase of an order of magnitude of the surface area. The synthesis of Z-PM starting from pumice mine waste as raw material was described in a recent patent [14]. The resulting material has a surface area of about 30–40 m^2/g and a high content (around 60%) of crystalline zeolite Pc which led to the development of some applications typical of zeolites [15–16].

In this paper, the use in catalysis – that is a further application field typical of zeolite [17] – is proposed. Zeolite catalysts have found extensive use in the petrochemical industry and show potential applications in fine chemical synthesis [18]. Nevertheless, the catalytic hydrogenation of unsaturated aldehydes was less investigated with zeolite materials and consequently the role of these supports in the promotion mechanism is still obscure. Blackmond et al. [19] reported the hydrogenation of 3-methyl crotonaldehyde over Pt, Rh or Ru metals supported on NaY and KY zeolites. They found that the selectivity to the unsaturated alcohol increased when support was less acidic due to a greater electron density on the metal particles. Other authors pointed out instead the benefit of geometrical effects of zeolite pores [20] or the peculiar catalytic properties of the smaller metallic particles located inside the zeolite cavities [21].

In this study, we report results obtained in the selective hydrogenation of campholenic aldehyde (CPA) to naturanol (NAT), a valuable fine chemical largely used in food and perfumery industry due to its particularly well defined sweet, natural and specific berry-like notes [22]. The reaction was carried out on either Pt or bimetallic Pt–Sn catalysts, both supported on Z-PM. A comparison with the corresponding Pt and Pt–Sn catalysts supported on silica is also reported.

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2. Experimental

2.1. Z-PM preparation and characterization

The synthesis of Z-PM was carried out by extracting from pumice mine waste as much silica as possible by a sodium alkali aqueous solution in hydrothermal conditions and by rinsing the unextracted residue with water up to neutral pH, according to a previous report [14].

BET surface area and porosity data were determined by adsorption–desorption of dinitrogen at 77 K using a Micromeritics ASAP 2010 instrument.

The chemical composition was determined by an energy dispersive spectroscopy (EDS) microprobe (Oxford INCA ENERGY-400 with PENTAFET Si(Li) detector).

X-ray diffraction (XRD) spectra were recorded on an Ital Structure mod. APD 2000 X-ray diffractometer using the Cu Kα radiation and mounting powder samples on a Plexiglass holder.

Scanning electron microscopy (SEM) analyses were carried out with a JEOL 5600LV electron microscope. The samples were coated with a thin layer of gold to prevent charging of the samples. Micrographs of the samples were recorded in the 10–20 kV accelerating voltage.

Transmission electron microscopy (TEM) studies of the catalysts were performed on a JEOL 2010 EX instrument operating at 200 kV and equipped with an EDX analyzer (Oxford). The specimens for electron microscopy were prepared by grinding the powder samples in an agate mortar, suspending and sonicating them in isopropanol, and placing a drop of the suspension on a holey coated carbon copper grid. After evaporation of the solvent, the specimens were introduced into the microscope column.

2.2. Catalysts preparation

Pt and Pt–Sn/Z-PM catalysts were prepared by (co)impregnation by using the incipient wetness technique of the Z-PM support with H_2PtCl_6 (hydrogen hexachloroplatinate(IV) hydrate 99.9%, Fluka) and $SnCl_2$ (Tin (II) chloride 99.99%, Aldrich) aqueous solutions having the appropriate metal concentration.

Pt and Pt–Sn/SiO_2 were also prepared in the same way, by using a commercial Silica support (SiO_2 Grace, BET surface area 276 m^2/g).

After impregnation, the catalysts were dried at 393 K in air for 1 h followed by reduction under flowing H_2 at 623 K for 2 h. On all catalysts Pt loading was 2 wt% and on bimetallic samples Sn was 0.48 wt%, corresponding to a Sn/Pt atomic ratio equal to 0.39.

2.3. Kinetic tests

Catalytic activity tests were carried out in a 100 ml five-necked flask, equipped with a reflux condenser. Constant temperature (343 ± 0.5 K) was maintained by circulation of silicone oil in an external jacket connected with a thermostat. The reactions were carried out as follows. The catalyst (250 mg) was added to 50 ml of cyclohexane through one arm of the flask. Before introduction of the substrate (CPA), the catalyst was reduced "in situ" by a H_2 flow (50 ml/min) for 30 min. at 343 K. Then 0.1 ml of the substrate and 0.1 ml of tetradecane were introduced (the latter was used as an internal standard for gas chromatographic analysis) in the reactor. The reaction mixture was stirred with a stirrer head at 600 rpm with permanent magnetic coupling which ensure a very efficient stirring under H_2 at atmospheric pressure. The progress of the reactions was followed analyzing by GC samples withdrawn from the reaction mixture at different times. Details are reported in a previous work [23].

In order to check the absence of diffusional limitations, preliminary runs have been carried out at different stirring conditions, loading and catalyst grain size. The dependence of hydrogenation rate upon the stirring speed, revealed that above 400 rpm the rate is independent on the stirring speed. The trend of CPA conversion at different amounts of catalyst was linear, confirming the absence of external mass transfer limitations. Experimental results have shown that the activity remained nearly constant when the grain size of the support was changed, indicating that the inner diffusion limitation was negligible.

3. Results and discussion

3.1. Z-PM preparation and characterization

Several previous studies report pumice powder as a silica source in the synthesis of zeolites by hydrothermal treatment in concentrated sodium hydroxide [24–26]. The aluminosilicate phase produced is dependent on the synthesis conditions, in particular temperature, NaOH concentration and Si/Al ratio [24,25,27].

The synthesis of Z-PM was carried out as reported above and described in detail in a recent patent [14]. The composition of pumice mine waste we used as starting material is shown in Table 1. Its Si/Al atomic ratio was 5.6–5.7. Chemical analysis of the product obtained after the silica extraction process is also reported in Table 1. Compared to pumice mine waste the resulting material contains much less silica, consequently the Si/Al atomic ratio is strongly reduced (about 2.2). On the other hand, Al_2O_3 and Na_2O were significantly found in higher concentration in the lightened residue and both involved in the formation of zeolite.

Accordingly to data reported in Table 1, the material obtained has a surface area of about 34 m^2/g, much higher with respect to the raw material (1 m^2/g). A certain degree of microporosity (micropore area 3.6 m^2/g), absent in the starting material, was also developed in connection with zeolite formation. Morphological and microstructural modifications of the raw material after the silica extraction process are reported in Figs. 1–3. The starting pumice mine waste material is essentially amorphous as confirmed by its diffraction pattern reported in Fig. 1. The product obtained is instead highly crystalline, an approximate quantification of which gives a value around 60%. A comparison of the diffraction peaks with reference compounds indicates that reflections observed are related to the presence of zeolite Pc. Zeolite P indicates a series of synthetic zeolite phases, of which the more common are the cubic, Pc, and the tetragonal zeolite, Pt [28], having a Si:Al ratio from 1.0 to 2.5 [29].

The morphology of the raw material and product obtained was examined by scanning electron microscopy. SEM analysis of pumice mine waste (Fig. 2a) shows irregular particles in a wide range of size. After processing, the material was deeply re-structured and a remarkable morphology change and reduction of the particle size was observed (Fig. 2b). TEM micrographs of the Z-PM material taken at different magnification are also shown in Fig. 3a–b. The aggregates observed at any magnification level are constituted by particles mainly homogeneous regarding both the size and, as evinced by EDX analysis, spatial distribution of the main components and impurities.

Pt and Pt–Sn catalysts supported on Z-PM have been then prepared by the impregnation technique as reported in the experimental section. A detailed characterization of these catalysts will be reported in a forthcoming paper.

3.2. Catalytic activity

The behaviour of Pt-based catalysts supported on Z-PM was investigated in the selective hydrogenation of CPA. This substrate