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Activation of natural mordenite by various acids: Characterization and evaluation in the transformation of limonene into p-cymene

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ABSTRACT

Natural mordenite originated from volcanic soils in Greek islands was treated with aqueous solutions of various acids (CH_3COOH, H_2SO_4, HCl, HNO_3). The samples were characterized by the joint use of N_2-physisorption, X-ray Diffraction, Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy, Transmission Electron Microscopy, ζ-Potential, and Equilibrium pH and evaluated for the transformation of limonene into p-cymene under air and N_2 atmosphere. The influence of reaction temperature and time on catalytic performance of the most promising sample (activated by HCl) was also examined.

The acid treatment brings about the removal of cations (mainly sodium cations) located inside the framework channels and in the inter-fiber mesopores without disturbing mordenite framework. The emptying of micropores and mesopores increases drastically the BET specific surface area which is mainly due to micropores. The samples studied exhibit fibrous morphology with fibers (10–100 nm) separated by slit-like mesopores. The emptying of micropores and mesopores unmasks negatively charged surface sites. These are transformed into surface acidic sites by adsorbing H^+/H_3O^+ ions.

The changes in the texture and acidity are converting the catalytically inactive natural mordenite into very active catalysts for the transformation of limonene into p-cymene. The increase in the conversion of limonene and the yield of p-cymene over the activated samples are following trends similar to that followed by the BET specific surface area. The catalytic performance is maximized over the sample resulted by the treatment of the original mordenite with hydrogen chloride solution. A quite high yield of p-cymene (65%) is obtained over this sample at 140 °C, limonene to catalyst ratio equal to 15 and reaction time equal to 7 h. A two-step mechanism established previously over sulfuric acid activated natural mordenite catalysts for transformation of limonene to p-cymene is followed regardless of the kind of acid used for activation of this clay.

1. Introduction

The utilization of renewable raw materials for producing useful molecules through green processes is a good prospect in the context of sustainable development. p- Cymene is an important molecule. It is used as the starting material for the synthesis of p-cresol [1] and as intermediate in the synthesis of fine chemicals for perfumes, fungicides and pesticides [2–4] as well as for improving the odor of industrial products and as a solvent of dyes and varnishes [5]. The conversion of limonene into p-cymene is a promising green route [6–10] because limonene is a cheap by-product of citrus industry. This conversion requires solid catalysts with dual functionality, namely acid sites for isomerization-disproportionation and metallic sites for the subsequent dehydrogenation step involved in the whole process. Thus, it is frequently attempted over metallic catalysts dispersed on high surface area supports, principally with moderate acidity [6–11]. The reaction network involves several pathways. The participation of each of them to the whole mechanism depends on the reaction temperature, the catalyst

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acidity and the reaction atmosphere (hydrogen, nitrogen, helium, argon, air).

For years the well accepted mechanism of the reaction under inert atmosphere or atmospheric oxygen [12–14] over metallic catalysts supported on acidic supports and non-metallic acidic catalysts includes: (i) the isomerization of limonene to other terpenes (α-terpinene, γ-terpinene, terpinolene, iso-terpinolene) through migration of the exocyclic double bond into the ring (Fig. S1) and (ii) the disproportionation of limonene and the aforementioned intermediate terpenes to 3-menthene, p-menth-1-ene, p-menthane and p-cymene (Fig. S1). In parallel, high-molecular weight compounds, "polymers", are produced by polymerization (Fig. S1). Isomerization, disproportionation and polymerization are catalyzed by the acid sites through carbenium ion mechanisms. The aforementioned small intermediate molecules are then dehydrogenated on metallic sites. As the dehydrogenation step is endothermic, relatively high temperatures are required for obtaining acceptable yields in p-cymene. In the particular case of hydrogen atmosphere a simpler route (formation of p-menthane by limonene hydrogenation followed by dehydrogenation to p-cymene) becomes important over metallic catalysts supported on low acidity supports [6].

The aforementioned general mechanism was recently questioned by us for the case where the reaction is taking place in contact to the atmospheric oxygen [15]. The questioning was motivated by earlier observations. In fact, it has been reported that air exposed limonene is auto oxidized slowly resulting to various organic products and hydrogen peroxide [16] whereas α-terpinene is auto oxidized faster resulting to allylic epoxides, p-cymene and hydrogen peroxide [17]. Moreover, γ-terpinene can be effectively transformed into p-cymene in oxygen atmosphere [18]. In all cases the aforementioned transformations are taking place without catalysts. We have recently demonstrated that the transformation of limonene into p-cymene over an acidic non-metallic catalyst, under air atmosphere and relatively low temperatures is following a mechanism involving a catalytic step followed by a non catalytic one [15]. The first step, involving isomerization of limonene to other terpenes and "polymerization", was described before. Catalyst-free dehydrogenation (aromatization) and "polymerization" of terpinolenes and terpinenes is following through free radical pathways [15].

The utilization of "physical catalysts", like minerals, instead of synthetic ones is a welcome possibility for decreasing the cost of the chemical processes. This is the reason for which natural mordenite originated from volcanic soils in Greece was activated by treatment with sulfuric acid solutions in order to improve its catalytic performance in the transformation of limonene into p-cymene using atmospheric oxygen as green oxidant [15]. The acid treatment caused the removal of sodium oxide located inside the framework micropores and the small inter-fiber mesopores of natural mordenite increasing dramatically the BET specific surface area and developing acid sites on its surface. Thus, the catalytically inactive natural mordenite transformed into very active catalysts [15].

In the present work we are attempting to improve further the physicochemical and catalytic properties of the natural mordenite via activation with solutions of various acids. An additional reason of testing acidic solutions of various acids, besides sulfuric acid, is to attempt minimizing the environmental burden due to the acidic treatment. Thus, sodium chloride will be the main "waste" of the acidic treatment with aqueous solution of hydrochloric acid whereas the pH of the releasing aqueous solutions will be not very low using acetic acid solutions. Moreover, we are further investigating the aforementioned mechanism, developed by us recently, concerning the transformation of limonene into p-cymene which is occurred in contact to the atmospheric oxygen.

2. Experimental

2.1. Catalysts preparation

Natural mordenite provided from the Greek company TECHNOTOPIA Ltd and originated from volcanic soils of Greek islands in the Aegean Sea. The extraction of the mineral was performed by the Greek company Bentomine Kimolian Enterprizes S.A. The material was cleaned with water and then treated with 2 M acidic solutions of HCl, H_2SO_4, HNO_3 and CH_3COOH (all purchased by Fisher scientific) at 70 °C for 4 h and mass solid to solution volume 1 g/20 mL. Full details have been reported previously [15]. The symbols TECHNOSA, TECHNOSA-H2, TECHNOSA-S2, TECHNOSA-N2 and TECHNOSA-A2 stand, respectively, for the non-activated mordenite and the catalysts resulted by activation of natural mordenite with 2 M hydrochloric, sulfuric, nitric and acetic acid aqueous solutions.

2.2. Catalysts characterization

Nitrogen adsoption–desorption isotherms recorded using a Micromeritics apparatus (Tristar 3000 porosimeter) and the corresponding soft-ware were elaborated for determining the BET and BJH specific surface areas, pore volume and pore size distribution. X-ray diffraction (XRD) patterns were recorded in a Brucker D8 Advance diffractometer equipped with nickel-filtered CuKα (1.5418 Å) radiation source. Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra were recorded on a FTIR spectrophotometer (Perkin-Elmer, Spectrum 100), using a multi-reflection horizontal ZnSe ATR accessory (Specac's Gateway ATR Accessory Kit). Scanning electron microscopy (SEM) measurements were performed using a Scanning Electron Microscope (SEMJEOLJSM6300) equipped with an Energy Dispersive Spectrometer (EDS). A JEOL JEM-2100 system, operated at 200 kV (resolution: point 0.23 nm, lattice 0.14 nm) was used for conducting transmission electron microscopy (TEM) and high resolution TEM (HRTEM) measurements. The "equilibrium pH" was determined for dense sample/water suspensions (0.5 g of the solid sample dispersed in 6.5 mL of distilled water) using a pH-meter (Radiometer Copenhagen ABU901 Autoburet) equipped with a combination pH electrode. Microelectrophoretic mobility measurements were performed for determination of ζ-potential of the samples in very dilute sample/electrolyte suspensions (10 mg/100 mL) with ionic strength 0.01 M $NaNO_3$ at 25 °C using a Zetasizer 5000 (Malvern Instruments Ltd). More details concerning the samples characterization have been reported elsewhere [15].

2.3. Catalysts evaluation

The catalytic tests concerning the conversion of limonene (Liquid limonene, purity 95%, extracted from natural orange oil, purified by distillation and supplied by VIORYL S.A.) into p-cymene were performed in the presence of atmospheric oxygen and under inert atmosphere (nitrogen). The experiments were performed in a three-necked round-bottom reaction flask at different time periods and temperatures and limonene/catalyst mass ratio equal to 15. Tetraethylene glycol dimethyl ether (Peroxide value < 1) was used as solvent. The reaction mixture was analyzed by gas chromatography and gas chromatography-mass spectrometry. More details have been reported in Ref. [15].

3. Results and discussion

3.1. Morphology and chemical composition investigated by SEM-EDS and TEM-HRTEM

The SEM images of the studied samples (Fig. S2) revealed that they have a fibrous morphology. This morphology is more clearly observed in the TEM images taken at much more higher magnifications (Fig. 1).