FRIEDEL-CRAFTS ALKYLATION OF *p*-XYLENE ON Zr-SBA-15 MATERIAL S:CONVENTIONAL HEATING VERSUS MICROWAVE IRRADIATION

M. D. Gracia, E. Losada, J. M. Campelo, D. Luna, R. Luque, J. M. Marinas, A. A. Romero

Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV, Km 396, E-14014 Córdoba, Spain. Email- q82grsem@uco.es

Introduction

Friedel–Crafts alkylations comprise a very important type of processes of common use in organic chemistry. The substitution of homogeneous mineral acids as catalysts in these reactions for more environmentally friendly solid acid catalysts including acidic microporous (zeolites) and mesoporous (M41S, SBA) is currently an important challenge in our aim to switch to more sustainable and minimum waste processes.

Friedel-Crafts reactions have been reported to be catalysed by metal-incorporated nanoporous materials (e.g. Al, Ga) as a consequence of the highly active acid sites generated after silicon substitution within the porous frameworks. The isomorphous substitution of Si for Zr in SBA type materials has been reported to generate Lewis acid sites[1]. Herein, we report the direct preparation of Zr-SBA-15 materials via sol-gel hydrothermal synthesis. The activity of the materials was subsequently investigated in the alkylation of *p*-xylene with benzyl alcohol.

Experimental

Materials were synthesized following a previously reported protocol by our group[2] using $ZrONO_3$ .x H_2O as Zr precursor. Samples were denoted as Zr-X where X stands for the Si/Zr ratio in the synthesis gel (e.g. Si/Zr 40, 20, 10 and 5). Well structured Zr-SBA-15 materials with high surface areas and narrow pore size distributions were obtained. Materials were characterized by adsorption of pyridine (PY) and 2,6-dimethyl pyridine (DMPY), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Thermal Analysis (TG/DTA), Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), and N_2 adsorption.

The solid acids were also tested for activity in the Friedel-Crafts alkylation of *p*-xylene with benzyl alcohol. Reactions were carried out under conventional heating and microwave irradiation.

Conclusions

Zr-SBA-15 materials were found to be highly active, selective and reusable in the Friedel-Crafts alkylation of *p*-xylene with benzyl alcohol under both conventional heating and microwave irradiation. Reaction rates were considerably increased under microwaves compared to conventionally heated reactions, reducing times of reaction from 24h to a few minutes. Zr-10 was the optimum catalyst for the alkylation reaction, providing quantitative conversion of starting material after 5 minutes of microwave irradiation. This novel methodology may pave the way to the utilisation of solid acids both to improve the green credentials of chemical products using low impact technologies (e.g. microwaves) and the utilisation of benign and reusable catalysts in chemical processes.

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