Applied Catalysis A: General 433–434 (2012) 179–187

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Zirconium doped mesoporous silica catalysts for dehydration of glycerol to high added-value products

C. García-Sancho, R. Moreno-Tost*, J. Mérida-Robles, J. Santamaría-González, A. Jiménez-López, P. Maireles-Torres

Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n., 29071 Málaga, Spain

ARTICLE INFO

Article history:
Received 28 March 2012
Received in revised form 7 May 2012
Accepted 13 May 2012
Available online 22 May 2012

Keywords:
Mesoporous silica
Glycerol
Zirconium oxide
Acid catalysis
Acrolein

ABSTRACT

A series of zirconium doped mesoporous silica, with different Si/Zr molar ratios, has been synthesized and tested in the gas-phase dehydration of glycerol. The surface characterization of these solids by using NH_3-TPD and pyridine adsorption coupled to FTIR spectroscopy has revealed the existence of well dispersed acid sites, mainly of Lewis type, associated to Zr(IV) species deficiently coordinated located on the pore walls of the siliceous framework. These acid catalysts are active in the glycerol dehydration, increasing the conversion with the zirconium content until values higher than 90 mol% for a Si/Zr molar ratio of 4, at 325 °C after 5 h of reaction. However, the catalysts suffer deactivation, which is more important when zirconium oxide is incorporated by impregnation of mesoporous MCM-41 silica. The main reaction products were acrolein, acetaldehyde and acetol. Moreover, the catalysts with a SiZr molar ratio higher than 5 are more selective to acetaldehyde. The acrolein yield was, in all cases, lower than 15 mol% after 24 h of TOS, but a pretreatment under a helium flow saturated with water vapour allows reaching an acrolein yield of 28 mol% and ameliorates the stability of catalysts. The selectivity towards acrolein and hydroxyacetone can be explained by considering the influence of the nature of active sites.

1. Introduction

Acrolein (2-propenal) is the simplest unsaturated aldehyde, with a high synthetic and technical potential due to the conjugation of the carbonyl group with a vinyl group. Acrolein is widely used as intermediate in the production of building materials, herbicides and algaecides, water treatment chemicals, and essential amino acids like methionine used as supplementary in fodder, especially for poultry. At low concentrations, it finds also application for protecting liquid fuels against microorganisms, H_2S scavenger and anti-algae agent.

The current industrial process for acrolein production is by partial catalytic oxidation of propylene. A variety of different catalysts are available for this reaction, the most efficient catalysts are complex mixed-metal oxides that consist largely of Bi, Mo, Fe, Ni, Co, and/or K and either P, B, W, or Sb [1]. The principal side reactions produce acrylic acid, acetaldehyde, acetic acid, carbon monoxide, and carbon dioxide [2,3]. Since propylene is obtained from crude-oil resources, it is desired to utilize a lower cost and renewable raw material for acrolein production, being glycerol a potential candidate. Glycerol is a natural by-product of the manufacture of soap from the hydrolysis of animal fats and vegetable oils. Due to the incessant increment of the worldwide production of biodiesel, the production of glycerol, a by-product of the biodiesel industry, has notably increased causing a drop in its price. In this way, glycerol has been turned into an interesting starting raw material for others chemical products, where the double dehydration of glycerol to acrolein is one of the proposed routes for glycerol valorization. This field of studying has attracted the attention of numerous research groups and in fact, recently, a critical review of acrolein production from glycerol has been released [4].

The dehydration reaction of glycerol yielding acrolein is known since the nineteenth century. Already in 1918, Sabatier et al. reported the decomposition of glycerol to different products, including acrolein, in the presence of alumina catalysts [5]. Because of crude glycerine is found diluted in water, the catalysts must be active and resistant to the presence of water avoiding a separation step of the glycerol from the water and therefore reducing the price of production of acrolein. Various solid acid catalysts have been tested in the dehydration of glycerol, including zeolites [6–10], supported heteropolyacids [11–14] and phosphoric acid impregnated activated carbon [15] or Al_2O_3 and TiO_2 [16], niobium oxide [17,18] and WO_3/ZrO_2 catalysts [19,20] in a gas phase reaction. Several studies have demonstrated that the catalytic activity depends on the textural, mainly the pore size, and acid properties of the solid catalysts, as recently reviewed by Pathak et al. [21]. Thus,

* Corresponding author. Tel.: +34 952132021; fax: +34 952131870.
E-mail address: rmtost@uma.es (R. Moreno-Tost).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.05.015