Catalysis Today 250 (2015) 226–238

Contents lists available at ScienceDirect

Catalysis Today

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

Vapor-phase hydrogenolysis of glycerol over nanostructured Ru/MCM-41 catalysts

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ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form 24 February 2014
Accepted 18 March 2014
Available online 13 April 2014

Keywords:
Glycerol
Hydrogenolysis
MCM-41
Ruthenium
1,3-Propanediol

ABSTRACT

A series of catalysts with different Ru contents supported on MCM-41 were prepared by microemulsion (ME) method. These catalysts were characterized by X-ray diffraction, BET-surface area, H_2-temperature programmed reduction, pore size distribution, XPS, transmission electron microscopy, and CO-chemisorption measurements. The catalytic properties of Ru/MCM-41 catalysts were evaluated during the vapor phase hydrogenolysis of glycerol on various reaction parameters. The catalysts have shown an unprecedented activity for the complete hydrogenolysis of glycerol at moderate reaction temperature under normal atmospheric pressure. The nanostructured ruthenium deposited on MCM-41 support plays a significant role in improving the catalytic activity and its stability. The glycerol conversion and the selectivity of 1,2propanediol (1,2-PD), 1,3-propanediol (1,3-PD) and various products were mainly depend on the method of catalyst preparation, effect of support and also on the Ru loading.

1. Introduction

Biodiesel is produced by transesterification of vegetable oil with methanol, generating significant amount of glycerol as a by-product [1]. Glycerol is one of the most important building block in the biorefinery feedstock, since enormous amount of glycerol is expected to be produced by the biodiesel production process as well as from traditional routes such as soap manufacture [2,3]. Thus glycerol can be used as a platform chemical for the production of more valuable chemicals. Among various valorization routes of glycerol, the hydrogenolysis of glycerol received considerable attention in the recent past for the production of propanediols. Hydrogenolysis is a catalytic chemical reaction that breaks a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to the resulting molecular fragments. Through the selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen, 1,2-propanediol (1,2-PD), 1,3-propanediol (1,3-PD), and ethyleneglycol (EG) could be obtained. Therefore, catalytic hydrogenolysis of glycerol is another alternative route to increase the profitability of biodiesel production plants as the products of glycerol hydrogenolysis. These can easily replace the chemical compounds, which at present are industrially produced mainly by using non-renewable sources [4].

In particular, propanediols are used for the production of antifreeze, aircraft deicer, lubricant, and more valuable polymers. Depending on the location of the removed hydroxyl group, 1,2-propanediol, ethylene glycol and 1,3-propanediol can be generated [3]. Whereas 1,2-propanediol is used for commodity chemicals, Another diol, ethylene glycol, mainly used as a raw material for synthetic fibers, explosives, etc. [3]. Among the chemicals that can be derived from glycerol, 1,3-propanediol is a very promising target because of the high cost of conventional processes of 1,3-propanediol production and the large-scale production of polyester and polyurethane resin from 1,3-propanediol [5]. Therefore, the development of an efficient conversion process of glycerol into propanediols will make the biodiesel process more profitable. However, selective hydrogenolysis of glycerol into1,3-propanediol is not easy. The production of these chemicals from biorenewable glycerol can be both environmentally and economically attractive [1]. As shown in Scheme 1 the hydrogenolysis reaction is suggested to proceed via dehydration of glycerol to acetol and 3-hydroxypropanal by acid catalysis and subsequent hydrogenation to the glycols by metal catalysts [6–9]. Besides the hydrogenolysis reaction, degradation reactions involving C—C cleavage also occur. The products from C—C cracking are mainly ethylene glycol, methanol, ethanol and methane. Therefore, the selective conversion of glycerol to propanediols requires a suitable catalyst with acid sites/metal surface, favoring the cleavage of the glycerol C—O bonds (dehydration/hydrogenation) by hydrogen. Many supported metal catalysts have been reported for this type of reaction in liquid phase. Tomishige and his co-workers [6–9] reported the use

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http://dx.doi.org/10.1016/j.cattod.2014.03.036
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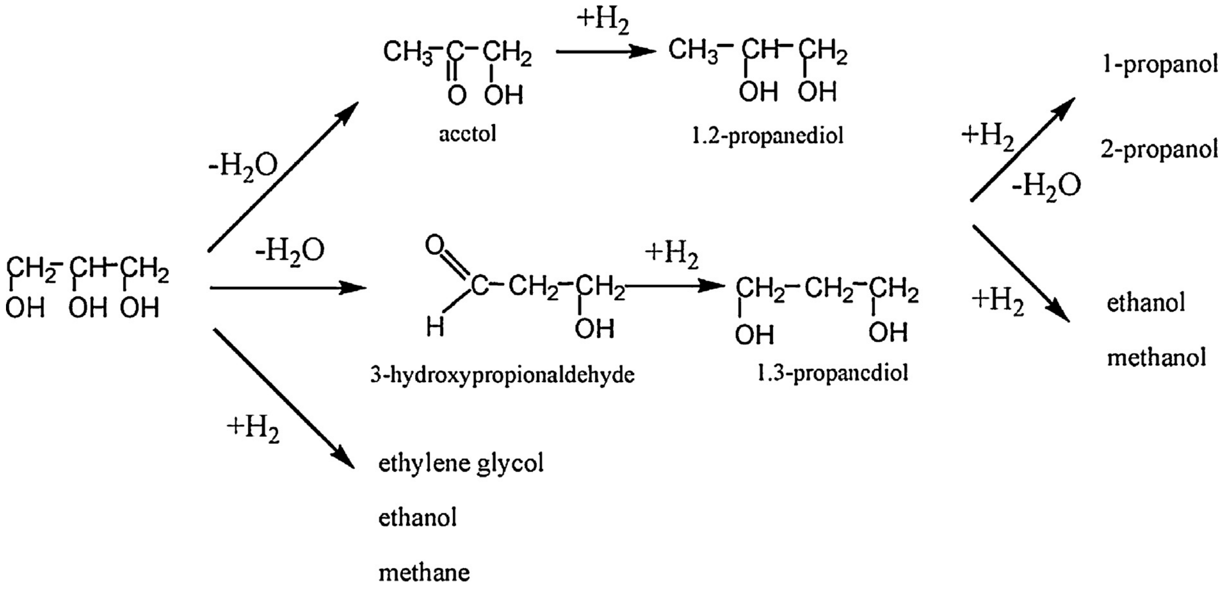

Scheme 1. Reaction mechanism of glycerol hydrogenolysis and degradation [15].

of supported group VIII metal (especially Ru/C and Rh/SiO_2) catalysts in combination with a strong solid acid (Amberlyst 15, 70) at mild temperatures of 120. 8 °C and H_2 pressures of 4–8 MPa. Other studies have demonstrated the use of Ru-supported catalysts on supports like carbon [10], TiO_2 [11,12] and acidic heteropoly salts [13]. Feng et al. [11] investigated the effect of various supports (TiO_2, SiO_2, NaY, γ-Al_2O_3 and active-carbon) on Ru catalysts and found that the support material can influence the metal particle size and the reaction routes, with TiO_2 yielding the most active and SiO_2 the most selective catalyst for propanediol production. Catalysts like Rh/C [12] and Pt/WO_3/ZrO_2 [13] have also been used in an attempt to selectively produce 1,2-PD and especially 1,3-PD [14]. Vasiliadou et al. [15] investigated the Ru-based (γ-Al_2O_3, SiO_2, ZrO_2) catalysts prepared by different precursors and found that the among the tested catalysts, Ru catalyst prepared with the chloride precursor exhibited the highest activity toward glycerol hydrogenolysis.

The present research work on vapor phase hydrogenolysis reaction is carried out on nanostructured Ru/MCM-41 catalysts. The word “nanostructured” deals with those materials having properties defined by features smaller than 100 nm. For practical applications the catalysts supports with high surface area are more attractive because the active catalysts component can be easily dispersed on their surface. MCM-41 is a member of a new mesoporous molecular sieve family and has attracted attention of researchers in academia and industry because of some unique properties like as very high surface area (>1000 m^2/g) uniform pore size (tunable from 20 to 100 Å) and relatively hydrophobic nature. The novel properties of MCM-41 are believed to be useful to increase not only the loading of transitional metal in the pores as high as possible, but also relatively with good dispersion. In recent years MCM-41 based materials have been employed as catalysts in various catalytic applications [16–18]. These properties exhibited by MCM-41 have attracted considerable attention recently for its potential application in catalysis [19–24] and many catalysts have been prepared by introducing noble metals. Among them ruthenium is one of the noble metal used for the glycerol hydrogenolysis for obtaining valuable propanediols. The production of these chemicals from biorenewable glycerol can be both environmentally and economically attractive on Ru/MCM-41. The choice of a suitable Ru precursor and optimized activation conditions also allow the controlled preparation of small ruthenium particles on mesoporous supports to yield better results on glycerol hydrogenolysis under vapor phase conditions [26]. The importance of vapor phase reaction, it can be performed as a continuous phase reaction at normal atmospheric pressure and also eco-friendly and economic viable for industrial applications compared to the liquid phase batch reactions.

In the present investigation we report the catalytic behavior of Ru/MCM-41 catalysts for the hydrogenolysis of glycerol. The catalytic properties are discussed in terms of characteristics such as Ru particle size and metal dispersion. The catalysts were also characterized by surface area, XRD, TPR, TEM, XPS, M-BET surface area, PSD, and CO-chemisorption measurements. The catalytic properties were carried out by varying metal loading, reaction temperature, effect of glycerol concentration, feed flow rate and effect of H_2 flow rate.

2. Experimental

2.1. Preparation of the MCM-41 and Ru/MCM-41

The mesoporous MCM-41 support was prepared by the procedure described in the literature [25]. The source of silicon is tetraethylorthosilicate (TEOS, 98%, Aldrich) and the structure-directing agent is cetyltrimethylammonium bromide (CTAB, Aldrich). The typical synthesis gel was prepared by adding 5.78 g of TEOS to an aqueous solution containing 1.01 g of CTAB and 0.34 g of NaOH and 30 mL of deionized water. After stirring for about 1 h at room temperature, the resulting homogeneous mixture was crystallized under static hydrothermal conditions at 373 K in a Teflon lined autoclave for 48 h. The molar composition of the initial gel mixture is 1.0:0.10:0.30:60 TEOS/CTAB/NaOH/H_2O. The solid product thus obtained was filtered, washed with deionized water to remove sodium ions from the sample and further the filterate was adjusted to pH 7 by hydrochloric acid. The filtered precipitate was dried at 383 K overnight and calcined in air at 773 K for 5 h to remove the CTAB.

The synthesized support MCM-41 (BET surface area > 1000 m^2/g) used for the preparation of supported ruthenium catalysts with varying Ru loadings from 1 to 6 wt% by micro-emulsion method [25]. 0.5 g of CTAB was added to 5.063 mL of n-butanol and 30 mL of cyclohexane until a clear solution formed. The solution was divided the solution in to two parts. To one part