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Selective transformation of glycerol into 1,2-propanediol on several Pt/ZnO solids: Further insight into the role and origin of catalyst acidity

V. Montes[a], M. Boutonnet[b], S. Järås[b], A. Marinas[a,*], J.M. Marinas[a], F.J. Urbano[a]

[a] Organic Chemistry Department, University of Córdoba, Campus de Excelencia Internacional Agroalimentario, ceiA3, Marie Curie Building, E-14014 Córdoba, Spain
[b] KTH (Royal Institute of Technology), Chemical Technology, Teknikringen 42, SE-100 44 Stockholm, Sweden

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ABSTRACT

Microemulsion technique allowed us to synthesize different ZnO solids with similar particle sizes and textural properties. Platinum was subsequently incorporated by deposition–precipitation and impregnation methods and solids tested for glycerol selective transformation into 1,2-PDO. Incorporation of platinum led to the creation of new (mainly Lewis) acid sites. A good correlation between conversion and acidity of Pt/ZnO solids was obtained. Interestingly, despite exhibiting some acidity, supports alone were inactive in the process which evidenced the role of the metal in dehydration of glycerol into acetol. Furthermore, as the reaction proceeded some chlorine coming from the precursor (H_2PtCl_6) was leached which led to the disappearance of the strongest acid sites, associated to side reactions (catalytic cracking) thus resulting in an increase in selectivity to 1,2-PDO. Eventual formation of Pt–Zn alloy upon reduction of the systems at ca. 400 °C was beneficial to 1,2-PDO selectivity.

1. Introduction

Glycerol is a by-product from biodiesel production (ca. 100 kg of glycerol per ton of biodiesel produced). Therefore, its valorization through transformation into other valuable chemicals is of great interest. One of those valuable products is 1,2-propanediol (1,2-PDO), which is used in food industry, as a less toxic alternative to 1,2-ethanediol in antifreeze and as a deicer or as a feedstock in the preparation of polyester resins, just to cite some examples of applications [1]. This chemical is traditionally obtained through the petrochemical route via hydration of propylene oxide. Alternatively, 1,2-PDO could be produced through a biomass route from glycerol via dehydration of primary hydroxyl group (thus forming acetol) followed by hydrogenation of acetol into 1,2-PDO [2].

There are different features affecting activity and selectivity of glycerol transformation on metals, such as the metal of choice (e.g. Pt [3,4], Rh [5,6], Pd [5,7], Ir [8], Cu [9–11]) the addition of a second metal [12,13], of acid or basic additives [5,14], the metal particle size [15,16] or the support [17,18], just to cite some of them.

As for the mechanistic studies, there are some discrepancies in the literature concerning the nature of active sites responsible for selective transformation of glycerol into 1,2-PDO, in particular for initial dehydration of glycerol into acetol. Selective dehydroxylation of polyols can proceed through 3 different mechanisms. (i) E1 (acid-catalyzed), involving protonation of a hydroxyl group which is then expelled as water, the resulting carbocation being neutralized by the elimination of a neighboring proton; (ii) E2 (base-catalyzed) involving simultaneous H^+ removal, loss of the OH and formation of C=C bond and (iii) homolytic cleavage of a C—O bond on a metallic surface (hydrogenolysis). Therefore, on acidic systems E1 mechanism is followed. In principle, dehydration of glycerol could take place through the primary or the secondary hydroxyl group, the former being thermodynamically favored [19].

According to Zhu et al. [20] Brønsted acid sites catalyze 1,3-propanediol formation whereas Lewis acid sites lead to 1,2-propanediol. On the contrary, Peng et al. [21] speculate on Brønsted acid sites being responsible for glycerol dehydration processes in aqueous medium given the fact that Lewis acid sites would be converted into Brønsted centers. As for the strength needed for the process, in a study on gas phase hydrogenolysis of glycerol

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* Corresponding author. Tel.: +34 957218622; fax: +34 957212066.
E-mail address: alberto.marinas@uco.es (A. Marinas).

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catalyzed by Cu/ZnO/MO*x* (MO*x* = Al_2O_3, TiO_2, and ZrO_2) solids, Feng et al. [22] concluded that strong acid sites were responsible for 1,2-PDO formation whereas weak acid sites led to 1,3-PDO. In the liquid phase, Vasiliadou et al. [18] found that moderate acid sites are sufficient to activate glycerol dehydration. Finally, some studies give support to the role of the metal not only in hydrogenation of acetol but also in glycerol activation [18,23,24].

In a previous paper, a screening of different partially reducible oxides to be used as supports for platinum was described, ZnO being selected for subsequent studies [4]. Moreover, systems reduced at 200 °C exhibited better catalytic performance than those reduced at 400 °C, a temperature at which Pt–Zn alloy was formed which was detrimental to activity. In a follow-up study [24], different solids consisting in a noble metal supported on ZnO were synthesized through the microemulsion method. This allowed us to obtain quite similar metal (Pt, Rh, Pd) particle sizes. Under our experimental conditions, reactivity followed the order Rh > Pt > Pd. Furthermore, the presence of some remaining surfactant seemed to somehow hinder hydrogenation activity of the metal, thus leading to an unusually high selectivity to acetol.

In the present paper, the good control of particle size ensured through microemulsion (ME) technique is used to synthesize diverse ZnO solids (either alone or modified with Al, Ce or Zr) with a view to tune acidity of the support. Platinum is subsequently incorporated onto the systems through deposition–precipitation technique or impregnation from H_2PtCl_6 aqueous solutions. For comparative studies, a system starting from a different precursor (platinum nitrate) was also synthesized. The final goal is to cast further light on the nature and origin of active sites responsible for the initial dehydration step of glycerol into acetol.

2. Experimental

2.1. Materials

Synperonic 13/6.5 was a gift from Croda. Zn(II)-2-ethylhexanoate (89%) dissolved in mineral spirit, Al(III)-2-ethylhexanoate, Zr(IV)-2-ethylhexanoate, Ce(IV)-2-ethylhexanoate, and 15% (w/w) Pt(IV) nitrate solution were purchased from Alfa Aesar. 8 wt% of H_2PtCl_6 aqueous solution, ZnO nanopowder, acetone (technical grade), glycerol 99%, 1,2-propanediol 99.5%, 1,3-propanediol 98%, (hydroxyacetone) acetol 95%, ethylenglycol 99.5%, *n*-propanol 99.5%, *n*-hexane > 99%, HCl 33% in water, and NaOH > 99% were purchased from Sigma–Aldrich. Milli-Q water was used for preparation of water solutions.

2.2. Synthesis of the solids

2.2.1. Synthesis of ZnO solids through ME technique

The solids, ZnO (either alone or doped with 5 wt% of Al, Zr or Ce) were synthesized using the commonly known method of oil in water (O/W) microemulsion (ME) [25]. The internal structure of the ME is determined by the relative fractions of three constituents: surfactant, oil and water. The ME is only formed for certain ratios of the constituents, outside which a two-phase system is formed. The first step was to determine the relative fractions of components where the ME was stable. So, different composition mixtures of surfactant and water were prepared at different temperatures. Then a solution of organometallic precursor was added dropwise in order to know the maximum soluble amount. Determination of this amount is easy because the microemulsions are isotropic and transparent, and when they destabilize the transparent dissolution turns into a cloudy system. These experiments allowed us to determine the region of relative fractions of constituents to form microemulsion. Under optimized conditions, the composition of microemulsions (ME) was surfactant: synperonic 13/6.5 (18.8 wt%), oil: organic precursor of metal (10 wt% of Zn) dissolved in *n*-hexane (24.5%), water: 56.7 wt%. In the case of doping of ZnO with Al, Ce or Zr, the oil is formed by 10 wt% Zn + (Al, Ce or Zr). Moreover, Al, Ce or Zr content was calculated to have 5 wt% of these metals in the resulting ZnO solid.

Once the microemulsion had been obtained in the presence of the Zn(II) ethylhexanoate aqueous solution, pH was increased up to 11 with NH_4OH in order to precipitate ZnO [26]. Resulting solids were aged under stirring for 7 h, centrifuged and carefully washed with 3 portions of 100 mL *n*-hexane. The solids were dried at 70 °C for 12 h and calcined at 400 °C for 2 h at a rate of 10 °C/min with a synthetic air flow of 2 L/h.

For comparative purposes, a commercial ZnO solid was also used as the support in the present study.

2.2.2. Incorporation of platinum

2.2.2.1. Deposition precipitation method. The synthetic procedure was as follows: a volume of 6.57 mL of chloroplatinic acid solution (or 1.67 mL of $Pt(NO_3)_4$ solution) was diluted to 200 mL with Milli-Q water and adjusted to pH 7 by adding 0.1 M NaOH. Then, an amount of 4.75 g of support was added and the mixture readjusted to pH 7 with 0.1 M HCl. The solution containing the support was refluxed at 70 °C under vigorous stirring for 2 h. Then, a volume of 10 mL of isopropanol was added, the temperature raised to 110 °C and refluxing continued for 30 min, after which the mixture was vacuum filtered and the filtrate washed with 3 portions of 25 mL of water each. The resulting solid was dried in a muffle furnace at 110 °C for 12 h, ground and calcined at 400 °C for 4 h with a rate of 1 °C/min. After calcination, the solid was ground again, sieved through a mesh of 0.149 mm pore size and stored in a flask.

2.2.2.2. Impregnation method. 200 mL of water containing the metal precursor (chloroplatinic acid) was adjusted to pH 7 with NaOH. Then, the corresponding amount of ZnO solid (in order to obtain 5 wt% Pt/ZnO in final systems) was suspended and pH readjusted to 7 with HCl. Suspensions were stirred for 5 h at room temperature and then the solvent was rota-evaporated and calcined at 400 °C. After calcination, the solid was ground, sieved through a mesh of 0.149 mm pore size and stored in a flask.

The nomenclature of the solids includes an N or Cl prefix indicating the platinum precursor (platinum nitrate or chloroplatinic acid, respectively), followed by the method of incorporation (dp or im for deposition–precipitation or impregnation, respectively) and the origin of the ZnO used (com or ME for commercial or synthesized through microemulsion, respectively). In the latter case, when applicable, Al, Ce or Zr refers to the metal doping ZnO. Finally, the name is followed by the reduction treatment. Therefore, for instance, a catalyst synthesized by deposition–precipitation method from chloroplatinic acid on an Al-doped ZnO solid synthesized through microemulsion and pre-reduced at 200 °C is denoted as Cl-dp-ME-Al-200 whereas N-dp-com-unred would indicate that platinum nitrate was incorporated on a commercial ZnO through deposition–precipitation method and tested in the reaction without any reduction pre-treatment.

2.3. Characterization

Elemental analysis of metal-containing samples was performed by the staff at the Central Service for Research Support (SCAI) of the University of Córdoba. It was performed using inductively coupled plasma mass spectrometry (ICP-MS). Measurements were made on a Perkin-Elmer ELAN DRC-e instrument following dissolution of the sample in a 1:3 HNO_3/HCl mixture with a soft heating. Calibration was done by using PE Pure Plus atomic spectroscopy standards, also from Perkin-Elmer.