Journal of Molecular Catalysis A: Chemical 368–369 (2013) 125–136

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Pt monometallic and bimetallic catalysts prepared by acid sol–gel method for liquid phase reforming of bioglycerol

M. El Doukkali[a,*], A. Iriondo[a], J.F. Cambra[a], L. Jalowiecki-Duhamel[b], A.S. Mamede[d], F. Dumeignil[b,c], P.L. Arias[a]

[a] University of the Basque Country (UPV/EHU), Engineering School, C/Alameda Urquijo s/n, 48013 Bilbao, Spain
[b] Université des Sciences et Technologies de Lille, CNRS UMR8181, Unité de Catalyse et de Chimie du Solide (UCCS), F-59655 Villeneuve d'Ascq Cedex, France
[c] Institut Universitaire de France, 10 Boulevard Saint-Michel, 75005 Paris, France
[d] Ecole Nationale Supérieure de Chimie de Lille, CNRS UMR8181, Unité de Catalyse et de Chimie du Solide UCCS, F-59655 Villeneuve d'Ascq Cedex, France

ARTICLE INFO

Article history:
Received 3 October 2012
Received in revised form 1 December 2012
Accepted 9 December 2012
Available online 20 December 2012

Keywords:
Platinum–nickel
Acid sol–gel
Promoting effect
Aqueous phase reforming
Glycerol
Hydrogen

ABSTRACT

PtFe, PtCo, PtNi, Ni and Pt-based γ-Al_2O_3 catalytic systems were prepared using the acid sol–gel method and characterized by appropriate techniques. Their catalytic activities in glycerol APR for H_2 production were investigated, and the most significant results will be fully discussed in this paper. The effect of operating conditions, the influence of different non-noble incorporated metals, the interesting promoting effect between Pt and Ni and their dispersion effect on the catalytic performance have been the main focus of this research. The analyses by TPR-H_2, XRD, XPS and TEM/EDX techniques confirmed high Pt and Ni dispersions and the promoting effect between both elements. All this explains the best catalytic activity of PtNiAl$^{(SGA)}$ catalyst, especially at moderate temperature/pressure reaction conditions. Highly dispersed Pt/Ni and Pt spillover effects were the key for obtaining high H_2 production. The Pt monometallic catalyst recorded lower conversions but fairly stable activity, while the Ni-containing catalysts recorded higher conversions, but some initial deactivation until steady state was reached.

1. Introduction

Fossil fuels have been the main resources used to meet energy demands all over the world. However, the use of large quantities of fossil fuels is causing the depletion of their reservoirs, global warming and climate change [1], as well as damaging the environment [2]. All these drawbacks in the use of fossil fuels have generated increasing interest in new sustainable and renewable clean fuels. In this sense, hydrogen is considered one of most promising future clean energy vectors.

Over the past decade, hydrogen generation from biomass-derived products and by-products has been considered one of the best alternatives when compared to traditional methods of hydrogen production, which use fossil fuels as raw materials. The conversion processes of biomass-derived materials, by contrast, present environmental benefits, as the CO_2 produced is absorbed during biomass growth, providing a neutral CO_2 balance [3–5]. One of the processes for producing hydrogen from biomass-derived products [6–8], namely, the aqueous phase catalytic reforming process [9–11] developed by Dumesic and co-workers, has received considerable attention because of its advantages: (i) low temperature, thereby reducing energy consumption because the feed needs not to be vaporized; (ii) limited decomposition reactions; (iii) the production of a gas stream rich in H_2 and CO_2 and very poor in CO in a simple chemical reactor. This last characteristic of the gas produced renders it suitable for use in fuel cells [5].

As reported in the literature [9–14], many aqueous solutions of oxygenated compounds have been used as feeds in aqueous phase reforming (APR). However, the aqueous solution of glycerol is widely used due to the possibility of revalorizing this by-product of biodiesel production through the transesterification of fats from biomass, as only small amounts of this glycerol can be absorbed by its traditional markets [15].

During the APR process, apart from the ideal reforming reaction ($C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2$) [2], other reactions take place, such as water-gas-shift (WGS), methanation or Fischer–Tropsch ones to produce alkanes, partial cracking of C—C/C—H/C—O bonds, dehydrogenation and dehydration/hydrogenation [9–13]. In the case of C—O bond cleavage, this reaction leads to diol and alkane production and is favored by catalyst acidity [16]. Moreover, the dehydrogenation and dehydration/hydrogenation of glycerol also generate diols [16]. The APR process therefore includes many reaction pathways that are highly dependent on the catalyst used [6]. Thus, it is important to develop an active catalyst for C—C/C—H bond cleavage and WGS

---

[*] Corresponding author. Tel.: +34 946 017 297; fax: +34 946 014 179.
E-mail address: mohamed.eldoukkali@ehu.es (M. El Doukkali).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2012.12.006

reaction in order to increase the selectivity toward H_2 production, while the parallel and consecutive reactions are either limited [5] or the intermediate products they generate fully reformed.

According to the literature [17,18], catalyst activity is highly influenced by the preparation method used. Conventional preparation methods, such as incipient wetness impregnation, also called wet impregnation, commonly produce active phase agglomeration on the support used. This phenomenon, which is attributed to large-sized particle formation, occurs especially when high contents of metal precursors are incorporated [17,18]. However, the sol–gel method presents some advantages when compared with impregnation methods, such as higher active metal dispersion, great thermal resistance to sintering and low deactivation rate [17–23], thus can lead to more stable catalysts [17]. Moreover, this method allows a better control of catalyst preparation via various parameters, such as: temperature, type and concentration of the alkoxide, the solvent, and the pH of the preparation medium. Therefore, varying these factors allows a more flexible control of the catalysts textural properties, such as surface area, pore size distribution and metal dispersion [23].

A variety of catalytic systems have been described in the literature for aqueous phase reforming of glycerol and other biomass-derived products [1,2,5,6,9–13,15,24–26]. These catalytic systems are based on Pt, Ni, Cu, Pd or Co monometallic catalysts and PtRe and PtNi bimetallic catalysts. Pt metal phase is usually used in both monometallic and bimetallic catalysts because of its high activity for C—C/C—H bond cleavage and WGS reaction, and low selectivity toward methane production via the methanation reaction [4]. According to Huber et al. [9], $Pt/Al_2O_3—SiO_2$ catalyst recorded higher activity in the APR of ethylene glycol than other silica-supported Group VIII metal catalysts. A similar conclusion was reached by Iriondo et al. [15], whereby both glycerol conversion and gaseous products increased when Pt and Ni were combined on γ-Al_2O_3 and γ-$Al_2O_3—La_2O_3$ supported catalysts. They concluded that Pt catalyst activity can be improved by the addition of Ni, Co and Fe.

Based on this background, and consistent with our previous research work [26], the main objective here is to study new Pt/transition-metal (Fe, Co and Ni) catalysts prepared via sol–gel method under acid conditions (SGA) and compare their catalytic activities and stabilities with those obtained using similar Pt/Ni catalysts prepared by sol–gel under basic conditions (SGB) and incipient wetness impregnation (IWI), which have been published in a previous work [26]. In fact, the selected catalytic systems consist of γ-Al_2O_3 with PtNi, PtCo and PtFe as active phases. Pt and Ni monometallic catalysts supported on γ-Al_2O_3 were also prepared for both comparative purposes and better understanding of the properties of PtNi catalyst and their influences on catalytic activity, as commented in Section 2.3. To facilitate a comparison between the results reported in this work and those shown in [26], all the parameters and the operating conditions remained unchanged. This research aims at the development of new catalysts for the aqueous phase reforming of glycerol, and therefore it investigates their catalytic activity and stability in order to maximize glycerol conversion, especially to gaseous products, and to maximize H_2 yield.

2. Experimental procedures

2.1. Catalyst preparation and reactants used

As mentioned above, PtFe, PtCo, PtNi, Ni and Pt-based γ-Al_2O_3 catalysts were prepared by the SGA method following a modified preparation procedure as described in [17–20,23,26].

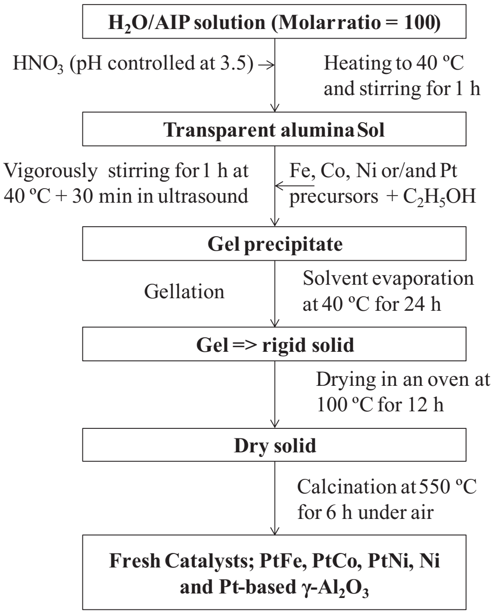

Fig. 1. Schematic flow of the methodology used to prepare the catalysts by the acid sol–gel method.

First, aluminum isopropoxide (AIP) $Al[OCH(CH_3)_2]_3$ (Sigma–Aldrich 99.995%) was hydrolyzed at 40 °C, using a molar ratio H_2O/AIP of 100. This solution was then peptized by adding HNO_3 to adjust the pH at 3.5. This pH was chosen to be under acid conditions while the preparation took place. This plays an important role in the evolution of the hydrolysis reaction [23]: H_3O^+ ions (acid medium) and OH^- (basic medium) do not have the same influence. The H_3O^+ cations, attracted by oxygen, facilitate the substitution of the groups $O—CH(CH_3)_2$ and, therefore, hydrolysis, while the OH^- anions attracted by the electronegative metal M favor the formation of M—O—M clusters by condensation. As a result pH selection will be decisive to determine the final texture of the materials prepared [23]. At the same time, another solution was prepared using absolute ethanol as solvent and the salt precursor ($H_2PtCl_6{\cdot}xH_2O$ (Sigma–Aldrich, 99.99%), $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich, 99.99%), $FeCl_3{\cdot}6H_2O$ (Panreac, 99.5%) and $CoCl_2{\cdot}6H_2O$ (Quimivita)) as solute. The metal concentration in the precursor solution was selected to obtain 3 wt% of Pt and 10 wt% of Ni, Co or Fe. This salt solution was added to the AIP-derived alumina sol at 40 °C and the mixture was vigorously stirred. After this, the sol formed was placed in ultrasound equipment for 30 min. The alcoholic solvent was removed by drying at 40 °C for 24 h. The rigid solid materials obtained by the SGA method were dried under air at 100 °C overnight and then calcined at 550 °C with a temperature ramp of 2 °C/min for 6 h. The calcination procedure was carried out under an air flow of $2\,L\,min^{-1}\,g_{cat}^{-1}$. The preparation procedure described above is schematically described in Fig. 1.

2.2. Catalyst characterization techniques

In order to understand the catalytic behavior of the tested catalysts, their physicochemical properties were examined at calcined state using different characterization techniques. The catalysts presenting the best performances were also characterized at their reduced state to get a better understanding of their functionalities.

Specifically, calcined catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), N_2 adsorption–desorption isotherms at 77 K, temperature programmed reduction (TPR-H_2), X-ray powder diffraction (XRD) and