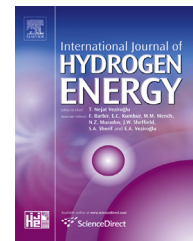




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H₂ production from oxidative steam reforming of 1-propanol and propylene glycol over yttria-stabilized supported bimetallic Ni–M (M = Pt, Ru, Ir) catalysts

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ABSTRACT

This paper reports hydrogen production from oxidative steam reforming of 1-propanol and propylene glycol over Ni–M/Y₂O₃–ZrO₂ (10% wt/wt Y₂O₃; M = Ir, Pt, Ru) bimetallic catalysts promoted with K. The results are compared with those obtained over the corresponding monometallic catalyst. The catalytic performance of the calcined catalysts was analyzed in the temperature range 723–773 K, adjusting the total composition of the reactants to O/C = 4 and S/C = 3.2–3.1 (molar ratios). The bimetallic catalysts showed higher hydrogen selectivity and lower selectivity of byproducts than the monometallic catalyst, especially at 723 K. Ni–Ir performed best in the oxidative steam reforming of both 1-propanol and propylene glycol. The presence of the noble metal favours the reduction of the NiO and the partial reduction of the support. The NiO crystalline phase present in the calcined catalysts was transformed to Ni⁰ during oxidative steam reforming. The adsorption and subsequent reactivity of both 1-propanol and propylene glycol over Ni–Ir and Ni catalysts were followed by FTIR; C–C bond cleavage was found to occur at a lower temperature in propylene glycol than in 1-propanol.

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1. Introduction

The use of bioalcohols for producing hydrogen is considered of great interest as in the mid-term, it may contribute, to the implementation of hydrogen production processes based on non-fossil resources. Currently, ethanol is the bioalcohol

produced in the greatest amount and it is also the higher alcohol that has been most studied with the goal of producing hydrogen using reforming processes [1–3]. Although the reforming of glycerol has also been widely studied [4–6] chiefly because glycerol is a byproduct in biodiesel production, there are few reports on the reforming of other C₃ and C₄ alcohols [7–12]. However, much effort is invested in the use

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biomass resources, including agricultural residues and lignocellulose materials, in the production of chemicals and fuels. The implementation of new processes for biomass transformation may provide new opportunities to obtain different biomass-derived alcohols, which could become available in large amounts in the near future [13–15]. In this context, the study of processes of reforming alcohols other than ethanol and glycerol for H₂ production emerges as an interesting research proposal. Moreover, the use of oxidative steam reforming (OSR) processes is energetically favourable compared with steam reforming, and it could be an appropriate compromise between the energy requirement and the hydrogen yield. Furthermore, the presence of O₂ in the reactants may also contribute to the elimination of carbon deposits, the build-up of which is one of the major causes of deactivation of reforming catalysts [1,2,16].

Co and Ni have been identified as appropriate active phases for the reforming of higher alcohols due to their high capacity for C–C bond cleavage [1,2]. The addition of a small amount of noble metal has been shown to have a positive effect on the catalytic behaviour of Co- and Ni-based materials for the processes mentioned [17–22]. Furthermore, the oxygen mobility of the support and the presence of alkaline cations as promoters can prevent carbon deposition, thereby contributing to less deactivation of such catalysts [17,23,24].

We recently reported that the OSR of 1-propanol (OSRP) can be effectively carried out over Ni catalysts supported on yttria-stabilized zirconia (YSZ), at 773 K [9]. The materials were used in the OSRP without previous reduction; characterization of the post-reaction catalysts showed that the initial NiO was transformed into metallic Ni⁰ during the OSRP. Together with the background relating to catalyst formulation for the OSR of higher alcohols laid out above, our previous results led us to study the effect of the addition of small amounts of different noble metals (Ir, Ru, Pt) to the bare Ni(K)/YSZ catalyst (10% Y₂O₃ wt/wt in the support) with respect to the OSR of 1-propanol and propylene glycol. Both processes, the OSRP and the OSR of propylene glycol (OSRPG), were studied in the temperature range 723–773 K using a reactant mixture with molar ratios of: total oxygen to carbon, O/C = 4 and H₂O/C = 3.2 (OSRP) or 3.1 (OSRPG). Catalysts were used in the reforming processes without a previous reduction step and were characterized before and after reaction using several techniques; any carbonaceous deposits on the post-reaction catalysts were analyzed by Raman spectroscopy and TPO experiments.

2. Experimental

2.1. Catalyst preparation

YSZ-supported monometallic Ni and bimetallic Ni–M (M = Pt, Ir, Ru) catalysts containing K as a promoter were prepared by incipient wetness impregnation. The YSZ (10% wt/wt Y₂O₃; BET surface area 79 m² g^{−1}) was prepared by a precipitation method and calcined at 873 K, as described elsewhere [9]. The Ni, K, and M (M = Ir, Pt, Ru) were loaded from an aqueous solution of Ni(NO₃)₂·6H₂O, KNO₃ and K₂[PtCl₄], IrCl₃·xH₂O or RuCl₃. The resulting solids were calcined at 773 K.

2.2. Catalyst characterization

The chemical composition of the samples was analyzed with inductively coupled plasma (ICP) apparatus: Perkin Elmer Optima 3200RL.

X-ray powder diffraction (XRD) patterns of the catalysts were acquired with a computer-controlled XPert-PRO diffractometer using Cu K α radiation with 0.017 steps in the range $2\theta = 4^\circ$ – 100° , with 50 s at each step.

Temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) experiments were performed using a Micromeritics Autochem 2920 analyzer. The sample was treated with a 12.5% (v/v) H₂/Ar mixture (TPR) or 10% (v/v) O₂/He (TPO) mixture and it was heated at 10 K/min. H₂ or O₂ consumption was measured by a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5500 Multitechnique System, using a monochromatic AlK α X-ray source (1486.6 eV, 350 W) which was placed perpendicular to the analyzer, working with an ultra-high vacuum (5×10^{-7} Pa). The binding energy (BE) values were referred to the C 1s peak, at 284.8 eV.

Infrared spectra of the solids were recorded using a Nicolet 520 FTIR spectrometer by collecting 256 scans with a resolution of 4 cm^{−1}. FTIR was used for studying both the adsorption of CO probe molecule and the adsorption of reactant vapours (1-propanol and propylene glycol). Adsorption experiments were carried out over the H₂-reduced (773 K) catalysts using a special greaseless infrared cell with ZnSe windows which allows thermal, vacuum and gas treatments. Self-supported wafers of the reduced samples were introduced into the cell, treated under high vacuum (10^{-3} Pa) at 673 K and then, in order to refresh the reduced samples and remove water and CO₂, they were treated with several hydrogen/vacuum pulses at the same temperature. The corresponding vapour of 1-propanol or propylene glycol was adsorbed onto the samples from the purified liquid. After the adsorption, the samples were outgassed at 10^{-2} Pa, and the initial spectra at 298 K were registered. The samples were then treated at successive increasing temperatures up to 723 K; after each treatment, the sample was cooled to 298 K and the spectrum of the solid phase and that corresponding to the gas phase were registered. The spectra of the solid catalysts were always referred to the background spectrum of the corresponding sample after the in-situ re-reduction.

The Raman spectroscopy was performed using a Jobin-Yvon LabRam HR 800 with a CCD detector cooled at 203 K and a 532 nm laser. The laser power was limited to 0.7 mW to minimize laser-heating effects. The samples were studied at room temperature at various points using 50 \times magnification.

2.3. Oxidative steam reforming of n-propanol and propylene glycol

Catalytic behaviour was studied using a Micro-Activity Reference unit (PID Eng&Tech). The sample was placed in a stainless steel 316 (i.d. = 9.2 mm) tubular reactor and the temperature was measured using a thermocouple in the catalytic bed. The liquid reaction mixture (alcohol and water) was

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