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Bimetallic MNi/Al_2O_3-La catalysts (M = Pt, Cu) for acetone steam reforming: Role of M on catalyst structure and activity

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ABSTRACT

The effect of Pt and Cu addition on the behaviour of Ni catalysts supported on Al_2O_3 modified with La for acetone steam reforming (as model molecule of bio-oil) was studied. Catalytic activity was found to depend strongly on the bimetallic formulation, achieving the bimetallic PtNi catalyst almost complete gasification of the acetone. The characterization results achieved with XRD, TPR and XPS showed differences in surface metal concentrations which depend on the presence of Pt or Cu in catalysts composition. The decrease in activity observed for the bimetallic CuNi catalyst is associated with changes in the acetone reaction mechanism due to the presence of metallic copper since formation of CuNi alloy was not formed in this catalyst. In the case of bimetallic PtNi catalyst, a lower carbon deposition and a higher thermal stability of the Ni crystallites under reaction conditions was observed with respect to monometallic Ni reference catalyst. It is suggested that the better dispersion of metallic nickel crystallites together with the enhanced H-atom mobility on Pt are responsible of the better catalytic behaviour of the bimetallic PtNi formulation in the steam reforming of acetone.

1. Introduction

There is an increasing interest in the development of technologies for the conversion of biomass derived hydrocarbons in hydrogen rich gas mixtures as a way to overcome the current technical limitations in hydrogen supply and storage. Recent developments in flash pyrolysis technologies make it possible to convert lignocellulosic biomass efficiently to a bio-oil (a mixture of aliphatic and aromatic oxygenates: aldehydes, ketones, acids, esters, alcohols, sugars, furans, etc.) which is easier for handling and transport [1]. Steam reforming of aqueous bio-oil fractions is therefore an interesting alternative to produce hydrogen in a renewable way. The direct steam reforming of bio-oil generates high amount of undesirable by-products and high coke/oligomer deposition on catalyst, which quickly deactivates it. Therefore, the successful extraction of hydrogen from bio-oils mainly depends on the development of new catalysts with high thermal stability and improved resistance towards coke formation.

Given the influence of the nature of both the metal and support on the catalytic characteristics of supported metals and to fulfil the above requirements, a careful choice of these elements is essential to develop supported catalysts. Due to complexity of steam reforming of bio-oils, reforming of model oxygenate components has been studied in last decades, focusing on acetic acid, acetone or ethylene glycol as the most representative compounds [2–6] in order to establish more clearly the structure-activity correlations on reforming catalysts. Most of the studies reported in literature have been focused on the reforming of acetic acid, whereas acetone steam reforming (Eq. (1)) has been less studied in spite that this compound could be the model of the carbonyl-containing compounds present in bio-oils (ketones and aldehydes).

$$CH_3COCH_3 + 5H_2O \rightarrow 3CO_2 + 8H_2 \qquad (1)$$

According to the literature, different catalysts have been used in steam reforming of oxygenated compounds: Ni/CaO–Al_2O_3 [2], Ni/Al_2O_3 [7] Ni–Zn–Al [8], Ni/ZrO_2 [9], Co–Ce/Al_2O_3 and Co–La/Al_2O_3 [10], Pt/CeO_2 and Pt/ZrO_2 [11–14]. Platinum-based catalysts have been the most used systems, however their high cost limit their practical application. Apart of Pt based catalysts, the high C—C bond-breaking activity and the relatively low cost of Ni make

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it a suitable active phase for oxygenates reforming reactions. However coke formation is an important problem in bio-oil reforming on Ni based catalysts. The platinum group metals have been reported to be more effective catalysts by preventing coke deposition since Pt crystallites do not dissolve carbon. Several authors have reported that the addition of small amounts of noble or semi-noble metals to Ni catalysts improve their catalytic performance decreasing the coke formation on the Ni surfaces [15–18]. The high hydrogenation activity of Pt or Cu could also help the formation of molecular H_2 from atomic H, improving the activity of nickel catalyst in the reforming of bio-oil.

The nature of support also influences the catalytic performance of supported metal catalyst for the steam reforming of oxygenated compounds since it affects both the dispersion and stability of the metal as well as it may participate in the reaction. Among oxide supports, alumina-based supports are often used as a substrate for the reforming catalysts because of their mechanical and chemical resistance under reaction conditions. However, the acid sites of alumina could participate in undesirable reactions during the acetone reforming such as aldol condensation [19] and oligomerization [12] that could form deposits on the catalyst surface. Thus, additives or promoters are often used in reforming catalyst formulations. For this purpose, rare earth elements are extensively used as promoters in the catalysts used in the reforming of oxygenated compounds. In particular, it is described the beneficial effect of lanthanum oxide in the stability of catalysts for steam reforming due to its known capability to remove carbon formation from metallic surfaces [20–22]. Additionally, lanthanum has been reported to prevent the thermal sintering of bare alumina [23].

With this background, in this contribution we study the effect of Pt and Cu addition on the behaviour of Ni catalysts supported on Al_2O_3 modified with lanthanum for acetone reforming (as model molecule of bio-oil). Careful investigation of the structure of catalysts were done in an attempt to establish a relationship between activity and the changes in structural and surface characteristics induced by Pt or Cu addition to Ni catalysts.

2. Experimental

2.1. Catalyst preparation

Lanthanum modified-Al_2O_3 support (15 wt% La_2O_3) was prepared by impregnation of a commercial γ-Al_2O_3 (Alfa Aesar, S_{BET} 235 m^2/g) with 0.09 M aqueous solution of $La(NO_3)_3{\cdot}xH_2O$ (Aldrich 99.9%) using 10 $mL/g_{support}$ as impregnation ratio. Previous to lanthanum impregnation, the Al_2O_3 support was previously stabilized by treating in static air in an oven at 1073 K for 12 h (A). The La-impregnated support (A-La) was dried under static air at 393 K for 3 h and subsequently calcined at 1073 K for 8 h.

Monometallic Ni reference catalyst (Ni/A-La, 12 wt% NiO) was prepared by impregnation of the lanthanum modified-Al_2O_3 support, with 0.16 M aqueous solutions of $Ni(NO_3)_2$ using 10 $mL/g_{support}$ as impregnation ratio. The sample was impregnated for 5 h, subsequently dried at 393 K for 2 h, and finally calcined in air at 773 K for 4 h.

MNi bimetallic catalysts (MNi/A-La, M = Pt or Cu, 1 wt%) were prepared by wet impregnation of the calcined Ni/A-La catalyst with aqueous solutions of the corresponding metal precursors (0.005 M of $Pt(NH_3)_4(NO_3)_2$ or 0.015 $MCu(NO_3)_2$), using 10 $mL/g_{Nicatalyst}$ as impregnation ratio during 2 h. After drying at 383 K for 14 h, the impregnated bimetallic samples were calcined under air at 773 K for 4 h.

2.2. Catalyst characterization

The chemical composition of the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Perkin-Elmer Optima 3300DV apparatus. The samples were first dissolved in acid solutions (a mixture of HF, HCl and HNO_3), microwaved for 15 min, and diluted to concentrations within the detection range of the instrument.

N_2 adsorption–desorption isotherms were obtained at 77 K over the whole range of relative pressures, using a Micromeritics ASAP 2100 automatic device on samples previously degassed at 423 K for 12 h. BET specific areas were calculated from these isotherms using the BET method and taking a value of 0.162 nm^2 for the cross-section of the physically adsorbed N_2 molecule. The pore size distribution was calculated by applying the Barrer–Joyner–Halenda method (BJH) to the adsorption branch of the N_2 isotherm. The total pore volume was calculated from the adsorption isotherms at $P/P_0 = 0.98$.

Temperature-programmed reduction experiments were carried out on a semiautomatic Micromeritics TPD/TPR 2900 apparatus equipped with a TC detector. Prior to reduction experiments, the samples (about 30 mg) were treated thermally under an air stream at 573 K to remove water and other adsorbed contaminants. TPR profiles were obtained by heating the samples under a 10% H_2/Ar flow (50 mL/min) from 233 to 1173 K at a linearly programmed rate of 10 K/min. The effluent gas was passed through a cold trap to remove water before measuring the amount of hydrogen consumed during reduction by the TC detector. The TCD signals were normalized by the measured weight of each sample.

X-ray powder diffraction patterns were recorded following the step-scanning procedure (step size 0.02°, 2θ scanning from 5° to 90°) using a computerized Seifert XRD 3000P diffractometer (Cu Kα radiation, $\lambda = 0.15418$ nm). A rate of 500 s per step was used during a continuous scan in the above mentioned range. Volume-averaged crystallite sizes were determined by applying the Debye–Scherrer equation from the line broadening (β_r) of the characteristic (2 0 0) NiO peak at $2\theta = 43.3°$ and the (2 0 0) Ni-metal peak at $2\theta = 53.8°$ after subtracting the instrument effect ($\beta_r = \sqrt{\beta_0^2 - \beta_i^2}$); β_0 = total line broadening, β_i = instrumental broadening = 0.058 rad).

X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition and oxidation state of the catalyst surfaces. Photoelectron spectra were recorded with a VG Escalab 200R electron spectrometer equipped with a Mg Kα X-ray source ($h\nu = 1253.6$ eV) and a hemispherical electron analyser operating at constant transmission energy (50 eV). The areas of the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of variable proportions. The reduction treatment was carried out ex situ at 823 K in H_2/N_2 (1/9 vol) flow for 90 min followed by re-reduction in situ at 773 K for 30 min. The C 1s, Al 2p, Pt 4d, Ce 3d and Ni 2p core-level spectra were recorded. Differential charging was observed in all samples. This charging effect was corrected by referencing the binding energies (accuracy ± 0.1 eV) to the C 1s signal arising from carbon contamination at 284.8 eV.

Temperature programmed oxidation analyses of spent catalysts were carried out using a thermo-gravimetric analyser (Mettler Toledo TGA/SDTA 851e) to determine the amount of coke deposited on catalysts. The standard protocol involved the weight change of the sample (20 mg) during its heating in 200 mL/min of N_2 as purge gas and 50 mL/min of O_2 as reactive gas from 298 to 1123 K at a heating rate of 10 K/min.