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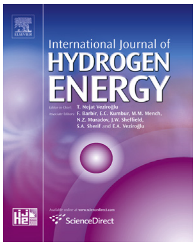

Furfural steam reforming over Ni-based catalysts. Influence of Ni incorporation method

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ABSTRACT

Catalytic steam reforming of biomass-derived compounds as furfural could be a promising option to produce renewable hydrogen; however efficient catalysts are still under study. Different commercial supports (SiO_2, Al_2O_3, ASA, MgO, $MgAl_2O_3$, ZnO, TiO_2, Natural Sepiolite) incorporating Ni by incipient wetness impregnation have been initially tested in the Steam Reforming of Furfural (SRF). Among them, Ni supported in natural sepiolite exhibited the best catalytic activity. In order to improve the catalytic performance of this sepiolite-based catalyst an alternative method for the incorporation of Ni was explored (precipitation). Precipitation method led to a Ni-based catalyst highly active and selective in the production of hydrogen. In addition, the production of undesired products (CO and acetone) decreased significantly. Characterization by BET area, XRD, TEM and TPR shows that precipitation method allows to synthesize a Ni-based catalyst with higher BET surface area and smaller metallic nickel particles. These particular physico-chemical properties seem to be the major responsible of the better catalytic performance exhibited by the material prepared by precipitation.

1. Introduction

Hydrogen has attracted much attention as an alternative fuels mainly due to environmental aspects [1]. Unfortunately, hydrogen is not freely available in nature and it must be produced by some means. Currently, about 75% of hydrogen we use today comes from natural gas reforming. Thus, the real environmental benefits in the use of hydrogen as fuel could be only achieved if its production was carried out from renewable sources [2]. A new eco-friendly reservoir of hydrogen is needed for a clean and sustainable production of energy. Biomass-derived compounds as furfural could be one of this source since it can be extracted directly from a variety of agricultural byproducts, including corncobs, oat and wheat bran, sawdust, and rice husk [3,4], and bio-oil derived from fast pyrolysis of biomass [5]. The option to obtain hydrogen from furfural is quite new. Thus, new process and catalytic materials need to be developed. The few works about the steam reforming of furfural are focusing in the use of catalytic materials based on transition metals, i.e. Ni or Cu, supported on oxides [6–8]. Economically, it is accepted that Ni, operating at moderate temperatures, behaves as an excellent and cheaper material, compared with precious metals. Particularly, in the steam reforming of biomass-derived compounds Ni has exhibited good performance favoring C–C bond and O–H bond rupture [9–25,40]. In general, the catalytic performance of each catalyst (activity, selectivity, and stability)

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depends on the nature of metal, type of precursor, preparation method, type of support, presence of additives and operating conditions. Among them, it is found that support plays an important role in the preparation of highly active and selective steam reforming catalysts since it helps in the dispersion of metal catalysts and enhances its activity via metal- support interactions [26,27]. In addition, synthesis methods and pretreatment conditions of supported nickel catalysts are also important issues to prepare highly active steam reforming catalysts. This way, the activity of the steam reforming catalyst can be improved achieving a good dispersion of metallic sites on the support, while coke formation could decrease using non-acidic supports that would avoid the ethylene formation [26–28]. In the present work we have explored the performance of Ni incorporated in several supports (SiO_2, Al_2O_3, ASA (Amorphous Silica Alumina), ZnO, MgO, $MgAl_2O_3$, TiO_2 and Sepiolite) in the SRF. The best results were obtained with sepiolite as support. Two different methods for the Ni incorporation in the sepiolite have been also explored, finding that the method of the incorporation of Ni has an important influence in its catalytic performance. The characterization of the sepiolite-based catalysts containing Ni by BET area, XRD, TPR, and TEM has allowed to establish interesting relationships between their catalytic activity and physico-chemical properties.

2. Experimental

2.1. Preparation of catalysts

Eight different commercial materials, SiO_2 (Basf), Al_2O_3 (Merck), ASA (Crossfield catalysts), MgO (Fluka), $MgAl_2O_3$ (Alfa Aesar), ZnO (Fluka), TiO_2 (Aldrich) and Natural Sepiolite (Tolsa S.A.), have been used as support of Ni. The incorporation of Ni was accomplished by incipient wetness impregnation with an aqueous solution containing the required amount of Ni $(NO_3)_2 6H_2O$ (Aldrich, 98%) to achieve a nominal concentration of 15 wt.% of Ni in the final catalysts. In addition, a second Ni incorporation method over the sepiolite support was performed according to the reference [29] with the proper modifications for the Ni incorporation (precipitation method). Specifically, to introduce the Ni two solutions were prepared, one with $Ni(NO_3)_2 6H_2O$ (Aldrich, 98%) as nickel precursor which was acidified with several drops of HNO_3 to achieve $pH = 2$ and other containing the natural sepiolite. Nickel solution was added to the sepiolite solution using a syringe pump (Kd Scientific) under vigorous agitation. After, NaOH was added to achieve a final pH of 11, in these conditions Ni species precipitate on the surface of the sepiolite as nickel hydroxide [29].

Supports containing Ni were calcined in muffle oven at 600 °C for 3 h before reaction.

2.2. Characterization techniques

The nickel content of all the samples and the chemical composition of the sepiolite sample before and after Ni incorporation methods were determined by atomic absorption spectrophotometry (AAS) in a Varian Spectra A-l0 Plus apparatus.

Textural properties were obtained from the nitrogen adsorption isotherms determined at 77 K in a Micromeritics ASAP 2000 equipment. Prior to the adsorption measurements the samples were outgassed at 200 °C for 24 h.

X-ray diffraction was used to identify the nature of the crystalline phases present in the catalysts. XRD patterns were obtained at room temperature in a Philips X'pert diffractometer using monochromatized CuKα radiation. The crystalline particle size was calculated by Scherrer equation from characteristic peaks of each phase [30].

Transmission electron microscopy (TEM) was used to determine the size of supported Ni metallic particles. The samples were ultrasonically dispersed in carbon tetrachloride and transferred to carbon coated copper grids. Micrographs were recorded using a Philips CM-10 microscope operating at 100 kV.

The reduction behaviors of the supported oxidized nickel phases were studied by temperature programmed reduction (TPR) in a Micromeritics Autochem 2910 equipment. About 50 mg of the calcined catalyst was initially flushed with 30 ml min^{-1} of Ar at room temperature for 30 min and then a mixture of 10 vol% of H_2 in Ar was passed through the catalyst at a total flow rate of 50 cm^3 min^{-1} while the temperature is increased up to 900 °C at a heating rate of 10 °C min^{-1}. The H_2 consumption rate was monitored in a thermal conductivity detector (TCD) previously calibrated using the reduction of CuO as reference.

The degree of reduction was determined from TPR experiments comparing the total amount of hydrogen consumed by each catalyst with the theoretical amount of hydrogen, which is necessary to complete the reduction of NiO present in the catalyst.

Ni^0 metal dispersions were estimated using two different procedures, first using the correlation between metallic particle size and dispersion reported in Table 1 of US patent US7813523 [31] and second using the equation $D = 101/d$ (nm) [32], where D is the percentage dispersion and d is the average particle size of Ni^0 in nanometers determined by TEM.

The amount of carbon deposited in the catalysts after steam reforming reaction was determined by elemental analysis using a Carlo Erba 1106 analyzer.

2.3. Catalytic study

Steam reforming of furfural (SRF) were carried out in a continuous fixed bed reactor at atmospheric pressure, H_2O/FUR of 18, GHSV of 2300 h^{-1} and a range of temperatures between 400 °C and 600 °C. Fresh catalyst was used for each temperature study. Before reaction the catalysts were reduced "in situ" in flow of H_2 (100 ml min^{-1}) at 600 °C for 2 h.

In a typical catalytic test the reactor was loaded with 0.5 g of catalyst (grain-size: 0.25–0.42 mm), diluted with the required amount of carborundum (SiC) (grain-size: 0.60–0.80 mm) to achieve a catalyst bed of 5 cm. The water and furfural were fed separately from pressurized container using a liquid flow controller (Bronkhorst), and vaporized at 160 °C into a stream of nitrogen. The total gas flow was 90 ml min^{-1}.