



Silica and zirconia supported catalysts for the low-temperature ethanol steam reforming

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ABSTRACT

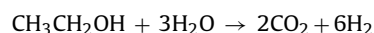
Ethanol steam reforming has been investigated in the low temperature range, focusing not only on H₂ productivity, but also on catalyst stability, very critical parameters under such conditions. Different supports (SiO₂ and ZrO₂), active phases (Ni, Co, Cu) and reaction temperature (300–500 °C) have been employed. Ni confirmed the best performing active phase to promote ethanol decomposition and reforming already at low reaction temperature. However, stability towards coking remains a key problem. The support plays a key role from this point of view. Indeed, the stabilization of the active phase in very dispersed form allowed to reach stable catalyst performance with time-on-stream. SiO₂, thanks to no Lewis acidity and sufficiently strong metal–support interaction, demonstrated an interesting support for Ni under the selected operating conditions.

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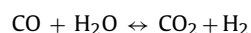
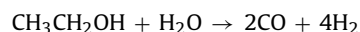
1. Introduction

The steam reforming of ethanol raised interest for the production of H₂ from a renewable source. Broad efforts have been devoted to develop active and stable catalytic systems for this application. Among non noble metal catalysts Ni and Co exhibited the most interesting performance, suggesting to optimize their formulation to achieve better results [1–9].

The steam reforming process is composed of many different possible reactions [9], of which we may summarize the most relevant as follows:



which may be seen as the sum of the syngas production and the water gas shift (WGS) reaction:



The latter is exothermal, in contrast to the former. Therefore, when operating under the typical steam reforming conditions the WGS reaction is often at equilibrium. Its degree of advancement may be deduced from the CO/CO₂ ratio.

Ethanol may be dehydrogenated to acetaldehyde, which can be further reformed. However ethanol may also undergo dehydration to form ethylene that can then polymerize to form carbonaceous deposits over the catalyst. Depending on the operating conditions other parasitic reactions induce coke formation, such as CO disproportion (Boudouard reaction), active at moderate temperature, or the decomposition of hydrocarbons, active at high temperature.

Differently prepared Ni-, Co- and Cu-based catalysts supported over TiO₂ have been recently tested for the steam reforming of ethanol. The results evidenced that the highest activity may be reached in general with Ni as active phase, but its tendency to form C filaments remains a key problem, besides possible coking due to support acidity [10–14]. It was also underlined that the interaction strength between the support and the active phase, tunable with the preparation procedure, determines the success of a formulation. For instance, the same 10 wt% Ni/TiO₂ sample was completely inactive when the support was calcined at 500 °C, whereas it was conveniently active and stable when calcined at 800 °C [12–14].

In addition, Ni proved much more stable against coking when prepared in very dispersed form also for the SR of CH₄ [15–18]. The

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possibility to disperse (and stabilize in dispersed way) the metal depends on the preparation method, but also on the support. ZrO₂ and SiO₂ demonstrated interesting supports for Ni, provided the right preparation route is chosen [12,13]. Therefore, in this work we investigated different Ni-, Co- and Cu-based catalysts supported over ZrO₂ or SiO₂. In particular a mesoporous SBA-15 support was chosen, trying at least the partial confinement of the active phase into the mesoporous framework. On the other hand, the mean pore size of SBA-15 is much larger than the kinetic diameter of ethanol, so that no significant mass transfer limitations are expected during the reaction.

All the samples were calcined at 500 °C in order to keep the active phase as dispersed as possible and we focused on low temperature activity testing in the temperature range 300–500 °C. Indeed, the possibility to operate at relatively low temperature, *i.e.* at 500 °C or below, is very attractive to limit the energy input to the reactor. Nevertheless, coking activity is particularly high in such a temperature range, especially with Ni-based catalysts.

In previous investigations [12–14] we managed the coking item by high temperature operation (500–750 °C), so to favour the gasification of the coke deposits in case formed. On the contrary, in the present work we focused on the optimization of metal dispersion and its interaction with the support to improve catalyst stability towards coking. This approach was successfully applied also with Pt-supported samples in this application [19]. Extensive characterization by means of various techniques of both the fresh and spent samples allowed to compare the main physical–chemical properties of the catalysts and to comment activity/stability data.

2. Experimental

2.1. Catalyst preparation

2.1.1. Support synthesis

The SBA-15 support was synthesized as previously reported [20,21], in the presence of Pluronic 123 (P123, Aldrich) as structure directing agent and calcined at 500 °C.

Zr(OH)₄ was prepared by a conventional precipitation method [21,22] at a constant pH of 10.

2.1.2. Addition of the active phase

The active phase was added to each support by incipient wetness impregnation with an aqueous solution of the metallic precursor (Ni(NO₃)₂·6H₂O, Sigma Aldrich, purity ≥98.5%; Co(NO₃)₂·6H₂O Sigma–Aldrich, puriss. p.a. ACS reagent; Cu(NO₃)₂·3H₂O Sigma–Aldrich, puriss. p.a.), in the proper concentration in order to obtain 10 wt% nominal metal loading. The catalyst was dried overnight at 110 °C and then calcined at 500 °C for 4 h.

Catalysts were labelled with a S or Z symbol, referring to SiO₂ or ZrO₂ carriers, respectively, followed by a symbol indicating the metal constituting the active phase (Ni, Co or Cu).

2.2. Characterization

The actual metal concentration in the catalysts was determined by atomic absorption spectroscopy (AA) measurements on a Perkin Elmer AAnalysis instrument after dissolution of the sample.

X-ray powder diffraction (XRD) analysis of the as prepared samples was performed in order to identify the crystalline phases. XRD patterns were collected on a Bruker D8 Advance diffractometer equipped with a Si(Li) solid state detector (SOL-X) and a sealed tube providing Cu K α radiation. Phase recognition was possible by comparison with literature data [23].

Specific surface area and pores size distribution were evaluated through N₂ adsorption–desorption isotherms at –196 °C

(Micromeritics, ASAP 2000 Analyser). Surface area was calculated on the basis of the BET equation [24], whereas the pores size distribution was determined by the BJH method [25], applied to the N₂ desorption branch of the isotherm. Prior to the analysis the sample was dried overnight at 110 °C and then outgassed at the same temperature for 2 h.

The TPR technique was employed to identify different metallic species possibly present in the catalysts according to the different reduction temperatures, in case used to assess the interaction strength between the active phase and the support. The catalyst was placed in a quartz reactor and heated by 10 °C/min from *r.t.* to 800 °C in a 5% H₂/Ar mixed gas stream flowing at 40 mL/min. TPO analysis was performed by feeding 40 mL/min of a 10 vol% mixture of O₂/He while heating by 10 °C/min up to 650 °C.

SEM images have been obtained using a Field Emission Gun Electron Scanning Microscopy LEO 1525, after metallization with Cr. Elemental composition was determined using Bruker Quantax EDS.

TEM images have been obtained using a Philips 208 Transmission Electron Microscope. The samples were prepared by putting one drop of an ethanol dispersion of the catalysts on a copper grid pre-coated with a Formvar film and dried in air.

FT-IR spectra have been recorded in static conditions by a Nicolet Nexus Fourier transform instrument, using conventional IR cells connected to a gas manipulation apparatus. Pressed disks of pure catalyst and support powders (~30 mg) were reduced in the IR cell by heating in pure H₂ at 500 °C and following outgassing at the same temperature. CO adsorption experiments have been performed at –140 °C, recording spectra upon warming.

Pivalonitrile (PN, Aldrich, pur. 98%) adsorption experiments have been performed over the reduced samples at room temperature and following outgassing at increasing temperatures.

Skeletal spectra have been recorded in air, after dilution of the catalyst powder with KBr (Aldrich, FT-IR grade) (0.1%, w/w).

Micro-Raman sampling was made by an OLYMPUS microscope (model BX40) connected to an ISA Jobin–Yvon model TRIAX320 single monochromator, with a resolution of 1 cm^{–1}. The source of excitation was a Melles Griot 25LHP925 He–Ne laser that was used in single line excitation mode at $\lambda = 632.8$ nm. The power focused on the samples was always less than 2 mW. The scattered Raman photons were detected by a liquid-nitrogen cooled charge coupled device (CCD, Jobin–Yvon model, Spectrum One).

UV–vis, NIR spectra of catalyst pure powders have been recorded in air, by a Jasco 570V instrument equipped with a DR cell.

2.3. Activity testing for ethanol steam reforming (ESR)

Details on the equipment for activity testing have been previously reported elsewhere [12]. The catalysts (*ca.* 0.5 g, 0.15–0.25 mm particle size) were diluted 1:3 (vol/vol) with SiC of the same size. The catalyst was activated in 50 cm³/min of a 20% H₂/N₂ gas mixture, while heating by 10 °C/min up to 500 °C for 1 h.

Activity testing was carried out by feeding 0.017 cm³/min of a 3:1 (mol/mol) H₂O:CH₃CH₂OH liquid mixture by means of a Hitachi, model L7100, HPLC pump, added with 56 cm³/min of N₂, used as internal standard, and 174 cm³/min of He. Such dilution of the feed stream was calibrated so to keep the reactants mixture in the vapour phase even at zero conversion at the reactor outlet.

The activity tests were carried out at atmospheric pressure, GHSV = 1750 h^{–1} (referred to the ethanol + water gaseous mixture) at 500 °C.

The analysis of the out-flowing gas was carried out by GC analysis. Repeated analyses of the effluent gas were carried out every hour and the whole duration of every test at each temperature was *ca.* 8 h. The raw data, expressed as mol/min of each species

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