

Dry reforming of ethanol over supported Ni catalysts prepared by impregnation with methanolic solution



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ABSTRACT

Nickel catalysts were prepared on single-oxide supports of Al₂O₃, CeO₂, MgO and ZrO₂ by impregnation of the oxide with a solution of Ni(NO₃)₂ in methanol. The catalysts were characterized by N₂ physisorption (BET method), TPR, XRD, SEM and Raman spectroscopy and tested in dry reforming of ethanol (DRE). It was observed that the interaction with the support and Ni reducibility depended on the support used. According to TPR results, NiO species supported on CeO₂ and Al₂O₃ were the easiest to reduce. Possibly, this behavior combined to redox properties of CeO₂ inhibited side undesirable reactions and contributed to the higher selectivity for H₂ on the NiCe catalyst. The catalytic test at 750 °C on NiCe showed better H₂ selectivity than the test at 700 °C, suggesting that the higher temperature enhanced CO₂ conversion and hindered carbon deposition in dry reforming of ethanol reactions.

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1. Introduction

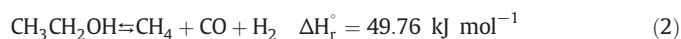
The reforming of ethanol with carbon dioxide has been investigated as a new way to produce synthesis gas. The use of ethanol as a fuel is attractive because it is derived from a renewable source—sugar cane or corn—and leads to a low net emission of greenhouse gases, mainly CO₂, which was first consumed from the atmosphere to form the cane biomass [1]. The net emission of CO₂ can also be reduced by sequestration of this gas [2,3] and its use in alternative processes, such as the carbon dioxide reforming of ethanol (dry reforming of ethanol, DRE).

Research on carbon dioxide reforming of ethanol is quite recent. Tsiakaras and Demin [4] studied the thermodynamics of this reaction but did not carry out experiments. Wang et al. analyzed the thermodynamics of dry reforming of ethanol (DRE) in terms of Gibbs free energy minimization and observed the effects of reaction conditions on H₂ and CO yields and concluded that high temperatures and high CO₂:C₂H₅OH molar ratios (especially above 1.2) favor ethanol and CO₂ conversions and inhibit coke formation [5]. Under conditions of complete conversion, the production of H₂ was around 95% and that of CO was around 97%.

Dry reforming of ethanol can be represented by the following main reaction:



Parallel reactions may happen, including reactions observed in the steam reforming of ethanol and reactions of carbon formation, such as:



Nickel catalysts are interesting for this reaction, in view of the low cost of nickel compared to noble metals and its high selectivity for cleaving carbon–carbon bonds [6,7]. There are many studies in the literature of Ni catalysts applied to ethanol steam reforming [8].

However, Ni-based catalysts are prone to coke formation, which may deactivate the catalyst. Therefore, new methods must be found to enhance the nickel catalysts, so as to prevent the deactivation and obtain high selectivity and activity.

Bellido and Assaf studied nickel catalysts supported on Y₂O₃–ZrO₂, synthesized by the polymerization method and by wet impregnation. The two synthetic methods were compared by a catalytic test of DRE. The maximum conversion of CO₂ was 61%, achieved by 5NiYZ, prepared by polymerization, with 5% Ni loading. The authors concluded that the catalysts synthesized by polymerization performed better than those prepared by impregnation [9].

The choice of support, heat treatment, synthetic reagents, solvent and the percent load of the active phase all influence the characteristics

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and properties of catalysts such as their reducibility, specific surface area and dispersion of the metal phase, these properties being responsible for the catalytic performance. There are reports of the use of ethanol as a solvent in the synthesis of supported Co catalysts by impregnation [10,11]. Song and Ozkan tested Co catalysts supported on CeO₂, prepared by wet impregnation and ethanol impregnation, in the steam reforming of ethanol [11]. They concluded that the solvent does not influence the size of the cobalt oxide species, but it can influence the size of cobalt particles and crystallites reduced by H₂ during TPR or activation before the reaction. Their results suggest that organic solvents suppress particle growth during reduction and may prevent the segregation of Co⁰ particles.

Lucredio et al. studied the effects of the solvent on catalyst properties, such as crystal size, and its influence on the catalytic performance in ethanol steam reforming. The authors compared the use of water and methanol as the solvents in the impregnation method and observed that supported cobalt catalysts prepared by impregnation with methanol as solvent had smaller crystallites of Co⁰ than catalysts prepared by impregnation with aqueous solution. Furthermore, it was observed that a larger specific surface area of the support and heat treatment led to smaller particles and also stabilized them because of the stronger Co–support interactions [12].

In the context of the above discussion, the aim of this study was to investigate the interference of the type of support in the catalytic activity of the supported Ni in the dry reforming of ethanol and to verify the use of methanol as solvent in the synthesis of supports and catalysts to obtain high specific surface areas and low crystallite sizes of Ni in order to improve activation of metal by reduction with H₂, respectively.

2. Experimental

2.1. Preparation

Initially supports were prepared by dissolving the respective precursor salts, Al(NO₃)₃·9H₂O, (NH₄)₂Ce(NO₃)₆, Mg(NO₃)₂·6H₂O and ZrO(CH₃COO)₂, in methanol, continuously stirred at 50 °C for 12 h. After drying at 80 °C for 12 h, the samples were heated at 2 °C min⁻¹ and then calcined in air at 750 °C for 2 h, to obtain respectively Al₂O₃, CeO₂, MgO and ZrO₂ as supports.

5 wt.% of Ni was added to the supports Al₂O₃, CeO₂, MgO and ZrO₂ by impregnation with a methanolic solution of Ni(NO₃)₂·6H₂O under constant stirring for 12 h, until complete methanol evaporation. After impregnation of Ni, the samples were dried at 80 °C and named NiAl, NiCe, NiMg and NiZr, to indicate the samples supported on Al₂O₃, CeO₂, MgO and ZrO₂, respectively. These catalysts were characterized and tested for catalysis of the DRE, without further calcinations.

2.2. Characterization

The composition of the catalysts was determined by energy dispersive X-ray spectroscopy (EDS), using a LEO 440 scanning electron microscope with a tungsten filament, coupled to an energy-dispersive X-ray detector. The samples were made up of pellets and coated with a layer of gold to avoid a build-up of charge.

The specific surface areas of the supports and catalysts were determined by the N₂ physisorption (BET) method, introduced by Brunauer, Emmett and Teller in (1938), in a Quantachrome NOVA 1000e surface area analyzer.

The crystal structures were investigated by X-ray diffraction (XRD) in a Rigaku Multiflex X-ray diffractometer with a Cu-Kα (λ = 1.5418) radiation source and a Bragg angle scan rate of 2° min⁻¹, from 3° to 80°. The samples were analyzed just after having been reduced ex-situ at 700 °C in flowing H₂ and also after the catalytic test. The Ni metal crystallite size was estimated by the Scherrer equation: $D = K * \lambda / \beta * \cos(\theta)$, where: D = crystallite diameter; θ = Bragg angle; β = line width at half the

maximum intensity in radians; K = 0.9, for a sphere-like particle and λ = 1.5406 Å.

Temperature-programmed reduction (TPR) of the catalysts was carried out in a quartz U-shaped tube reactor with a mixture of H₂ (1.96%)/Ar flowing at 30 mL min⁻¹. 100 mg of the catalyst was heated from room temperature to 1000 °C at the rate of 10 °C min⁻¹. Water produced in the reaction was removed by driving the exit stream through a tube containing silica gel. The dried outlet gas was analyzed by a thermal conductivity detector (TCD) and the H₂ content was recorded continuously. The amount of hydrogen consumed during a TPR peak was determined by comparing the area under the curve with that of a standard CuO sample. TPR of the supports was recorded to measure the H₂ consumption needed for support reduction and this value was subtracted from the H₂ consumption found for the catalysts.

Raman spectroscopy was used to characterize the carbon after the reaction. The Raman spectra were collected in a Lambda Solution Dimension-P2 spectrometer equipped with a CCD detector. The samples were excited with a laser at wavelength of 785.01 nm and power of 36.0 mW and the spectra were acquired in five scans of 180 s for each sample.

Scanning electron microscopy (SEM) images were obtained in a LEO-440 electron microscope with an Oxford detector, operated with a 20 kV electronic beam. The spent catalysts, collected after the reaction, were suspended in ethanol, sonicated and, after being air-dried, covered with a sputtered gold layer in a Bal-Tec MED 020 sputter-coater.

2.3. Catalytic tests

The catalytic tests were carried out at atmospheric pressure, in a fixed-bed tubular quartz micro-reactor (i.d. = 10 mm). The gaseous products were analyzed in-line by gas chromatography in a CP-3800 Varian chromatograph with two TCDs, detecting the effluents from parallel Porapak N and Molecular Sieve columns. Prior to the reaction, 150 mg of the catalyst was introduced into the reactor and reduced in situ in flowing H₂ (30 mL min⁻¹) at 700 °C (10 °C min⁻¹) for 1 h, to activate it. A thermocouple was located in the catalyst bed, to control the temperature. The reaction was started in a hydrogen-free feed by purging the sample with a flow of pure N₂. The catalysts were tested in the dry reforming of ethanol at 700 °C (NiCe) and 750 °C (NiCe^a), with a feed of molar ratio CO₂:C₂H₅OH = 1.5:1, flowing constantly at 2.5 mL min⁻¹.

The catalyst sample that performed best, NiCe, was also tested in a catalytic reaction with a feed of molar ratio CO₂:C₂H₅OH = 1:1, at 750 °C (NiCe^b).

During the reaction, the liquid products were condensed in a cold trap kept at 0 °C. At the end of the reaction, the condensed liquid products collected were analyzed in a gas chromatograph (Hewlett Packard 5890) with HP-FFAP capillary column (25 m × 0.2 mm i.d.) and FID detector. During the sample preparation, the solution was kept at a temperature lower than 10 °C, to avoid any liquid product evaporation.

The total ethanol conversion during the test was taken as the total volume of ethanol fed to the reactor minus the volume of condensed ethanol, expressed as a percentage of the total fed ethanol. The selectivity of each product (i = H₂, CH₄, CO₂, CO or C₂H₄) was calculated by the following equation:

$$\text{Selectivity for } i = F_i \text{ produced} / F_{\text{ethanol converted}} \quad (5)$$

where:

$$F_i \text{ produced} \quad \text{molar flow rate of } i \text{ produced in outlet stream}$$

$$F_{\text{ethanol converted}} \quad \text{molar flow rate of ethanol converted.}$$

Carbon deposition was determined by gravimetric analysis.

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