



Study of preparation method and oxidization/reduction effect on the performance of nickel-cerium oxide catalysts for aqueous-phase reforming of ethanol



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HIGHLIGHTS

- The ratio of Ce₂O₃ to CeO₂ in catalysts increased during use in the APR reactor.
- The Ce³⁺ reduces nickel in situ, so reduction prior to use is not important.
- The oxygen mobility through reduced CeO_x leads to less CO in product gas.
- Difference in the metal particle size affect the catalytic efficiency.
- SG catalysts with smaller Ni are superior for APR of EtOH than the SCS samples.

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ABSTRACT

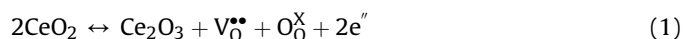
The effect of preparation method and oxidation state of the active metal on the catalytic activity of Ni–Ce–O catalysts was studied for aqueous phase reforming of ethanol. A sol-gel (SG) route and a solution combustion synthesis (SCS) method were used for the preparation of 10 wt% Ni loaded catalysts. The catalytic activity of three groups of catalysts; reduced at 425 °C (HR, metallic Ni), reduced at 1000 °C (FR, metallic Ni), and not reduced (NR, as NiO) were tested at different operating conditions. The difference in the metal particle sizes, governed by the preparation method, affects the catalytic efficiency most, not the reduced or oxidized state of Ni. The SG samples were superior for ethanol conversion and selectivity for H₂ and CO₂ compared to the SCS samples. The X-ray photoelectron spectroscopy (XPS) analysis of the samples demonstrated that the relative ratio of Ce₂O₃ to CeO₂ increased inside the reactor. While Ni doping increases oxygen mobility in the Ce–O lattice, Ce³⁺ converts Ni²⁺ to metallic Ni inside the reactor. This can explain why the reduction stage for Ni–Ce–O system in APR is irrelevant. Higher oxygen mobility through the support helps oxidation of CO to CO₂ leading to improved catalytic performance.

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1. Introduction

Cerium oxide (CeO₂) a fluorite structured ceramic oxide either as a sole support or as an additive is well known to enhance the catalytic activity of metal-oxide catalyst systems. It increases oxygen storage capacity, buttresses the metal dispersion of the three way auto catalysts, and enhances CO to CO₂ conversion as a consequence [1–7]. In case of pristine CeO₂, CO oxidation occurs by a Mars–van Krevelen-type mechanism, according to which the

ceria surface is capable of undergoing alternate reduction (Ce³⁺) and oxidation (Ce⁴⁺) with the formation of surface oxygen vacancies (as the key step) as shown in the following equation and giving high oxygen mobility through the lattice [8].



Oxygen atoms in CeO₂ are very mobile and leave the ceria lattice easily, giving rise to a large variety of non-stoichiometric oxides with the two limiting cases CeO₂ and Ce₂O₃. Ni doping in CeO₂ can create oxygen vacancies as follows [9–13]:



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This high oxygen mobility prevents carbon deposition on the surface.

An aqueous-phase reforming (APR) study of ethylene glycol over different metallic systems manifested the superiority of Pt and Pd metal catalysts for selectivity of producing H₂ and Pt shows higher catalytic activity in terms of feed conversion. Higher cost, combined with limited availability of these metals, make it advantageous to develop catalysts based on less expensive metals, such as Ni [14]. Studies show that in order to achieve high H₂ selectivity on a catalyst for the APR of an oxygenated hydrocarbon, a high C–C bond breaking rate, a low C–O breaking rate, and a low methanation reaction rate on metal, and low acidic catalyst supports are required [15]. For Ni, C–C bond breakage is reported to be high with reasonably good water gas shift activity compared to Co, Pt, Pd, Fe, Ir, and Rh [15–18].

For metal-ceramic oxide catalyst systems, it is a generally accepted normal practice to reduce the metal oxide to the active, metallic form which acts as the center of interaction with the reactants, intermediates, and products. In fact it has been claimed in many cases that the formation of a surface oxide layer causes deactivation of metal-oxide catalyst systems [19–21]. However, we observed in our previous work for aqueous-phase reforming of ethanol over Ni/Al₂O₃ catalysts that according to X-ray photoelectron spectroscopy (XPS) data had no surface Ni left in metallic form in the used catalysts, yet the activity of the catalysts were appreciably high. Dueso et al. recently reported the reactivity of a NiO–Al₂O₃ oxygen carrier system for chemical-looping combustion of methane. They showed that depending on the relative ratio of NiO and spinel, the conversion of alkanes and formation of H₂ and CO may vary and the oxide species is more reactive than the spinel [22]. This raises the question regarding the mechanism of catalytic activity of metal-ceramic oxide systems for APR of biomass. It is well known that existence of synergism between components can affect the efficiency of the oxide based catalysts tremendously [22–25].

In this paper, we present a study regarding the effect of catalyst preparation methods and the reduced and oxidized state of the metal on the performance of nickel-cerium oxide catalysts for aqueous-phase reforming of EtOH. 10 wt% metal loaded catalysts were prepared in two different ways; the first one is a direct sol-gel (SG) method and for the second one the ceria support was made by a solution combustion synthesis (SCS) route and then the metal was loaded by standard wet impregnation. The catalytic activity of these catalysts was compared at different temperatures, pressures, feed flow rates, and feed concentrations. X-ray diffraction data has been used to obtain information on the phase content and particle size, while H₂-pulse chemisorptions were used to depict the dispersion percentage and average particle size of the active metal phase. Temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) have been used to understand the metal-support interaction, and temperature program desorption of ammonia (NH₃-TPD) has been used to analyze acidity of the support. X-ray photoelectron spectroscopy (XPS) has been used to characterize the surface chemistry of catalysts.

2. Experimental

2.1. Preparation of catalysts

The Ni loaded CeO₂ catalysts were prepared by using two procedures; a sol-gel method and a solution combustion method (SCS). For the second one the CeO₂ support was made and then the metal was loaded by the wet impregnation method.

The classical Pechini sol-gel route [26] was used for the preparation of catalyst. Cerium(III) nitrate hexahydrate [(Ce(NO₃)₃·6H₂O,

Fisher, >99%] and nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O, Fisher, >98%] was mixed with DI water-ethanol solution. Little diluted HNO₃ was added in the solution. Equimolar citric acid and polyethylene glycol, was added as for chelating and cross linking purposes, respectively in this solution. The solution was continuously stirred at 70 °C until a light blue-greenish color transparent gel was obtained. Then the gel was dried at 110 °C for 12 h and calcined at 350 °C for 3 h in air.

The method for the preparation of CeO₂ powder by solution combustion synthesis has been described elsewhere [27] in detail. No post combustion heat treatment was applied on this powder. The metal (10 wt% Ni) was loaded in the SCS powder by a standard wet impregnation method. The Ni loaded samples were heat treated at 350 °C in air to convert the Ni(NO₃)₂·6H₂O to NiO [28].

2.2. Characterization

X-ray diffraction (Siemens D 500 system with a CuK_α radiation, operated at 40 kV and 30 mA) of all the samples was performed over a range of 20°–80° 2θ to identify the phases present and the crystallinity of the powders. The grain size (*D*) was calculated by using the Scherrer's formula.

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (3)$$

where, λ = wavelength of the CuK_α radiation, ~1.54 Å, θ = Half of the peak position in 2θ and, $B = (B_m^2 - B_s^2)^{1/2}$, where B_m is the measured full width at half maxima (FWHM). The instrumental broadening (B_s ~ 0.1°) was determined by measuring a standard polycrystalline Si sample under the same scanning and data acquisition rates. In general, the maximum grain size that can be measured by XRD is 1000 Å.

The XPS spectra were acquired by a Kratos AXIS Ultra X-ray photoelectron spectrometer using monochromatic Al K_α source operating at 300 W. The operating pressure was 3 × 10^{−9} torr. Charge neutralization using low energy electrons was used for charge compensation. Following a survey of each area, high-resolution spectra of C 1s, O 1s, Ce 3d and Ni 2p were acquired. A linear background was used for quantifying the C and O spectra and Shirley background for quantifying Ni and Ce spectra. All the spectra were charge referenced to the aliphatic carbon at 284.8 eV. Individual peaks of constrained FWHM, position and 70% Gaussian/30% Lorentzian line shape were used for curve fitting. For species identification, the Ni 2p spectrum has been deconvoluted based on the constraints of equal spin-orbit splitting. The height ratio of Ni 2p 3/2 to Ni 2p 1/2 was constrained at 2:1 with the same FWHM.

Temperature programmed reduction (TPR), temperature programmed oxidation (TPO), H₂-pulse chemisorption, and BET surface area of the samples were characterized by a Micromeritics Autochem–II 2920 catalyst characterization system with a thermal conductivity detector (TCD). TPR was carried out under flowing 10% H₂–Ar of 10 cm³ min^{−1} and the sample was heated up to 1050 °C at 10 °C/min rate.

For TPO the samples were reduced first. TPO experiments were carried out under flowing 10%O₂–He, at 10 cm³ min^{−1} and the sample was heated at 10 °C/min with simultaneous recording of the TCD reading with temperature.

The H₂-pulse chemisorption analyses have been carried out to determine percent metal dispersion, average active particle size, and active surface area of metal on the support by applying measured doses of reactant gas to the sample. For pretreatment, the sample was reduced by flowing 10% H₂–Ar of 25 cm³ min^{−1} over the sample, while ramping the temperature up to 1050 °C at 10 °C/min. The maximum temperature was held for 2 h with flowing He

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