Carbon dioxide reforming of methane over co-precipitated Ni–Ce–ZrO₂ catalysts

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An active and relatively stable Ni–Ce–ZrO₂ catalyst has been designed and prepared conveniently by a novel one-step co-precipitation/digestion method. This catalyst exhibited higher stability compared with a catalyst having the same composition but prepared using the conventional impregnation method. It was found that 15% Ni (w/w) co-precipitated with Ce–ZrO₂ making the cubic phase of Ce₀.₈Zr₀.₂O₂ gave synthesis gas with CH₄ conversion more than 97% at 800 °C and that the activity was maintained for 100 h during the reaction. The higher activity, conversion and stability of these catalysts are mainly related to the nano-crystalline nature of cubic Ce₁₋ₓZrₓO₂ producing strong interaction with finely dispersed nano-sized NiO crystallites.

KEY WORDS: co-precipitation/digestion; cubic Ce₁₋ₓZrₓO₂; CH₄; CO₂; Ni; reforming.

1. Introduction

During the last decade, the CO₂ reforming of CH₄ (CDR) has received much attention for the production of synthesis gas as a complementary process over the well-established steam-reforming process because of both environmental and commercial reasons [1,2]. Nickel-based catalysts on various support materials showed high activity in this reaction comparable to noble metals [3–6]. However, Ni catalysts easily deactivate by coke formation and/or sintering of the metallic and support phases [4,6,7].

Recently, there has been interest in mixed oxide catalyst systems containing CeO₂–ZrO₂ [8]. It has been reported that the addition of ZrO₂ to CeO₂ leads to improvements in the oxygen storage capacity of CeO₂, the redox property, thermal resistance and promotion of metal dispersion [8–10], resulting in better performance in certain reactions such as CO oxidation [11] and combustion of methane [12]. This was found to be due to the partial substitution of Ce⁴⁺ with Zr⁴⁺ in the lattice of CeO₂, which results in a solid solution formation [9]. Because of better thermal stability as well as their enhanced oxygen mobility, the Ce₁₋ₓZrₓO₂ system has appeared as a promising candidate to be used as a support material in nickel-based catalyst systems. Only a limited number of papers have been concerned with this objective [13–15]. Lercher et al. [6] have reported that Pt/ZrO₂ showed excellent performance in CDR. However, Ni/ZrO₂ with a high Ni loading is not viable for CDR due to coke formation. Li et al. [16,17] have reported that Ni/ZrO₂ catalysts with more than 10 wt% Ni loading showed high activity at 750 °C for 30 h in CDR despite producing a large amount of carbon. However, its stable activity can be obtained only under diluted reaction conditions, namely dilution of reactants with N₂ and dilution of catalysts with quartz sand. Previously, Ni catalysts supported on a tetragonal Ce–ZrO₂, prepared by the molten salt method, were applied to steam reforming of methane (SRM) [18,19], oxygen-reforming of methane (ORM) [20,21], and oxygen-SRM (O-SRM) [18,21]. Montoya et al. [22] applied Ni supported on a tetragonal CeO₂–ZrO₂ support for the CDR reaction; however, the problem of support sintering at 800 °C could not be avoided completely.

It has been reported that the cubic phase of CeO₂–ZrO₂ has more oxygen storage capacity and is more easily reducible than the tetragonal phase [7,23]. It is also known that Ni dispersion using the co-precipitation method is higher than that employing the conventional impregnation method [9]. To the best of our knowledge, cubic Ce₀.₈Zr₀.₂O₂ support containing nickel has not yet been tried in the CDR reaction. In the work described in this paper, a novel one-step chemical co-precipitation/digestion method was used to prepare a nickel-based catalyst on a cubic Ce₀.₈Zr₀.₂O₂ support for evaluation in CDR.

2. Experimental

Cubic Ce₀.₈Zr₀.₂O₂ catalysts with varying NiO concentrations were prepared by a one-step co-precipitation/digestion method. Stoichiometric quantities of zirconyl nitrate solution (20 wt% in ZrO₂ base, MEL...
Chemicals), cerrous nitrate (99.9%, Aldrich) and nickel nitrate (97%, Junsei Chemicals) were dissolved in distilled water, and the resulting solution was transferred to a round-bottomed flask. To this solution an aqueous solution of 20% KOH (w/w) was added drop-wise at 80 °C with constant stirring to attain an alkaline pH (9.5–10.5). During the entire course of co-precipitation reactions, the pH was maintained in this alkaline range. The precipitates were digested at 80 °C for 72 and 96 h. Later, they were thoroughly washed with distilled water several times to remove any potassium impurity and then initially air-dried for 48 h followed by drying at 120 °C for 6 h. The dried mass thus obtained was then finely ground to a particle size less than a micron. This material was finally calcined at 500 °C for 6 h in an aerobic environment to get the final catalyst material. Many synthesis parameters such as pH, digestion time, addition sequence and use of tetrpropyl ammonium bromide, i.e., TPABr (4.3% by weight), were systematically varied. This was done to optimize conditions in order to get high surface area in 30% Ni loaded (w/w) on cubic Ce0.8Zr0.2O2 material after calcination at 500 °C for 6 h. Furthermore, Ni content was gradually varied from 5 to 15% in the Ce0.8Zr0.2O2 supports in order to optimize the Ni loading. Simultaneously, for comparison, a Ce0.8Zr0.2O2-supported Ni catalyst system with optimized Ni loading (15%, w/w) was prepared by the conventional impregnation method. This was achieved by impregnating appropriate amounts of Ni(NO3)2·6H2O onto cubic supports of Ce0.8Zr0.2O2 (prepared by the co-precipitation methodology described previously), followed by drying at 100 °C and later calcining the material at 800 °C for 6 h in air. Similarly, a Ce0.8Zr0.2O2-supported 15% Ni catalyst system was also prepared by calcining the one-step co-precipitated material at 800 °C for 6 h in air.

The BET specific surface area was measured by nitrogen adsorption at −196 °C using a Micromeritics (ASAP-2400) surface area measurement apparatus. The XRD patterns were recorded using a Rigaku 2155D6 diffractometer (Ni filtered Cu Kα radiation, 40 kV, 50 mA). Pulse chemisorptions were performed in a multifunction apparatus. About 250 mg of catalyst was placed in a quartz reactor. Before pulse chemisorption, the sample was reduced in 5% H2/Ar at 700 °C for 3 h. Then the sample was purged in Ar at 720 °C for 1 h and cooled to 50 °C in flowing Ar. Hydrogen was pulsed over the catalyst to measure the chemisorption at 50 °C using 5% H2/Ar and continued at 8 min intervals until the area of the hydrogen peak on the chromatograph was identical. Based on the hydrogen uptake, the surface area of Ni was calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni = 1).

Activity tests were carried out using a fixed-bed micro-reactor [18]. The reactant feed comprised a gaseous mixture of CH4:CO2:N2 (1.00:1.04:1.00). N2 was employed as the reference for calculating CH4 and CO2 conversion. Each catalyst was reduced in the reactor with 5% H2/N2 at 700 °C for 2 h prior to each catalytic measurement. The CDR reaction was tested at 800 °C. Effluent gases from the reactor were analyzed by a Chrompack CP9001 gas chromatograph (fitted with a fused silica capillary column (CarboPLOT P7)) equipped with a thermal conductivity detector (TCD).

3. Results and discussion

3.1. Synthesis and catalyst characterization

An aim of the present study was to optimize the preparation parameters in a one-step co-precipitation/digestion methodology toward the co-precipitation of nickel, cerium and zirconium hydroxides, and thus obtain a novel NiO dispersed cubic Ce0.8Zr0.2O2 matrix with high surface area. Another aspect of this work was to evaluate the performance of the catalyst systems in the CDR reaction for elevated time periods in order to test catalyst stability.

Table 1 summarizes characteristics of the supports and catalysts prepared by the one-step co-precipitation/digestion after the calcination step at 500 °C for 6 h in static air. The highest surface area (181 m²/g) was obtained at a pH of 10.5. However, if the pH is 9.5, then the surface area decreases to 62.3 m²/g. The increase in digestion time from 72 to 96 h resulted in lowering the surface area from 181 to 154 m²/g. The addition of TPABr and reverse addition of cationic solution to the precipitant are not beneficial to improving the surface area. Hence, the optimized reaction condition to obtain high surface area materials is achieved by the addition of 20% precipitant, viz. aqueous KOH, to an aqueous solution containing stoichiometric concentrations of cerium, zirconium and nickel nitrates for a digestion time of 72 h at 80 °C.

For a comparison of the surface area of the various catalytic materials, samples of cubic Ce0.8Zr0.2O2 and CeO2 were synthesized by the one step co-precipitation/digestion methodology described above. It was observed that the surface area of Ce0.8Zr0.2O2 was 115 m²/g, whereas that of CeO2 was 112 m²/g after calcination at 500 °C for 6 h. The surface-area values are quite comparable with reported data for similar compositions prepared by other chemical routes such as a sol-gel, hydrothermal, microwave hydrothermal, micro-emulsion and high-energy ball milling [3,24,25].

In order to understand the phase composition, crystallinity and size of crystallites in these materials, XRD patterns of the 30% Ni on cubic Ce0.8Zr0.2O2 samples were obtained (figure 1). All the patterns showed reflections typical of the cubic fluorite structure of Ce0.8Zr0.2O2 corresponding to the (111), (200), (311), (222) and (400) planes. The lines corresponding to