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Iron–ceria spinel ($FeCe_2O_4$) catalyst for dry reforming of propane to inhibit carbon formation

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ABSTRACT

Dry reforming of propane (DRP) with CO_2 was examined over iron–ceria spinel ($FeCe_2O_4$) that was synthesized on mesoporous alumina foam by the sol–gel method. The $FeCe_2O_4$/Al-F catalyst exhibited significant catalytic activity for the DRP with propane and CO_2 conversions of 93% and 76%, respectively. Moreover, the redox behavior of the spinel was found to greatly reduce the deposition of carbon, which could be attributed to the oxidation of surface carbon to CO via the interaction with $FeCe_2O_4$ lattice oxygen. The $FeCe_2O_4$/Al-F catalyst with good catalytic activity, long-term stability and coke resistance may be a promising candidate for the DRP.

Introduction

The production of synthesis gas (syngas; a mixture of H_2 and CO) is an important industrial process in the conversion of natural gas to liquid fuels, petrochemical products and essential building blocks for chemicals [1,2]. In this regard, dry reforming has received much attention as a technology to produce syngas for the production of sulfur-free liquid fuels and oxygenated chemicals at a low H_2/CO ratio by syngas [3,4]. Dry reforming of methane with CO_2 is a well-known process that has been extensively studied owing to its industrial importance to produce syngas [5–7]. Recently, considerable attention has been paid to the dry reforming of light hydrocarbons such as ethane and propane as an alternative hydrocarbon for the production of syngas [8–14]. More precisely, propane has many advantages as a hydrogen source over natural gas; it can be stored as a compressible liquid and is easily transportable [15]. Propane was expected to produce more surface carbon species compared to natural gas due to a higher carbon atom content, consequently, creating an ideal environment for the challenge that needed to be overcome. Moreover, utilizing higher hydrocarbon substrate is preferred as it requires less energy for the bond breakup. Furthermore, higher hydrocarbons are known to have a lower flammability limit which is 5.3–15% for methane and 2.2–9.6% for propane. It exists in gaseous form at standard temperature and pressure. The overall reaction for the dry reforming of propane (DRP) is as follows:

$$C_3H_8 + 3CO_2 = 6CO + 4H_2 \quad \Delta H^0_{298k} = 644.8\,kJ\,mol^{-1} \tag{1}$$

Up to now, many previous studies on the catalytic DRP using noble metals such as Pt, Ru, Rh, and Re have been reported [11,16–19]. Even though the noble metals have high catalytic activity and selectivity for the dry reforming process, the high cost and limited availability restrict their applications in industry. Several transition-metal-based catalysts, typically nickel can be a cost-effective alternative (compare to noble metals), and many researchers have found that Ni-based catalysts also have good activity for dry reforming reactions [15,20]. However, Ni-based catalysts undergo rapid deactivation due to sintering as well as coke formation. Apart from the metal oxides, bimetallic catalysts, such as Ni–MgO, Ni–CeO_2, and Co–Ni, have been studied for dry reforming reactions; however, even though these catalysts were reported as being highly reactive in dry reforming, they led to the formation of a significant amount of coke and the sintering of catalysts [21]. One method to improve the coke-resistance is to design a catalyst with a site at which the phase (Fe, Ni) could be activated within a well-defined structure. In this regard, perovskite and spinel compound were reported to be an exciting catalytic material [22–25]. These structures increase the metal reduction

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temperature such that it is closer to the reaction temperature. An example is a noble spinel compound, which showed high reactivity and stability towards the dry reforming of methane [26]. A highly dispersed active phase could be obtained in this way with decreased coke formation. This method could also enhance the metal-support interaction, the formation of the solid solution, and thermal stability. Spinel compounds represented by the general empirical formula AB_2O_4 where A and B represent divalent and trivalent metal cations, respectively, have been extensively studied as a heterogeneous catalyst [27]. Guo et al. reported a comparison of the $MgAl_2O_4$ spinel oxide catalyst with MgO-γ-Al_2O_3 and γ-Al_2O_3. The authors observed high activity and coking resistance to enhanced control over sintering [28]. Khoo and Tan have reported that a bimetallic NiFe catalyst increases the catalytic stability and Fe actively reduces the carbon deposition via Fe redox to FeO [29]. During the last decade, researchers have used lanthanide oxides such as La_2O_3 and CeO_2 as highly oxidative agents that are able to readily store and release oxygen [30]. CeO_2 has the ability to release lattice oxygen and be quickly re-oxidized, thereby enhancing the catalytic performance [13,29,31]. In this work, the use of iron as an A-site cation was investigated, because iron has redox properties and Fe can oxidize the carbon to CO during dry reforming to prevent deactivation [32]. Cerium was selected as a paired B-site cation since cerium oxides showed prominent oxidation activity and as a basic rare-earth metal it is capable of preventing coke formation. An iron ceriate spinel compound, prepared by the sol-gel method using citric acid as a chelating agent, was used in the DRP [33–35].

In this work, we have used propane as the primary reactant. Various other support materials have been investigated such as SiO_2, TiO_2, ZrO_2 and MgO [11,36]. In many cases, Al_2O_3 has been used as a catalyst support [37]. According to reports in the literature, the mechanism of dry reforming is strongly dependent on the support materials. Suitable supports have to be resistant to high temperature and should be able to maintain metal dispersion during operation [12,38–40]. In the experiments described in this paper, mesoporous alumina foam was used as a catalyst support. The alumina foam has 60 pores per inch (PPI), and it can easily be used as a commercial system due to the low drop in pressure of packed bed reactors [41,42]. The present study aims to discuss the results obtained for the dry reforming and the inhibition of coke formation by the combination of iron with cerium in the definite structure, in order to stabilize the structure and to limit the sintering of the active metal species. In addition, we also studied the stability of the catalyst in terms of DRP to syngas.

Materials and methods

Catalyst preparation

The $FeCe_2O_4$ spinel, NiO–CeO_2 and CeO_2 catalysts on commercial alumina foam (Al-F) support were synthesized by the sol–gel method. The commercial Al-F supports were purchased from ShengQuan Ltd., China. The default size of commercial Al-F foam was 70 mm × 70 mm × 14 mm (length × width × height) and then cut into cylindrical shape pellets (14 mm in length and 10 mm OD) by a puncher. Each pellet weighs ~0.8 g. The Al-F support was pretreated for 2 h at 150 °C to remove moisture. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) and citric acid were used as catalyst precursors. The chemicals were purchased from Daejung Chemicals Ltd., South Korea. The Fe-Ce spinel catalysts were formed by preparing 0.5 M aqueous solution of iron and cerium nitrates (each 20 mL). An appropriate volume (20 mL) of citric acid solution (1.0 M) was poured into metal nitrate solution. The initial citric/nitrate stoichiometric molar ratio was equal to 1. The mixed solutions were heated at 80 °C and stirred continuously until a viscous gel was obtained. The pretreated Al-F pellets were poured into the gel solution to allow the solutions to be entirely absorbed by Al-F. The resulting foam was further dried at 110 °C for 12 h. During the drying at 110 °C, the gel started boiling with bubbling and foaming and with the rapid evolution of a massive quantity of gases, producing a foamy and voluminous powder. The Al-F after drying contained carbonaceous residues. These residues were eliminated by further heating the Al-F at 700 °C for 2 h in air. Finally, the ~20 wt.% of Fe–Ce spinel catalyst on Al-F ($FeCe_2O_4$/Al-F) was obtained. The same procedure was used to prepare Ni-Ce (NiO–CeO_2/Al-F) and CeO_2/Al-F catalysts. The total loaded weights of metal oxide in all catalysts on the surface of the Al-F were the same which was measured by the weight of the Al-F before and after synthesis.

Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the prepared catalysts were obtained with a Rigaku powder diffractometer (Japan) using nickel-filtered CuKα radiation (λ = 0.154 nm) operated at 40 mA and 40 kV. The X-ray diffractograms were analyzed using X'Pert ScorePlus software. The measurement was carried out in the 2θ angle range from 20° to 90° with a step of 0.04°. The crystallite size was calculated using Debye-Scherrer's Eq. (2) as follows:

$$D = \frac{K\lambda}{(\beta \cos \theta)} \quad (2)$$

where D is the average crystallite size, K is a constant, λ is the wavelength of the X-ray radiation, β is the full width at half maximum of intensity peak, and θ is the diffraction angle. The Brunauer–Emmett–Teller(BET) surface area of the prepared samples was determined with a Quantachrome Auto absorber by N_2 adsorption at −196 °C after outgassing the sample at 300 °C for 3 h. The Raman spectra of the samples were analyzed using a LabRam HR Evolution Raman spectrometer (Horiba, Japan). The instrument was operated at an Ar laser power of 10 mW, and an excitation wavelength was 514 nm. The surface morphology of the catalyst was evaluated by field emission-electron scanning microscopy(FE-SEM) (JSM-6700F: JEOL Ltd., Japan), operated at an accelerating voltage of 20 kV and 10 μA. The chemical characteristics of the catalyst surface were examined using X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, U.K) with monochromatic Al Kα radiation (1488.6 eV) operated at 15 kV and a 150-W X-ray excitation source.

The temperature programmed reduction and temperature programmed oxidation (TPR/TPO) measurements were studied in a conventional flow system monitored by the gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). In the TPR experiments, all the catalysts were examined in the temperature range of 25–900 °C, using 100 mg catalyst samples. Each sample was pretreated at 400 °C for 1 h under Ar flow before TPR. After cooling down to room temperature under Ar flow, TPR experiments were conducted under a flow of a 5% H_2/Ar at a total flow rate of 50 mL min^{-1}, with a linear temperature increase of 5 °C min^{-1}. In the TPO experiments, all the catalysts that were studied in the temperature range of 25–900 °C, in a stream consisting of the mixture 5% O_2/Ar (a gas flow rate of 50 mL min^{-1}, at a heating rate of 5 °C min^{-1}) to determine the nature of carbon and to estimate the coke after DRP. The TPO was carried out with 100 mg of used catalyst sample at 500 °C with 10% O_2 flowing through the catalyst bed to oxidize the carbon deposited on the catalyst surface. The CO_2 formed from the oxidation of carbon was

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