



A study on characterization and methane dry reforming performance of Co–Ce/ZrO₂ catalyst



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ABSTRACT

The overall purpose of this study is to propose an effective Co-based non-PGM bimetallic carbon dioxide reforming of methane (CDRM) catalyst, and to find the optimal reaction conditions to be used in production of synthesis gas. In catalyst formulation, ZrO₂, which has ability to produce surface oxygen, is used as a support. Ce is used as a promoter in order to increase oxygen storage capacity and to regulate surface oxygen transfer. Freshly reduced and spent catalysts were analyzed by SEM–EDX, HRTEM–EDX, TPO, Raman Spectroscopy and XPS. The reaction conditions were optimised through the use of an experimentally designed procedure using reaction temperature, CH₄/CO₂ feed ratio and space velocity as the parameters. XPS analysis of Co 2p indicated that additional oxidation of Co was limited during CDRM which may only lead to a small decrease in activity. EM measurements showed well dispersion of Co and Ce on the surface. No significant metal sintering was observed. Local changes in Co/Ce ratio were found to have pronounced effect on carbon formation. It is well known that methane dehydrogenation produces surface carbon as the side product covering the active site. The comparative analysis of extent of carbon coverage on Co and Ce sites of the freshly reduced and spent samples through metal mapping by SEM–EDX indirectly confirmed methane dehydrogenation is the primary function of Co sites, and there is no methane activation on Ce sites. A comparative evaluation of XPS Ce 3d obtained from freshly reduced and spent samples on the other hand showed the surface oxygen storage/transfer function of Ce through redox cycle. In the performance tests, high activity with stable performance was observed for 1/1CH₄/CO₂ feed ratio for CDRM over Co–Ce/ZrO₂ catalyst.

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1. Introduction

Carbon dioxide reforming of methane (CDRM) is a catalytic process that produces valuable synthesis gas from methane and carbon dioxide. Compared to other reforming routes, such as steam reforming (SR) or partial oxidation (POX), CDRM has the advantage of utilizing carbon dioxide, which is the most thermodynamically stable greenhouse gas whose concentration rise in the atmosphere has been accepted as the most plausible reason for the recent climate change. CDRM can be directly used without any pre-separation in producing syngas from natural gas, which may have large amount of CO₂ [1]. The low H₂/CO ratio obtained in CDRM is preferable in production of valuable, especially olefinic, hydrocarbons and alcohols via further reactions, like Fischer–Tropsch. Since the reaction is highly endothermic, CDRM can be also used in chemical energy transmission and storage systems [2]. Moreover, the process is suitable to be used in recovering

excess heat from gas turbine exhaust, and as a source of CO and H₂ for flame stabilization in low temperature methane fired gas turbines [3].

The main drawbacks of CDRM are coking and metal sintering. Methane decomposition and carbon monoxide disproportionation through Boudouard reaction are possible reasons of coke formation and deposition. The former is favored at high temperatures and low pressures, whereas the latter is favored at low temperatures and high pressures [4]. The high temperature window required for CDRM, and the formation of H₂O by the reversed water gas shift reaction make the catalysts sensitive to metal sintering [5].

Although noble metals exhibit good activity and suffer less from carbon deposition, they have the drawback of high cost and limited availability [6,7]. As they are relatively cheap and possess high activity, industrial nickel-based catalysts have been preferred for reforming reactions. However, at high CDRM temperatures, they deactivate quickly due to metal sintering and coke deposition.

In designing non-noble metal based catalysts, coke resistance and stable performance can be achieved through the use of a suitable metal(s)–support combination leading beneficial synergy between metal and support [8,9]. The carbon formation in CDRM

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can be controlled by using a support, like ZrO_2 , favoring surface oxygen production via dissociative adsorption of CO_2 ; the carbon formed on the active metal centers is cleaned by this surface oxygen [5,10]. ZrO_2 also has high thermal stability and an appreciable ionic conductivity led by its readiness to form defects and surface oxygen vacancies [11]. Additionally, it is mentioned in literature that the use of supports with low concentration of Lewis acid sites and/or that have basic sites, such as ZrO_2 , MgO , and La_2O_3 , lead to high and stable CDRM performance [12].

In CDRM catalysts, Co is a promising choice as a primary metal owing to its stable performance, abundance and relatively low cost. It has been reported that deactivation of Co based catalysts may be due to metal oxidation under reaction conditions as well as coke deposition. Cobalt oxidation and coke deposition can be avoided through optimizing Co loading, using different supports, promoters and reaction conditions [13,14]. Introducing a second metal(ic) component to form a bimetallic catalyst system also improves the anti-coking property of catalysts [15]. Ceria and ceria-based substrates may enhance the catalytic performance by increasing metal dispersion [9]. It has been previously shown by our group that, owing to its redox properties enabling release and restore of oxygen atoms, Ce is an effective promoter for CDRM catalysts regulating surface oxygen transfer to active metal sites [16,17]. These oxygen species react with methane constituents on the surface of the primary metal, which are formed upon CH_4 disproportionation, resulting in reduced coke formation [5]. Besides, the addition of Zr to CeO_2 increases thermal resistance, redox property and oxygen storage capacity of CeO_2 [18].

The overall purpose of this initial study, which is the first paper of a series, is to propose Co–Ce/ ZrO_2 system as an effective Co-based non-PGM CDRM catalyst, and to find the optimal reaction conditions to be used in production of synthesis gas leading high and stable activity. In order to increase the oxygen storage capacity of the catalyst, Ce was used as a promoter. The freshly reduced and spent catalyst samples were characterized by using SEM–EDX, HRTEM–EDX, TPO, Raman Spectroscopy and XPS in order to analyze dispersion of the active phases, oxidation state of Co and Ce, extent of carbon coverage of the active sites and types of the carbon formed on those sites. The reaction conditions are optimized through the use of an experimentally designed procedure using reaction temperature, CH_4/CO_2 feed ratio and space velocity as the parameters.

2. Experimental

2.1. Catalyst preparation and pretreatment

5% Co–2% Ce/ ZrO_2 catalyst was prepared for the experiments. Zirconia support was first ground and sieved to 45–60 mesh size, and then calcined at 1073 K for 4 h in muffle furnace for high thermal stability. To obtain Co–Ce/ ZrO_2 catalyst, impregnation of aqueous precursor solution of Ce (cerium(III) nitrate hexahydrate) was performed first. The slurry obtained after the impregnation step was dried at 388 K overnight. This was followed by heat treatment at 773 K for 4 h and impregnation of aqueous cobalt(II) nitrate hexahydrate solution. Upon Co impregnation, the slurry was again dried at 388 K overnight. Prior to the performance tests, the catalysts were calcined *in situ* in dry air (30 mL/min) for 4 h at 773 K and subsequently reduced *in situ* in H_2 (50 mL/min) for 2 h at the same temperature.

2.2. Catalyst characterization

SEM, energy dispersive X-Ray (EDX) and HRTEM tests were conducted on freshly reduced (*i.e.*, calcined and reduced) Co–Ce/ ZrO_2

catalyst samples in order to elucidate their micro-structural properties. The SEM micrographs of the spent catalyst samples tested under different reaction conditions were also used to observe whether there is a change in metal dispersion and the morphology of the deposited carbon. SEM analyses were conducted by using a Philips XL 30 ESEM–FEG system, having a maximum resolution of 2 nm. The experiments were performed at the Advanced Technologies Research and Development Center of Boğaziçi University. HRTEM analyses were carried out at the Institute of Materials at TUBITAK–MAM by using JEOL 2100 LaB6HRTEM operating at 200 kV.

In order to understand the nature of interaction between the dispersed metal species and the support, fresh and spent Co–Ce/ ZrO_2 catalyst samples were analyzed by XPS by using Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer at Advanced Technologies Research and Development Center of Boğaziçi University. All binding energies were referenced to the C1s line. For data analysis, the peak intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped Shirley-type background, and by fitting the curve to a combination of Lorentzian (30%) and Gaussian (70%) lines.

The coke deposited spent catalyst samples were analyzed by temperature programmed oxidation (TPO) and by Raman spectroscopy. The TPO experiments were performed via an Intelligent Gravimetric Analyzer (Hiden Isochema) connected online to a dynamic sampling mass spectrometer (Hiden Analytical) for monitoring the combustion products with the following procedure: (i) The spent catalyst sample (~25 mg) was outgassed at 383 K for one hour and then at 298 K overnight to eliminate humidity and trapped gasses, (ii) The sample was subjected to 50 mL/min flow of 5% O_2 –95% He mixture at 1 bar, and then heated to 1023 K with 2 K/min heating rate in order to complete coke oxidation. Results from repeated experiments showed that the TPO profiles were reproducible. Raman spectra of the spent catalysts were obtained by using a Renishaw inVia Raman microscope (Advanced Technologies Research and Development Center of Boğaziçi University) with the following operation parameters: 514 nm 20 mW Ar^+ laser as the excitation source; laser intensity of ~2 mW; 5 s acquisition time; a total of 20 accumulation per spectrum. Before measurements, Raman spectrum was calibrated by using a silicon wafer peak at 520 cm^{-1} . All the samples were analyzed under atmospheric condition without pre-treatment with the de-focusing technique.

2.3. Catalytic performance evaluation

Carbon dioxide reforming of methane was carried out in a fixed-bed down-flow tubular 12 mm ID, 70 cm long quartz microreactor under atmospheric pressure over the Co–Ce/ ZrO_2 catalyst to see the effects of temperature, CH_4/CO_2 feed ratio and space velocity. Prior to each reaction test, the catalyst was calcined and reduced *in situ*. The reaction tests were performed at the temperature interval of 873–973 K with CH_4/CO_2 feed ratios of 1/1, 2/1, 1/2 and space velocities of 30,000, 20,000 and 10,000 mL/h g-catalyst. Hewlett Packard HP5890, temperature-controlled and programmable gas chromatograph equipped with a thermal conductivity detector (TCD) and a HayeSep D column was used for analyzing the feed and product streams.

3. Results and discussion

3.1. Characterization of Co–Ce/ ZrO_2 catalyst

Freshly reduced catalyst samples were characterized by SEM–EDX and HRTEM aiming to study micro-structural properties of the catalysts and dispersion of Co and Ce.

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