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Catalytic conversion of methane and carbon dioxide (greenhouse gases) into syngas over samarium-cobalt-trioxides perovskite catalyst

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ABSTRACT

The catalytic behaviour of samarium-cobalt-trioxides perovskite catalyst was investigated for the mitigation of greenhouse gases (carbon dioxide and methane) to provide cleaner energy (hydrogen and carbon monoxide) and environment. X-ray photoelectron spectroscopy analysis of the as-synthesized catalyst showed peaks corresponding to complexes of cobalt (II), dual oxygen species, and samarium (III) ions. X-ray diffraction pattern showed a monophasic samarium-cobalt-trioxides perovskite structure, while post-reaction analysis showed modification of the perovskite. The temperature-programmed reduction analysis showed peaks corresponding to reduction of cobalt (II) to Co^o. The temperature-programmed desorption displayed peaks ascribed to medium strength basic and acidic sites. Performance test carried out on the catalyst via methane dry reforming, showed excellent reactants conversions of above 90% which was maintained for the duration (30 h) of the experiment. The catalyst remained active over the time of experiment, even though the temperature-programmed oxidation, scanning electron microscopy and energy dispersive X-ray spectroscopy analyses of the used catalyst showed evidence of carbon deposit.
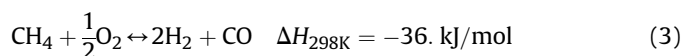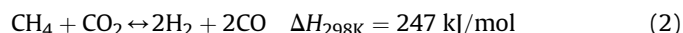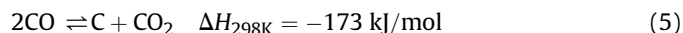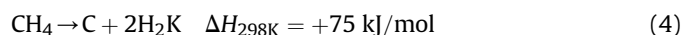
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1. Introduction

Several methods have been employed in the utilization of greenhouse gases. Amongst these methods is the already established steam reforming. Methane conversion to yield H_2 and CO using the steam reforming process occurs by the following reaction (Eq. (1)) (Krylov et al., 1998):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (\Delta H_{298k} = 206 \text{ kJ/mol}) \quad (1)$$
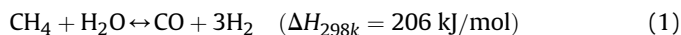
Steam reforming of methane produces syngas with H_2/CO ratios greater than 3. However, the production of methanol, higher alcohols, light alkenes and the Fischer-Tropsch to diesel process requires lower ratio (Tsipouriari and Verykios, 2001). These processes require H_2/CO values of less than 2 (Khalesi et al., 2008). Lower syngas ratio can be obtained from CO_2 reforming and by partial oxidation of methane as stated in Eqs. (2) and (3) (Goldwasser et al., 2005)

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad \Delta H_{298K} = 247 \text{ kJ/mol} \quad (2)$$

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow 2H_2 + CO \quad \Delta H_{298K} = -36. \text{ kJ/mol} \quad (3)$$

In the reaction (Eqs. (2) and (3)), H_2 production (clean energy) is favoured at high temperature (973—1073 K). This could be of great disadvantage as high temperature causes catalyst metal sintering, unstable behaviour of the catalyst and carbon deposition arising from Eqs. (4) and (5) (Richardson and Paripatyadar, 1990):

$$CH_4 \rightarrow C + 2H_2K \quad \Delta H_{298K} = +75 \text{ kJ/mol} \quad (4)$$

$$2CO \rightleftharpoons C + CO_2 \quad \Delta H_{298K} = -173 \text{ kJ/mol} \quad (5)$$

The reforming reaction requires the presence of a good catalyst in order to achieve desired products. Mixed metal oxides possessing the structure and composition of the perovskite have attracted interest from researchers, because they exhibit fantastic solid-state properties (Lombardo and Ulla, 1998). In methane dry reforming, the use of perovskite type oxides (ABO_3) as a catalyst, where the 'A' site cation is a rare earth and the 'B' site cation is a transition metal, has been reported (Goldwasser et al., 2005). The ideal perovskite (ABO_3) has cubic crystal structure in which the larger 'A' site cation

is surrounded by 12 oxygen anions and the smaller 'B' site cation is surrounded by 6 oxygen anions (Zhu et al., 2014). Perovskite fulfil the stability requirements for reforming reactions and also form well dispersed and stable metal particle catalysts (Tomishige et al., 2002). They allow for small metallic particles to be stabilized in the 'B' site over an 'A' site metallic oxide in order to minimize carbon deposition in the dry reforming of methane. Numerous publications on perovskite particularly, La and Ni based perovskite have been reported (Jahangiri et al., 2013; Zheng et al., 2015). It has also being established that Ni possesses a high activity in the methane dry reforming of methane (Gallego et al., 2006). However, Co was used to synthesize the perovskite in this study due to the fact that the ionic radius of Co^{2+} in the octagonal coordination which is required for the formation of a perovskite is 55 pm, while that of Ni^{2+} is 56 pm. The proximity of their ionic radii (Co and Ni) indicates that they could possibly serve similar purpose in terms of their metallic activity. In addition, there is scarcity of data involving rare earth metal such as Sm in literature. Interestingly, to the best of our knowledge, Sm and Co compositions have not being reported in literature as perovskite catalyst for the utilization of greenhouse gases via methane dry reforming. Therefore, the objectives of this study were to synthesize, characterize, and investigate the catalytic behaviour and performance of $SmCoO_3$ perovskite applied as catalyst for consumption of greenhouse gases via methane dry reforming. In addition, the effects of reactant gas (CO_2 and CH_4) partial pressure on the consumption of these greenhouse gases and production of synthesis gas have also been carefully studied.

2. Experimental

2.1. Catalyst synthesis

The synthesis of $SmCoO_3$ perovskite catalyst was carried out using the sol-gel citrate method already established in previous studies (Moradi et al., 2014). Mixture of the transition metal; $Co(NO_3)_2 \cdot 6H_2O$ (99.99% purity, Sigma Aldrich) and citric acid (anhydrous, Sigma Aldrich) was prepared at room temperature in a molar ratio of 1:2. The nitrate of the rare earth metal; $Sm(NO_3)_3 \cdot 6H_2O$ (99.99% purity, Acros Organics), was added to the mixture in the ratio of 1:1 with the transition metal, and stirred at room temperature until a clear solution was attained. The resulting homogeneous solution was continuously stirred and heated at 353 K for 4 h to obtain a gel, before being dried to powder at 383 K. The powder was ground and annealed in a furnace (carbolite AAF 11/3) at 1123 K with a heating rate of 5 K min^{-1}. In addition, the oxides of the individual metals were prepared by mixing their nitrates in distilled water, and then drying at 383 K for 4 h. The dried powder was then annealed in a furnace with heating rate of 5 K min^{-1} at 1123 K.

2.2. Catalyst characterization

Temperature-programmed calcination (TPC) and temperature-programmed oxidation (TPO) were carried out on a TA instruments (Q 500 series) to analyse the solid-state phase change before calcination and after reaction. These analyses were carried out at temperature ranged 298–1173 K using a temperature ramping of 10 K min^{-1} in pure N_2 and O_2 flow during the TPC and TPO study, respectively. Temperature-programmed reduction (TPR) profiles were determined using a TPDRO 110 apparatus equipped with a TCD detector. Prior to reduction, the sample (50 mg) was flushed in a quartz reactor tube, at 393 K for 2 h under N_2 flow with a rate of 5 K min^{-1} and cooled afterward to ambient temperature. The sample was blanketed with 5% H_2 in N_2 from ambient temperature to 1173 K, while employing a 20 K min^{-1} rate and holding time of 1 h.

CO_2 and NH_3-temperature programmed desorption (TPD) experiments were carried out using the same equipment as TPR. 50 mg of fresh catalyst was charged into a quartz reactor tube, pre-treated in 20 mL min^{-1} N_2 flow at 313 K for 30 min and then cooled to ambient temperature. After the pre-treatment, adsorption of CO_2 (or NH_3) was carried out while the temperature was retained at 393 K for 1 h, and then the sample was flushed with He flow for 30 min. The CO_2 (or NH_3) -TPD was carried out in He flow, while increasing the temperature from ambient to 1173 K with a ramping of 20 K min^{-1} for 1 h. The amount of CO_2 (or NH_3) desorbed was measured by a thermal conductivity detector. To determine the textural properties of the catalyst, N_2 multi-layer adsorption isotherms data was obtained. The isotherm data was analysed and processed by a Thermo Scientific acquisition analyser, furnished with degasser station and surfer acquisition (version 1.2.1) software. HITACHI table top SEM-EDX microscope (TM 3030 plus) was used to determine the elemental composition, particle dimension and morphology of the fresh and used catalysts. Photoelectron spectra (XPS) was acquired using a PHI-5000 VersaProbe spectrometer equipped with a hemispherical electron analyser and non-monochromated Al $K\alpha$ ($hv = 1486.6$ eV) x-ray source to determine the surface composition and binding energy of the fresh catalyst. The background pressure in the analysis chamber which was fixed at 2.7×10^{-4} Pa during data acquisition was operated with energy at 117 eV for wide scan spectra and 58 eV for narrow scan spectra. Peak intensities were estimated by calculating the integral of each peak by a least-square routine using Gaussian and Lorentzian lines. Atomic percentages of each element were calculated from the intensity ratios normalized by atomic sensitivity factors. All binding energies were referenced to the C 1s hydrocarbon peak at 284.8 eV. The crystalline phase of the catalyst was detected by performing an X-ray diffraction (XRD) analysis. A RIGAKU miniflex II X-ray diffractometer from 3° to 80° in 2θ scanning range using monochromatized $CuK\alpha$ radiation with wavelength (λ) of 0.154 nm at a rate of 0.02° (2θ) and a counting speed of 1 s was employed. The crystallite size of the catalyst was computed using the Debye-Scherrer equation (Eq. (6)) (Bradford and Vannice, 1996)

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl}\cos\theta} \tag{6}$$

where the crystallites size of the $SmCoO_3$ perovskite is D_{hkl}, λ is the wavelength of Cu-$K\alpha$, β_{hkl} is the peak full width with half maximum and θ is the Bragg diffraction angle.

2.3. Catalyst test

A stainless steel reactor (10 mm ID) containing 0.1 g of solid catalyst supported on quartz wool was employed for the catalyst test at reaction conditions; 1073 K, and a total flow of 50 mL min^{-1}, which culminates to gas-hourly-space-velocity (GHSV) of 30,000 mL h^{-1} g^{-1}. In all the experiments, the calcined perovskite catalyst was reduced by H_2 in a 50 mL min^{-1} of 50% H_2/N_2 mixture at temperature ramping of 5 K min^{-1}, and held at 1023 K for 1 h. The product gases were analysed using a gas chromatography instrument (GC-Agilent 6890 N series) equipped with a thermal conductivity detector for detecting CO_2, CH_4, H_2 and CO. The conversion and yield from the product stream were calculated using Eqs. 7(a)–(e), as previously reported in literature (Moradi et al., 2014), where F is molar flowrate and X is the conversion:

$$X_{CO_2}(\%) = \left[\frac{F_{CO_2}(in) - F_{CO_2}(out)}{F_{CO_2}(in)} \right] \times 100 \tag{7a}$$