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

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A B S T R A C T

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 Coo. 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 H2 and CO using the steam reforming process occurs by the following reaction (Eq. (1)) (Krylov et al., 1998):

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (\Delta H_{298K} = 206 \text{ kJ/mol}) \quad (1) \]

Steam reforming of methane produces syngas with H2/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 H2/CO values of less than 2 (Khalesi et al., 2008). Lower syngas ratio can be obtained from CO2 reforming and by partial oxidation of methane as stated in Eqs. (2) and (3) (Goldwasser et al., 2005)

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{H}_2 + \text{CO} \quad \Delta H_{298K} = -36 \text{ kJ/mol} \quad (3) \]

In the reaction (Eqs. (2) and (3)), H2 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):

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2\text{K} \quad \Delta H_{298K} = +75 \text{ kJ/mol} \quad (4) \]

\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \quad \Delta H_{298K} = -173 \text{ kJ/mol} \quad (5) \]

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 (ABO3) 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 (ABO3) has cubic crystal structure in which the larger ‘A’ site cation

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