Dry (CO₂) reforming of natural gas over pyrochlore catalysts for sustainable and clean energy production

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Introduction

With the depletion of fossil fuels and exponential increase in energy demand [1], there is a need to investigate other means to utilize the available abundant resources, like natural gas reserves, to produce fractions of compounds obtained from fossil liquid fuels [2]. Reforming natural gas to synthesis gas is one way of utilizing this resource for synthesis of hydrocarbons and oxygenates by Fischer-Tropsch process [3, 4]. Dry (CO₂) reforming of methane (DRM) is one reforming technique that converts CH_4 and CO_2 to commercially important syngas with H_2/CO ratio of ≤ 1 . This is a highly endothermic reaction and requires temperatures as high as 800-1000°C to attain equilibrium conversions. DRM is usually accompanied by simultaneous reactions like methane decomposition and boudouard reaction resulting in carbon formation which deactivates the catalyst. Thus, it is imperative to use catalysts that resist deactivation due to sintering and carbon formation.

In this work we study Rh, Pt and Ru substituted lanthanum zirconate pyrochlores; designated LRhZ, LPtZ, and LRuZ respectively. These catalysts are studied by means of temperature programmed surface reaction to determine the light-off temperatures of these catalysts for DRM. The stability of these catalysts against carbon formation and sintering is determined by performing DRM for extended period of 100 h. The formation of the La₂Zr₂O₇ pyrochlore phase was confirmed by X-ray diffraction (XRD). The reducibility of the metal in the pyrochlore was studied by H₂-temperature programmed reduction.

Materials and Methods

The pyrochlore catalysts were prepared using a variation of the Pechini method. The DRM 10 hr experiment was performed in a packed-bed AMI-200, Altamira instruments reactor with $CH_4/CO_2 = 1$, gas mixture of 10% CH_4/He and 10% CO_2/He , a GHSV = 48,000 ml h⁻¹ g_{cat}⁻¹, 650°C, and 1 atm. The product stream was analyzed in the Ametek quadrapole mass spectrometer. The carbon formed during the 100 hr run was characterized by temperature programmed oxidation by flowing 10% O_2/He over the spent catalyst from 30°C to 950°C.

Results and Discussion

TPSR results show that the light-off temperature of LRuZ was much lower than that of LRhZ and LPtZ. This could be attributed to increased surface concentration of Ru on LRuZ due to weak stability of Ru within the pyrochlore structure which causes the Ru from the bulk to migrate to the surface of the catalysts unlike LRhZ and LPtZ. The light-off temperature for LRhZ and LPtZ was observed to be similar and the reactant conversion increased with increasing temperature.

It is shown that CH_4 molecule activates on the metallic suite and CO_2 activates on the support. This phenomenon was observed to be true for the pyrochlores used in this study. Due to increased Ru concentration on the surface, LRuZ shows higher CH_4 and CO_2 conversion compared to LRhZ and LPtZ.



Figure 1. TPSR results showing that the light-off temperature for (a) LRuZ is much lower than that for (b) LRhZ.

Significance

The substitution of the active metals into the pyrochlore structure changes the reduction behavior of the metal as compared to the conventional supported catalysts as suggested by the H_2 -TPR results. The LRuZ possess different active sites from LRhZ which result in difference in the light-off temperature as seen in **Figure. 1**.

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