

Effect of reaction temperature on activity of Pt- and Ru-substituted lanthanum zirconate pyrochlores (La₂Zr₂O₇) for dry (CO₂) reforming of methane (DRM)

Devendra Pakhare^a, Christopher Shaw^a, Daniel Haynes^b, Dushyant Shekhawat^b, James Spivey^{a,*}

^a Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

^b National Energy Technology Laboratory, U.S. Department of Energy, 3610 Collins Ferry Road, Morgantown, WV 26507, USA

ARTICLE INFO

Article history:

Received 16 January 2013

Received in revised form 28 March 2013

Accepted 4 April 2013

Available online 28 May 2013

Keywords:

Dry reforming

Lanthanum zirconate

Pyrochlores

Methane decomposition

Isomorphous substitution

Reverse water gas shift

ABSTRACT

Dry (CO₂) reforming of methane (DRM) is a highly endothermic reaction ($\Delta H = +59.1$ kcal/mol) producing syngas (H₂ and CO) with the H₂/CO ratio of ~1. DRM requires reaction temperatures above ~800 °C for complete equilibrium conversion to CO and H₂, and is inevitably accompanied by carbon deposition. Here we examine lanthanum zirconate (La₂Zr₂O₇) pyrochlores, with the larger trivalent cation La and a smaller tetravalent cation Zr occupying A and B sites, respectively. Three catalysts are tested: La₂Zr₂O₇ [LZ] and two pyrochlores in which Zr in the B-site has been isomorphically partially substituted with (a) Ru (2.00 wt%) [LRuZ] and (b) Pt (3.78 wt%) [LPtZ]. The levels of substitution by weight correspond to identical atomic levels of substitution at the B-site. Here, activation energies are determined as a function of Ru or Pt substitution on the B-site. The results show that activation energies based on both CH₄ and CO₂ reaction rates are much lower for LRuZ than LPtZ. Conversion of CH₄ (X_{CH_4}) and CO₂ (X_{CO_2}) was greater for LRuZ compared to LPtZ at 525 °C, 575 °C, and 625 °C throughout an on-stream time of 600 min. After each 600-min run, temperature programmed oxidation (TPO) showed that total carbon formation decreased with increasing reaction temperature, although the stability of the deposited carbon increased with increasing reaction temperature.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Dry reforming of methane (DRM) produces synthesis gas with H₂/CO ratio of ~1 [1], which can be used for processes like Fischer–Tropsch or synthesis of various chemicals [2–6]. Both CH₄ and CO₂ are potentially valuable feedstocks for synthesizing commercially important higher-value products [7]. However, one of the major problems associated with DRM is catalyst deactivation due to carbon deposition [2,4,8]. In addition to carbon deposition, DRM is highly endothermic reaction and requires temperatures above ~800 °C to achieve high equilibrium syngas yields. These temperatures lead to deactivation due to sintering of conventional supported metal catalysts [9–12].

Pyrochlores are thermally stable ternary metal oxides with general formula of A₂B₂O₇ [13,14]. Large cations like rare earth elements usually occupy the A-site and transition metals occupy the B-site [15]. Isomorphous substitution of catalytically active metals like Ru or Pt in the B site produces thermally stable and active catalysts that are resistant to carbon formation due to

increased oxygen conductivity within the lattice [15]. Perhaps the most widely studied catalysts for the DRM reaction are based on Ni due to its low cost and availability; however, many Ni-based catalysts undergo severe deactivation due to carbon deposition [8,16–19]. Metals like Pt and Ru can be used to inhibit carbon formation [7].

Despite the well-known thermal stability of pyrochlores [13,15], we are aware of only one study of these materials for DRM other than our group, i.e., by Ashcroft et al. [20]. In that paper, Ashcroft et al. studied Eu₂Ir₂O₇ pyrochlores with Eu occupying the A-site and the catalytically active metal Ir occupying the B-site. Above 342 °C, these materials completely decomposed to Eu₂O₃ and Ir metal.

Here, we report the DRM reaction over two substituted pyrochlores in which Ru or Pt is substituted at the B site at equal atomic levels. These materials have been characterized and reported in our earlier work [21]. Here, we determine the activation energies for the reaction rates based on both CH₄ and CO₂ over these materials. The DRM reaction was carried out at 525 °C, 575 °C, and 625 °C for 600 min and the conversion of CH₄, CO₂ and formation of H₂ and CO was monitored as a function of time. The reaction was followed by temperature programmed oxidation to characterize the carbon formed over the catalyst.

* Corresponding author. Tel.: +1 225 578 3690; fax: +1 225 578 1476.

E-mail address: jjspivey@lsu.edu (J. Spivey).

2. Experimental

2.1. Catalyst synthesis

The Ru and Pt substituted pyrochlores were synthesized by modified Pechini method and the obtained metallic composition of these materials determined by ICP-OES has been reported in our earlier work [21].

2.2. Activation energy (Arrhenius plot)

The reactions for determining the activation energies were performed in an AMI-200 lab-scale fixed bed reactor. The composition of reactant gases used for the reaction was 10 mol% CO₂/He and 10 mol% CH₄/He. The catalysts were first mixed/diluted with α -alumina with mass ratio catalyst:alumina = 1:11 so that the total mass of mixture was 120 mg. The temperature range was carefully selected so as to limit the reactant conversion below 15%, minimizing the temperature and concentration gradients across the catalyst bed. The reaction time was 60 min at steady state at each temperature. The activation barrier energies were calculated based on the rates of CH₄ and CO₂ determined by monitoring the rate of consumption at temperatures low enough to avoid both transport and equilibrium limitations. Due to higher activity of LRuZ compared to LPtZ, the temperature range chosen for LRuZ (510–530 °C) was lower than that for LPtZ (660–680 °C).

2.3. Activity study

We studied the activity of the catalysts for DRM at different temperatures 525, 575, and 625 °C. A blank run with only the α -alumina was carried out to determine the extent of reaction without any catalysts. The mass spectrometer (MS) connected to the reactor gave the mole fractions of the reactants in the blank condition. The reaction gases of 10 mol% CO₂/He and 10 mol% CH₄/He were used for calibration of CO₂ and CH₄, 5 mol% CO/He and 10 mol% H₂/He were used to calibrate the mass spectrometer for CO and H₂ respectively. DRM was performed with an equimolar reactant feed of 20 mL/min of each of the reactant gases to give a total gas space velocity of 48,000 mL/gcat/h. For each run, 50 mg of the catalyst (without alumina) was loaded in the U-tube reactor. Before each reaction run, the catalyst was purged with He flowing at 20 mL/min and heated to the reaction temperature removing

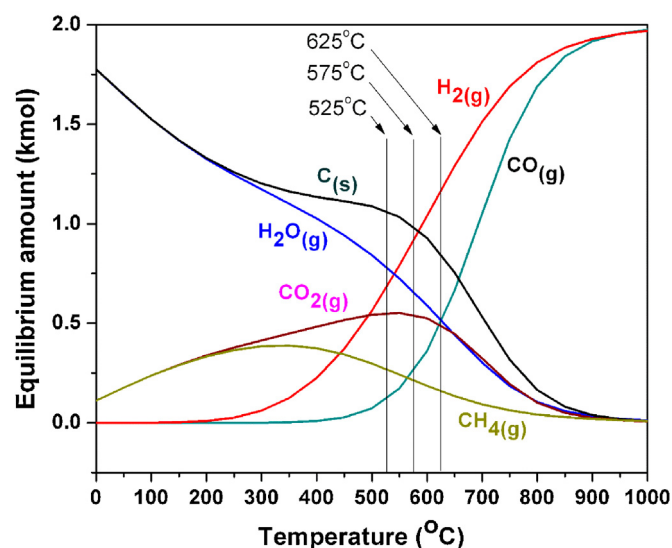


Fig. 1. Thermodynamic equilibrium composition for 1 kmol of CH₄ and CO₂ each at 1 atm as calculated by HSC Chemistry 7.1.

any surface species and moisture. No reduction of the catalyst was performed before DRM. The reactants CO₂ and CH₄ were introduced after this into the reactor at desired flow rates once the specified bed temperature was reached. The mole fractions of the reactants and products were measured by the Ametek quadrupole mass spectrometer.

2.4. Temperature programmed oxidation (TPO)

Immediately after each steady state DRM run, a TPO was conducted to characterize the carbon formation as a function of run temperature. The catalyst was cooled to room temperature (ca. 35 °C) in flowing He at 20 mL/min. The TPO was carried out by flowing 5 mol% O₂/He at 30 mL/min from room temperature to 950 °C at a ramp rate of 5 °C/min. The conditions were maintained isothermal at 950 °C for 30 min. The CO and CO₂ formed during the TPO were tracked using the mass spectrometer (MS) connected to the reactor outlet. The concentration of CO and CO₂ formed during TPO was calculated using the calibration gases of 5 mol% CO/He and 10 mol% CO₂/He.

3. Results and discussions

3.1. DRM reaction study

3.1.1. Thermodynamic equilibrium

The thermodynamic equilibrium composition of all compounds as a function of temperature at 1 atm is shown in Fig. 1. These molar compositions are calculated using Gibbs free energy minimization simulations using HSC Chemistry 7.1. These simulations were performed by assuming an initial equimolar mixture of CH_{4(g)} and CO_{2(g)}, with H_{2(g)}, CO_(g), H₂O_(g), C_(s) allowed as components of the equilibrium mixture. This accounts for the simultaneous occurrence of RWGS and methane decomposition along with DRM. The equilibrium compositions and H₂/CO ratios at different temperatures are shown in Fig. 1.

3.1.2. Arrhenius plot

The experimental apparent activation energies based on CH₄ and CO₂ disappearance are shown in Table 1. The apparent activation energies obtained over LPtZ and LRuZ are significantly different from those reported in the literature for Pt/Al₂O₃ [22] and Ru/Al₂O₃ [7], indicating that the mechanisms of the DRM reaction over the LPtZ and LRuZ are different than over conventional supported metals, as expected because Pt and Ru are bound within the pyrochlore structure rather than supported on an oxide.

The Arrhenius plots for LPtZ and LRuZ are shown in Fig. 2(a) and (b) respectively. The activation energy based on the consumption of CH₄ is greater than that based on CO₂ for both LPtZ and LRuZ. This agrees with the kinetic and mechanistic studies reported in the literature on Pt- and Ru-supported catalysts including Pt/Al₂O₃ [22] and Ru/Al₂O₃ [7], suggesting that activation of CH₄ is the rate limiting step during DRM [12,23,24].

The activation energy for both CH₄ and CO₂ reaction is significantly lower for LRuZ than LPtZ, meaning that there is a difference in the transition state and thus mechanism over the two catalysts. Lower activation barriers over LRuZ could also be due

Table 1
Summary of the activation energies.

Catalyst	E_{app} (CH ₄) (kcal/mol)	E_{app} (CO ₂) (kcal/mol)	Reference
LPtZ	36.5 ± 0.4	27.9 ± 0.2	This work
LRuZ	14.5 ± 0.7	11.5 ± 0.8	This work
Pt/Al ₂ O ₃	22.5	20.2	[22]
Ru/Al ₂ O ₃	26	18	[7]

Download English Version:

<https://daneshyari.com/en/article/63506>

Download Persian Version:

<https://daneshyari.com/article/63506>

[Daneshyari.com](https://daneshyari.com)