



Kinetic and mechanistic study of dry (CO₂) reforming of methane over Rh-substituted La₂Zr₂O₇ pyrochlores



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ABSTRACT

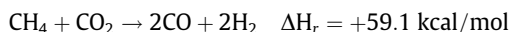
The active sites and kinetics of dry reforming of methane (DRM) on lanthanum zirconate (LZ) pyrochlore catalysts are studied as a function of Rh substitution, temperature, and partial pressures of CH₄ and CO₂. In this work, we focus specifically on determining the catalytic active sites for CH₄ and CO₂ activation and their role in the DRM mechanism over the two Rh-substituted pyrochlores, i.e., 2 wt% Rh, designated L2RhZ and 5 wt% Rh, designated L5RhZ. Kinetic rate modeling suggests dual-site mechanism, where CH₄ and CO₂ are activated on different sites (dual-site mechanism). Eleven different rate models were tested against the kinetic rate data obtained over these two Rh pyrochlores. Statistical analysis shows valid and similar fits for only two of eleven models: one in which activation of CH₄ is rate-determining and one in which CO₂ activation is rate-determining. This dual-site mechanism is studied further in detail to test the validity of the intermediate steps predicted by the kinetic model. CH₄/CD₄ isotope switching shows a strong deuterium kinetic isotope effect on CH₄ and CO₂ conversion, suggesting that CH₄ dissociation is the rate-determining step. Higher apparent activation energies of CH₄ (E_{a, CH_4}) versus CO₂ (E_{a, CO_2}) on both catalysts also confirm that CH₄ activation is rate-determining. Basic nature of La–O sites activates mildly acidic CO₂ to form La₂O₂CO₃ complexes as confirmed by FTIR. From different polymorphs of La₂O₂CO₃, the spectator and reactive species were distinguished by pulsing CH₄ over La₂O₂CO₃. Alternating pulses (CH₄/Ar → CO₂/Ar → CH₄/Ar) at 550 °C showed simultaneous formation of CO and H₂, suggesting that surface carbon, formed by CH₄ decomposition, is oxidized by H₂O; a crucial step in understanding the catalytic behavior of pyrochlores in the reaction mechanism. These experiments were used to identify the two types of sites taking part in the dual-site DRM mechanism. The work reported here helps in determining a single set of kinetically significant steps that most closely represent the mechanistic scheme of DRM over L2RhZ and L5RhZ.

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1. Introduction

In the past decade, methane-reforming processes such as steam reforming of methane (SRM), partial oxidation of methane (POM), autothermal reforming of methane (ARM), and dry reforming of methane (DRM) have been investigated. These processes differ in the final H₂/CO product ratio and energetics. From among these reforming processes, DRM is shown to have lower operating cost [1]. However, DRM has certain disadvantages such as high endothermicity, requiring high reaction temperatures (~900 °C) to

attain equilibrium conversions, and deactivation by carbon deposition and sintering [2,3].



Thus, there is a need to develop catalysts that will resist deactivation due to sintering and decrease carbon formation during DRM [4–7]. A balance between formation and oxidation of surface carbon is necessary for DRM catalyst stability. There are several ways to increase deactivation resistance, such as increasing and maintaining the dispersion of the active metal [8–10] improve the oxidation rate of surface carbon by increasing the concentration of an oxidizing agent such as CO₂ [11]. Since CO₂ is mildly acidic in nature, increasing the basicity of the catalyst will increase

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CO₂ activation and decrease carbon formation [12–14]. Addition of basic promoters such as La₂O₃, CeO₂, and alkaline earth metal oxides such as MgO, CaO, and BaO help in CO₂ activation, thus increasing reactive oxygen for surface carbon oxidation [2,15–21]. Basic promoters also help increase the active metal dispersion [13]. A comprehensive review on DRM kinetics and mechanism by Pakhare and Spivey [22] suggests various ways to control deactivation of DRM catalyst.

Activation of CH₄ is a crucial step in DRM mechanism [17,22–24]. However, there is no consensus in the literature on the mechanism of CH₄ activation on catalytic sites, even on the same metal. For example, Luntz and Winters [25] and Wei and Iglesia [26] proposed that on Pt and Pd [27] clusters, the activation of CH₄ occurs by direct decomposition where all C–H bonds simultaneously dissociate resulting in C_(s) and evolution of H_{2(g)}. However, theoretical calculations by Seets et al. [28] suggest activation of CH₄ by the formation of reactive intermediates such as formates or CH_x species. Yamaguchi and Iglesia [27] observed that C–H bond activation in CH₄ is structure sensitive and its rate increases with decreasing Pd clusters size.

For DRM, the activity decreases in the order Ru, Rh > Ir > Ni, Pt, Pd > Co > Fe, Cu [29], with noble metals showing higher activity and greater resistance to carbon deposition [30–33]. DRM has been studied on various catalysts; however, we are aware of no papers where pyrochlores have been studied for DRM other than those reported by our group [34–36]. Pyrochlores are crystalline thermally stable ternary metal oxides with a cubic unit cell and general formula of A₂B₂O₇. The A-site is usually a large cation (typically rare earth elements) and the B-site cation has a smaller radius (usually transition metal) [22,37]. These materials have two important properties that make them interesting for this reaction. The first is oxygen ion conductivity; vacancies at the O sites, created during synthesis, facilitate oxygen ion migration, which minimizes carbon deposition formed by CH₄ dissociation [38]. The second is the ability to isomorphically substitute catalytically active transition metals into the B-site, where they do not sinter at high DRM temperatures. Candidate catalytically active transition metals for B-site substitution include Ru, Rh, and Pt [34,35]. The most closely related paper for DRM over pyrochlores is by Ashcroft et al. [39] who studied Eu₂Ir₂O₇ for DRM. However, the pyrochlore structure in that study decomposed to Eu₂O₃ and metallic Ir under DRM gases above 340 °C.

Here, we report a systematic study of the active sites and kinetics of DRM on two Rh-substituted lanthanum zirconate [LZ] pyrochlores: 2 wt% [L2RhZ] and 5 wt% [L5RhZ]. A detailed characterization and activity study of these materials has been reported in our earlier work [36] where we confirm the formation of the pyrochlore phase and substitution of Rh at the B-site. Here, the process of CH₄ and CO₂ activation as a function of temperature and Rh substitution in the pyrochlore structure was studied by Fourier transform infrared (FTIR) spectroscopy. The role of CH₄ in rate-limiting step in DRM mechanism is examined by studying the CH₄/CD₄ kinetic isotope effect. The elementary steps involved in oxidation of surface carbon were studied by transient pulsing of CH₄ and CO₂ with Ar tracer. Kinetic rate models based on postulated mechanisms were validated by statistically fitting the kinetic data obtained over the L2RhZ and L5RhZ pyrochlores.

2. Experimental section

2.1. Catalyst synthesis

The LZ, L2RhZ, and L5RhZ pyrochlores studied in this work were prepared by the modified Pechini method [40]. The metal precursors of lanthanum nitrate hexahydrate [La(NO₃)₃·6H₂O] (GFS Chemicals, 99.9%), zirconium oxynitrate [ZrO(NO₃)₂·xH₂O] (Alfa

Aesar, 99.9%), and rhodium nitrate [Rh(NO₃)₃·2H₂O] (Alfa Aesar, 99.9%) were used. The dissolved metal salts were combined in a beaker with continuous stirring. Complexing agent citric acid (CA) solution with molar CA:metal ion ratio of 1.2:1 was added to the metal solution beaker and heated to 70 °C to which the polymerizing agent ethylene glycol (EG) was added with 1:1 M ratio of EG:CA. The solution was stirred until a clear viscous gel remained in the beaker. The gel was then heated to 130 °C to promote the polyesterification reaction. The resulting amorphous polyester-type resin was calcined at 1000 °C for 8 h to form pyrochlore catalyst.

2.2. Activation energies

The activation energy was obtained in the AMI-200 Altamira Instruments reactor using the catalyst:alumina of 1:10. Because the activity of L5RhZ was higher than L2RhZ, the temperature range chosen for L2RhZ (585–605 °C) was higher than that for L5RhZ (520–560 °C) to limit the conversion in both cases and to minimize any effects of concentration/temperature gradients across the catalyst bed. Gas composition and flow was 10% CH₄/He and 10% CO₂/He at 20 mL/min each.

2.3. Kinetic rate modeling

The equipment details and catalyst dilution ratio were the same as reported previously (Section 2.2). The partial pressure dependence of CH₄/CO₂ reaction rate was determined by keeping partial pressure of one reactant (CH₄ or CO₂) constant at 0.05 atm and varying that of the other (CO₂ or CH₄) as 0.03, 0.035, 0.04, and 0.045 atm (balance He). These set of experiments were performed at 570 °C, 590 °C, and 610 °C for L2RhZ and at 520 °C, 540 °C, and 560 °C for L5RhZ. The conversion was kept below 15%, so as to approach differential conditions.

2.4. CH₄/CD₄ kinetic isotope effect

Deuterium kinetic isotope effect was studied by using 10% of CD₄/He, 10% CH₄/He, 10% CO₂/He (all 99.99% pure). The reactor is same as mentioned previously (Section 2.2). Before testing for DRM, the catalysts were reduced in 4% H₂/He by ramping from 25 °C to 600 °C and maintaining isothermal conditions at 600 °C for 30 min then purged in He for 15 min. For testing the change in the rate of consumption of CH₄ and CD₄, alternate cycles of CH₄/CO₂/He and CD₄/CO₂/He of 30 min each were performed on L2RhZ and L5RhZ.

2.5. In situ FTIR and transient pulsing

For *in situ* FTIR studies, a Thermo Electron Nexus 670 spectrometer with a liquid N₂ cooled MCT detector and a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell from Pike Technologies was used. KBr beamsplitter provided spectra in the wavenumber range of 4000–500 cm⁻¹. Prior to spectrum collection, catalysts were reduced in flowing 4% H₂/He (20 mL/min) by heating from 25 °C to 550 °C and maintaining at 550 °C for 30 min. The reduced catalysts were then flushed by He for 15 min for background collection. The DRIFTS cell was connected to an 8-port valve which allowed rapid switching of gases without interrupting the continuous He flow, thus avoiding pressure drop across the cell. The valve was fitted with 0.5 cm³ loop, allowing injection of known amount of reactant gas pulses in the continuous He flow.

After background collection at 550 °C, the catalysts were treated in flowing 10% CO₂/He (20 mL/min). This resulted in the formation of carbonate on the catalysts and the gas-phase CO₂ was later

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