Ab Initio Derived Reaction Mechanism for the Dry Reforming of Methane on Rh Doped Pyrochlore Catalysts

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Abstract

The conversion of methane into syngas is of growing importance given recent increases in methane production world-wide. Furthermore, using CO₂ as the co-feed offers many environmental advantages. To this end, experimentalists have shown that Rh-substituted lanthanum zirconate pyrochlore (LRhZ) catalysts are active and stable at the high temperatures needed for the dry reforming of methane (DRM). To enable further improvements to these catalysts, the reaction mechanism for DRM on LRhZ catalysts was attained using density functional theory (DFT). Following the identification of favored reaction sites for all elementary reactions, reaction and activation energies were calculated and used to discern the primary reaction pathway. Simulations show that inclusion of Rh decreases activation barriers, including the barrier for the two rate limiting steps (CH₂ oxygenation and CHO dehydrogenation), which makes the plane (111) catalytically active for DRM. The slow steps are on the CH₄ dehydrogenation/oxygenation path, which agrees with experimental observations.

Keywords: Dry reforming
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1. Introduction

Syngas is a mixture of H₂ and CO, which has proven to be a versatile feedstock for the production of a variety of chemicals and fuels, including methanol and diesel fuel. This energy rich mixture is widely used for electricity and heat generation and is a key intermediate for many methane gas-to-liquid processes that yield products more easily shipped via pipeline. [1] In recent years, considerable effort has been put toward the development of organic waste to syngas processes, but with the advent of low-cost shale

gas, traditional syngas production from methane is also receiving renewed attention. There are several technologies available for syngas production from methane, such as Steam Methane Reforming (SMR), Partial Oxidation (POX), Autothermal Reforming (ATR) and Dry Reforming of Methane (DRM).

Steam methane reforming is currently the main route to produce hydrogen from natural gas. This reaction is highly endothermic, and therefore is carried out at very high temperatures. Nickel catalysts are often the most suitable for this reaction due to their observed high turnover rates, low cost and long term stability. The advantage of SRM is that carbon deposition on the catalyst surface can be substantially reduced by the use of excess water and temperatures around 1073 K. [2] However, the generation of the required super-heated steam is very expensive, significant amounts of carbon dioxide are produced via the reverse water gas shift (RWGS) reaction, and the H_2 to CO ratio is in excess of what is required for most downstream syngas conversion processes to other chemicals. Alternative strategies for syngas production, such as partial oxidation, offer several advantages, including the reaction being exothermic, the resulting syngas H_2 to CO ratio being ideal for methanol synthesis and the CO_2 concentration in the product gases being low (which otherwise CO_2 must be removed before further use of synthesis gas). Since PO_x produces very high yields of synthesis gas, oxygen is often added to the SMR process to keep the temperature high and promote methane oxidation. This combined methane reforming route is known as Autothermal Reforming. [2]

The work described herein, focuses on the Dry Reforming of Methane, as the reactants involved are two greenhouse gases, and unlike other syngas production methods, there is neither a significant water supply dependence nor is a purified oxygen supply required. Although DRM using CO_2 has long been considered a viable method for converting methane from geologic or biological sources into syngas, the high temperatures required for the reaction ($\sim 1000 \text{ K}$) have made it very difficult to find catalysts that exhibit high activity for extended periods. Several factors often lead to the deactivation of these catalysts, including the sintering of active metals, the structural rearrangement of the catalyst support causing a reduction in surface area, and the accumulation of carbon on the catalyst surface. To-date, many catalyst materials have been investigated for this reaction, for example, zeolites, supported group VIII metals, transition metal carbides and sulfides, bimetallics, and more recently, perovskites and pyrochlores have received attention. The

pyrochlore materials are of particular interest because of their exceptional thermal stability and high selectivity to desired products.[3]

Pyrochlores are crystalline oxides having high thermal stability and a general formula of $A_2B_2O_7$, where A represents a rare-earth metal and B represents a transition metal. Early experimental efforts indicated that pyrochlores are active for DRM, but the tested catalysts exhibited poor long term stability [4, 5]; whereas, more recent data suggests that this trend in deactivation may not be applicable to all pyrochlores. For example, $La_2Zr_2O_7$ (LZ) is a pyrochlore catalyst that has shown good long term stability [6-8], and it exhibits a propensity to accept a wide variety of metal substitutions into the lattice. Thus, efforts have been made to tailor its catalytic properties by incorporating select transition metals into the lattice. Specifically, the use of Rh as a dopant has been shown to enhance catalytic performance for DRM [9]. When tested for DRM activity, a 2% Rh-doped LZ catalyst (LRhZ) showed conversions of 95% and 98% for CH_4 and CO_2 , respectively; whereas, a similar Ni-based pyrochlore catalyst deactivated rapidly due to coke deposition on the catalyst [3]. Despite the high conversions and enhanced catalyst stability of the Rh-based pyrochlore, the required reaction temperature remains high (~ 1000 K), and the reaction mechanism is not well understood.

Some insight into the DRM reaction on LRhZ pyrochlores can be discerned from prior kinetic studies that examined the CO_2 and CH_4 dissociation mechanisms of catalysts somewhat related to the LRhZ pyrochlores. For instance, Gronchi et al. [10] compared the catalytic performance of Rh and Ni metals supported on SiO_2 and La_2O_3 , concluding that there is considerable influence of the support on the reaction performance. Most notably, increased CO production is obtained with the use of a lanthana support, which is presumed to activate CO_2 decomposition. Múnera et al. [11] also performed kinetic studies on Rh/ La_2O_3 and concluded that lanthanum plays an important role in CO_2 adsorption, in contrast to the data reported by Wei and Iglesia [12] for Rh supported on Al_2O_3 , which showed that CO_2 is only weakly bound to the alumina. Matsui et al. [13] also observed CO_2 activation on the support for Ru/ La_2O_3 and only CO_2 physisorption on Al_2O_3 . Research examining the DRM activity of multiple transition metals (e.g., Pt, Ni, and Rh) showed that methane cracking is the slow reaction step [14-17]. This was also observed by Munera et al. [11], due to the constancy of r_{CH_4} with increasing hydrogen pressure, but they also identified the reaction of surface carbon species with the oxycarbonates present in the working catalyst (Rh/ La_2O_3) as another slow step.

Considerable effort has been put towards understanding the reactivity of CH_x species on metals, and it is well known that the high activation barrier associated with C-H cleavage is

believed to directly influence the rate of transformation of natural gas into syngas. In addition to experimental efforts, several theoretical studies employing *ab initio* methods have also sought to understand the surface chemistry and quantify the activation energy required for methane dehydrogenation on different transition metals, as summarized in [18], but to our knowledge, there are no *ab initio* studies on how this occurs on pyrochlore structures and even less how the whole reaction mechanism for DRM proceeds on transition metal substituted pyrochlores.

Thus, this work seeks to describe the overall DRM reaction mechanism on Rh doped pyrochlore catalysts and more specifically, the role played by Rh in the formation of syngas. To understand and quantify reaction energetics, density functional theory (DFT) methods were used to calculate the structural stability of the LRhZ pyrochlores, identify minimum energy surface structures and favored adsorption sites for reactants and products, as well as quantify activation barriers for all DRM possible elementary reaction steps. Though a number of DFT simulations are reported for pyrochlore structures, these studies were not focused on catalytic uses for pyrochlores, but instead dealt with the structural stability, mechanical and electronic properties of the oxide [19-25]. To our knowledge, the work done by Mantz [26] is the only DFT-based work that deals with the interactions of adsorbed species with pyrochlore surfaces, where O₂ adsorption on selected La₂Zr₂O₇ pyrochlore surfaces is studied.

To validate the computational results obtained in this work, our findings are compared to experimental reaction and surface characterization data from collaborators [9, 17] as well as experimental data by others for non-pyrochlore rhodium-based oxide catalysts [10, 11, 13].

2. Experimental

First principles calculations were performed employing the Vienna *ab initio* simulation package (VASP) [27-30], which is based on a plane-wave DFT code. Previously, it was shown [31] that the lattice parameter calculations as well as the trends in surface stability and reactivity for Rh₂O₃ surfaces were very similar using DFT or DFT+U methods. Therefore, to reduce computational efforts, in the present study it was decided to only use DFT methods. To describe the interaction between the core and valence electrons, the projector augmented wave (PAW) pseudopotentials were used [32, 33]. Three different exchange correlation functionals were tested to find the optimum lattice parameters for both LZ and LRhZ. For these studies, predicted crystal structure parameters, including bulk density, were compared with experimental observations. The functionals tested were: the local density approximation (LDA) [34], the generalized gradient approximation using the

implementation of Perdew, Burke and Ernzerhof (GGA-PBE) [35], and the GGA implementation of Perdew and Wang (GGA-PW91) [36]. The lattice parameters predicted by the GGA-PBE exchange-correlation functional were found to accurately match experimental data, and thus, GGA-PBE was employed in all further calculations. A plane wave cutoff of 500 eV is used in all calculations, and all geometries are optimized until the forces on the atoms are less than 0.001 eV/Å for bulk catalyst optimization and 0.03 eV/Å for all further calculations. During electronic optimization, the energy is converged to within 1×10^{-6} eV/atom for the bulk catalyst optimization and 1×10^{-4} eV/atom for all further calculations. For some special cases where force convergence was difficult to obtain, the electronic iterations were further converged to within 1×10^{-9} eV. A Monkhorst-Pack k-point sampling scheme [37] (2x2x2 for bulk, 2x2x1 for surfaces and 1x1x1 for isolated species) is used and electronic occupancies are determined using the Methfessel-Paxton scheme [38], with an energy smearing (σ) of 0.1 eV. All calculations are spin-polarized.

Activation energies were calculated for selected elementary reactions using the climbing image nudged elastic band method (CI-NEB) via scripts developed previously in the Henkelman Research Group at UT Austin [39, 40]. A test using five and three structural images between reactants and products for a select reaction step was performed. This test showed that three structural images are sufficient to describe the energetics of the reaction barrier (see Supporting Information for further details); therefore, for computational efficiency three images were used for all CI-NEB calculations. A 5.0 eV/Å² spring constant was used in all CI-NEB calculations. The force and energy convergence criteria were 0.03 eV/Å and 10^{-7} eV, respectively, during the electronic optimization. To reduce computational effort and increase simulation convergence when employing CI-NEB, only the adsorbed atoms involved in the respective chemical reaction were allowed to move while fixing the atoms in the catalyst surface. Initial simulation studies and subsequent BEP analysis (see later discussion) indicated that the transition state structure for reaction intermediates more closely resembled the combined product species from addition reactions or the reactant from a dissociation reaction. Therefore, the slab structure used in all final CI-NEB calculations was for the product slab of the respective association reaction. To correct for this simplification, the energy values obtained from single species adsorption were used to address the influence of surface relaxation (see later discussion). Prior to performing CI-NEB calculations for an elementary reaction step, the intermediates were placed in their most favorable adsorption site and structure optimization was performed to allow for readjustments of the species on the surface when being nearby other surface species.

The complete set of elementary steps considered in the reaction network consists of 130 reactions, counting both forward and reverse reactions. Some activation energies were derived from rigorous DFT calculations (CI-NEB method), while others were estimated by a Bronsted-Evans-Polanyi (BEP) relation derived from our DFT data.

Due to the heterogeneity of the surface, studies of optimum vacuum height and slab thickness were carefully performed, so as to yield systems that accurately represent experimental catalyst samples and at the same time reduce computational expenses, so that the scope of the work can be covered in a time-effective manner.

2.1 Bulk catalyst model

LZ and LRhZ are cubic oxide pyrochlores of space group $Fd-3m$. Within this work, origin choice 2 [41] is used. The ideal stoichiometric pyrochlore has eight formula units (88 atoms) per unit cell and within it there are four crystallographically nonequivalent atom types: the cations La and Zr (or Rh) and the oxygen ions O and O'. The La atoms are eight coordinate, whereas the Zr (or Rh) atoms are six coordinate. The dimensions of the pyrochlore unit cell are described by the lattice parameter (a), and the location of lattice oxygens (O) are specified by the oxygen positional parameter (x).

DFT calculated energy versus lattice parameter (a) data for the bulk catalyst were fit to the Murnaghan equation of state [42] to obtain optimum lattice parameters that yield the lowest energy structure. These optimum parameters were cross-checked with experimental pyrochlore characterization data [9, 43] to further validate the optimized simulation parameters. The results obtained using different exchange correlation functionals and the available experimental data for comparison can be found in Supporting Information.

The computational results are in good agreement with the available experimental data for both the LZ and LRhZ pyrochlores, and there is only a moderate difference between the computational results obtained using the tested functionals. However, careful inspection of the data shows that the LDA functional underestimates the lattice parameter, as has been previously reported [20]. Based on these data, both GGA-PBE and GGA-PW91 accurately describe the pyrochlore structure. The GGA-PBE functional is used for all further calculations involving the LRhZ pyrochlore, and the lattice parameter is set to 10.88 Å, which corresponds to an error of 0.2% in the lattice parameter and an error of 0.6 % in the crystal density.

2.2 Optimization of slab dimensions

To create a catalytically active surface, the bulk pyrochlore structure must first be cleaved through a specific crystallographic plane. Using experimental XRD data [9], the pyrochlore structure was cleaved along the (111) plane, leaving one Rh atom at the surface. Further corroboration of the likelihood of appearance of the plane (111) on the pyrochlore catalyst surface is provided in section 2.3.

The catalyst surface is modeled using the periodic slab technique, in which a slab model with a vacuum region is periodically replicated in three dimensions to obtain a 2D infinite surface. The presence of adjacent replica slabs parallel to the catalyst surface can diminish the accuracy of the calculations if these surface replicas interact significantly with each other. Due to this fact, the adsorption energy for CH₄ on the same active site on the surface (111) is tested for different heights of the vacuum region. A stoichiometric slab model is employed, which contained 4 formula units (44 atoms) and has lateral dimensions of $a/\sqrt{2} \times a/\sqrt{2}$. Additionally, the metal and oxygen layers are intercalated in the slab and the two bottom layers are kept fixed.

Since the top of the slab is metal terminated and the bottom of the slab is oxygen terminated, a strong dipole moment is to be expected. The value of this dipole moment depends both on the termination of the slab and on the proximity of the slab replicas above and below. Calculations showed that having a vacuum region of 12 Å yields a methane adsorption energy that differs by less than 0.001 eV from the calculated most accurate value (at 18 Å of vacuum); furthermore, it was found that beyond a vacuum region of 11 Å the value of the adsorption energy is unaffected by the inter-slab distance. The data corresponding to the adsorption energy of methane on the plane (111) and the dipole moment of this pyrochlore slab with respect to the vacuum space between slabs is shown in Supporting Information.

Though extending the vacuum space between adjacent pyrochlore slabs reduces the overall slab dipole moment, the inherent asymmetry caused by terminations of the slab layer ensures that some residual dipole will continue to exist. To further address this issue, an extra metal layer is added to the bottom of the pyrochlore slab and full relaxation is allowed, reducing the slab dipole moment from -15.9 to -1.6 Debye (without embedded dipole moment correction as implemented in VASP 5.2). Independent of the inclusion of this extra metal layer, the adsorption energy of CH₄ is unaffected due to its lack of a molecular dipole. Nevertheless, reducing the dipole moment in the system decreases the overall computational effort considerably and thus, an extra metal layer was added to the non-reacting surface of all simulated pyrochlore slabs.

To ascertain the optimum pyrochlore slab thickness that most accurately mimics real systems and yet is computationally achievable, simulations of CH₄ adsorption on the (011) surface of metal terminated pyrochlore slabs (both ends) of varying thickness were compared. These simulations indicated that a 9-layer fully relaxed pyrochlore slab (48 atoms) is sufficiently thick, as the adsorption energy for CH₄ differed by only 0.02 eV for slabs containing 9 layers and a much thicker system containing 13 layers (70 atoms). For all subsequent simulations, parallel slabs are separated by 12 Å of vacuum and the slab thickness is maintained at a value equal to or greater than 7.50 Å (approximately a 48-atom slab).

2.3 Surface energy

Specific species adsorption and the overall reaction mechanism for a given catalyst are strongly dependent on the prevalence and spacing of surface atoms, which themselves are a function of the crystallographic planes exposed on the catalyst surface. To determine what planes are most likely to appear on the pyrochlore surface, the surface energy is calculated for multiple low index planes that were suggested by experimental X-ray diffraction studies. The surface energy for smooth crystallographic planes can be defined as the energy needed to cleave the bulk crystal along that specific plane. The lower the surface energy, the more thermodynamically stable is the plane.

As mentioned in the previous section, to reduce the dipole moment in the slab, nonstoichiometric slabs were created so that the terminations at the top and bottom of the slab are equivalent and the dipole moment is reduced. To calculate the surface energy independently of the termination used to adsorb the species, both metal terminated and oxygen terminated slabs are created, and their energies are used to calculate the surface energy as follows:

$$E_s = (E_{slab1} + E_{slab2} - nE_{bulk})/(4S) \quad (1)$$

When calculating the surface energy (E_s), S is the surface area of the 2D unit cell, E_{slab1} is the total energy of the metal terminated slab, E_{slab2} is the total energy of the oxygen terminated slab, n is the stoichiometric factor describing the fraction of bulk unit cells that are equivalent to the atoms contained in the two slabs (1 and 2), and E_{bulk} is the total energy of a crystallographic or bulk unit cell. Mastrivok et al. [44] used the software VASP and the GGA-PW91 correlation functional to calculate surface energies of the LaMnO₃ perovskite structure (structure similar to pyrochlore). The surface energy calculations using stoichiometric and non-stoichiometric slabs gave similar results. In addition, Evarestov et al. [45] used hybrid HF-DFT LCAO simulations to calculate surface energies of SrTiO₃ and SrZrO₃ cubic perovskites using stoichiometric and non-stoichiometric slabs and surface energy values did not show any significant difference. These previous studies indicated that

significant improvements in overall computational efficiency with minimal loss in accuracy are obtained by modeling non-stoichiometric oxide slabs, which is even more important for simulating systems with species in dilute concentration (such as Rh in the LRhZ pyrochlore). Thus, non-stoichiometric slabs were used to perform all surface energy calculations for the LRhZ pyrochlore in the present work.

To calculate the surface energy at a moderate computational effort and to reduce future computational expenses, a fraction of the plane after cutting the bulk structure was used as representation of the whole plane for the planes showing slow convergence. This means that the dimensions of the planes used for the surface energy calculations were $a \times a$ for the plane (001), $a \times a/\sqrt{2}$ for the plane (011) and $a/\sqrt{2} \times a/\sqrt{2}$ for the plane (111), where a equals the length of a side of the pyrochlore cubic unit cell. Fig. 1 shows the top and the side view (one of them) for both metal terminated and oxygen terminated slabs of the planes (001), (011) and (111).

Fig. 1 Top view and the side view (one of them) for both metal terminated and oxygen terminated slabs of the planes (001), (011) and (111) of the LRhZ pyrochlore.

The surface energy simulation results indicated that the planes (111) and (011) are the most thermodynamically stable ($E_{s(111)} = 0.09 \text{ eV}/\text{\AA}^2$ and $E_{s(011)} = 0.14 \text{ eV}/\text{\AA}^2$). In contrast, the plane (001) was found to have the highest surface energy ($E_s = 0.19 \text{ eV}/\text{\AA}^2$), suggesting that it is the least thermodynamically stable.

Computational results from Mantz [26] also showed the planes (011) and (111) are the most thermodynamically stable for the LZ pyrochlore, which is in good agreement with our results for the LRhZ pyrochlore. For the present work, all catalytically relevant simulations are performed using metal terminations of both the (011) and (111) pyrochlore planes, enabling us to evaluate the extent to which DRM proceeds on each plane.

3. Results and Discussion

3.1 Species adsorption

To achieve an accurate description of the DRM reaction mechanism on the pyrochlore surface, multiple pathways for the reaction are considered based on experimental observations [9, 12, 17, 46-48] and prior computational results [49]. This network of elementary reaction steps is shown in Fig. 2. Methanol formation was not detected in the experiments but is included in the reaction network as a way to cross-check the model, because inhibition of alcohol production should be predicted by calculated activation energy values. Additionally, water formation was observed experimentally due to the Reverse Water Gas Shift Reaction (RWGS, $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) but in negligible amounts. All reactions involved in the RWGS mechanism are shown implicitly in Fig. 2, and a separate figure showing the detailed mechanism for RWGS on LRhZ catalysts is shown in Supporting Information. Finally, CH_xOH (where $x = 0, 1, 2, 3$) dehydration was ruled out from the reaction network because no stable configuration for CH_x and H_2O was found using DFT methods when these species were placed close to each other on the same pyrochlore slab.

Fig. 2. Proposed reaction network for the dry reforming of methane on a pyrochlore catalyst.

The preferred adsorption sites of the species on both planes and the corresponding adsorption energies (ΔE_{ads}) are calculated as follows,

$$\Delta E_{\text{ads}} = E_{\text{ads+surf}} - E_{\text{surf}} - E_{\text{ads}} \quad (2)$$

where $E_{\text{ads+surf}}$ is the calculated energy of the combined slab and adsorbate; E_{surf} is the energy of the clean slab without any adsorbate, and E_{ads} is the energy of the isolated

adsorbing species, which was simulated in a 20.0 x 20.5 x 21 Å box, including as well spin-polarized considerations. According to this definition of adsorption energy, the more negative the value of ΔE_{ads} , the stronger the binding between the adsorbate and the surface. Analogously, as the value of ΔE_{ads} approaches zero, the weaker the adsorption of the molecule on the surface.

Planes (011) and (111) of the LRhZ pyrochlore present a variety of possible active sites for adsorption and conversion of the different species. After carrying out structure optimization simulations for all of the reactants and intermediates shown in Fig. 2, certain sites provided stronger adsorption for specific species and on some sites no stable adsorbate structure was found. Specifically, no stable structure for COH was found on any site on the (111) plane. Thus, all reactions involving this intermediate are not considered for this plane. The specific reactions excluded from studies of the (111) surface are:

Further insight into the chemisorption behavior of CO₂ and CO on pyrochlores can be garnered from prior experimental studies examining related metal oxides. For example, Múnera et al. [11] working with Rh/La₂O₃ catalysts and Matsui et al. [13] working with Ru/La₂O₃ and Ru/ZrO₂ catalysts arrived at similar conclusions, namely, that La facilitates CO₂ adsorption. Additionally, Gronchi et al. [10] concluded from experiments with Rh/La₂O₃ that La activates CO₂ decomposition. This is in very good agreement with our computational results, since all sites where CO₂ adsorbs both on planes (011) and (111) involve at least one La atom, see Fig. 3.

Fig. 3. Favored adsorption sites and energies predicted by DFT simulations for CO₂ and CO on the (011) and (111) LRhZ pyrochlore planes.

Validation of Simulation Results

In an effort to verify the predicted adsorption behavior of CO₂ and CO, our simulation results were compared to available experimental data. In previous IR spectroscopy studies of tightly bound CO₂ on LRhZ pyrochlores [17], two relatively sharp absorption bands were observed at frequencies of 1509 and 1367 cm⁻¹ (see Fig. 4) after flowing CO₂/He for 15 min followed by 15 min of He flush, removing then any weakly bound species. The difference between the frequencies of the two CO₂ absorption bands ($\Delta\nu = 142$ cm⁻¹) agrees remarkably well with the calculated (via DFT) difference between the highest frequencies for the two most stable configurations of adsorbed CO₂ on the (011) plane ($\Delta\nu = 152$ cm⁻¹), namely, at the bridge Zr-La and 3-fold Zr-La-La sites. When computing the difference between the highest frequencies for the two most stable configurations of adsorbed CO₂ on the (111) plane, at the 3-fold Zr-Zr-La and Rh-Zr-La sites, this difference is considerably less ($\Delta\nu = 53$ cm⁻¹). Considering the computational results presented in Fig. 3 for CO₂ adsorption energy, it is expected that the experimental IR data for strongly bound CO₂ [17] would more closely match that of the (011) LRhZ pyrochlore surface because CO₂ binds more strongly to the (011) surface and is only weakly bound to the (111) LRhZ surface.

Furthermore, our DFT results show that the most favorable CO₂ adsorption sites for LRhZ planes (011) and (111) involve La species, which is congruent with Pakhare et al. [17], who concluded that oxycarbonates form on the LRhZ surface at La sites.

Fig. 4. FTIR spectra after 15 min of CO₂/He flow → 15 min of He flush over reduced LRhZ. Reprinted from J. Catal., 316, Devendra Pakhare, Viviane Schwartz, Victor Abdelsayed, Daniel Haynes, Dushyant Shekhawat, James Poston, James Spivey, Kinetic and mechanistic study of dry (CO₂) reforming of methane over Rh-substituted La₂Zr₂O₇ pyrochlores, 78-92, Copyright (2014), with permission from Elsevier. [17]

Separate DRIFTS studies of Rh supported on different oxides (Al₂O₃ and SiO₂) [50, 51] indicated that the dominant surface species under reaction conditions is CO bound in linear and bridge schemes to metallic Rh. A similar adsorption behavior was observed in our simulations of Rh doped pyrochlores. Specifically, stable, linear atop binding of CO on Rh sites was observed on the (011) and (111) pyrochlore planes, but as expected, no bridge adsorption of CO on Rh sites was observed due to the high dispersion and low concentration of Rh surface sites.

As the limited experimental observations for species adsorption on LRhZ pyrochlores are in reasonable agreement with the computational results, it is assumed that the DFT simulation scheme used in this study is adequate to describe the energetics for the overall reaction process.

Adsorption behavior for DRM reactants, intermediates and products

DFT simulations were used to quantify the energetics of adsorption for all DRM reactants, intermediates and products on multiple LRhZ pyrochlore surface sites. The sites for species adsorption on one or both of the studied LRhZ surfaces included atop (on Rh, Zr, and La), bridge (on Rh-Zr, Zr-La, Rh-La, and La-La), and three fold sites (on Rh-Zr-Zr, Rh-La-La, Zr-La-La, and Zr-Zr-La). A summary of the strongest adsorption energies for

all relevant species on the (011) and (111) surfaces are shown in Fig. 5. In general, a low adsorption energy (negative but close to zero) suggests that the tested site is not preferred for that intermediate or that it only physisorbs to the catalyst surface. In contrast, a very high adsorption energy (negative value far from zero) suggests that the surface site may become poisoned by that particular intermediate. Species having moderate adsorption energies on a given site are those most likely to actively participate for multiple turnovers in the mechanism to convert methane and CO₂ into syngas. A detailed list of the adsorption behavior for all species on all tested sites along with a summary of the most important adsorption sites for the dry reforming of methane is provided in the Supporting Information.

Fig. 5. Predicted adsorption energies (ΔE_{ads}) of species involved in the dry reforming of methane for the (011) and (111) LRhZ pyrochlore planes.

From the DFT simulations, it is observed that the DRM reactants (CH₄ and CO₂) can adsorb on both the (011) and (111) LRhZ pyrochlore planes, and thus, DRM reactions are possible on both surfaces. It is also observed that neither pyrochlore plane considerably favors the adsorption of any intermediate.

For physisorbed molecular species, such as CH₄ and H₂, the favored adsorption sites identified in this study can only be interpreted as the approximate region where these molecules associate because DFT methods are insufficient to accurately describe van der Waals forces. Along these lines, multiple adsorption sites are expected for physisorbed species such as CH₄ and H₂. Likewise, H₂O presents multiple adsorption sites since it is weakly bound ($E_{\text{ads}} \sim -1\text{eV}$). In contrast, the majority of reaction intermediates are chemisorbed to the pyrochlore surface; thus, it was possible to clearly identify favored adsorption sites for these species via DFT minimization methods. It should also be noted

that hydrogen and other possible reaction products, such as methanol, are more readily adsorbed on the pyrochlore surface via a dissociative pathway, yielding molecular fragments that chemisorb to select sites on the LRhZ pyrochlore surface.

On the plane (011), an adsorbed structure for C in the bulk was found after structure optimization ($\Delta E_{\text{ads}} = -7.11$ eV) and it exhibits stronger adsorption than the surface C adsorbed in the 3-fold Zr-La-La position. The C adsorbed in the bulk was however not considered as a reactive species for further analysis, due to steric interactions that would limit its reaction with other surface adsorbed species.

3.2 Reaction and activation energies

3.2.1 Reaction energy

A greater understanding of the overall DRM reaction pathway can be discerned by examining the reaction enthalpy (ΔH_{rxn}) for each possible mechanistic step. These values can also prove useful in calculating the corresponding activation barrier associated with each of these mechanistic steps. Therefore, the heats of reaction were calculated for all possible reaction processes using the optimized system energies for reactants and products, which were calculated using DFT. For the example, for the surface catalyzed dissociation reaction, $\text{AB}^* + * \rightarrow \text{A}^* + \text{B}^*$ ($*$ denotes a surface site or surface bound species), the heat of reaction was calculated as follows:

$$\Delta H_{\text{rxn}} = E_{\text{slab-A}} + E_{\text{slab-B}} - E_{\text{slab-AB}} - E_{\text{slab-empty}} \quad (3)$$

where $E_{\text{slab-A}}$, $E_{\text{slab-B}}$, and $E_{\text{slab-AB}}$ equal the energy of a pyrochlore slab with A, B or AB adsorbed, respectively, and $E_{\text{slab-empty}}$ is the energy of a pyrochlore slab without adsorbates. Full atom relaxation (slab and adsorbates) is allowed in all these calculations.

To calculate activation energies using the CI-NEB method, all DFT simulations of multiple reactants/products involved in a given reaction were placed upon the same pyrochlore slab. More specifically, the species were placed at the preferred adsorption site identified from earlier DFT all-atom energy minimization simulations involving each individual species adsorbed on a pyrochlore slab. In some cases, the final minimized energy structure for systems with two adsorbants indicated that there were lateral interactions between adsorbed species but that no chemical bond existed between them. To account for pyrochlore surface relaxation effects, the enthalpy of reaction for every elementary reaction step was calculated as in eq. (3), and the value of the activation energy calculated via CI-NEB (see later discussion) was adjusted to the value of ΔH_{rxn} considering surface relaxation effects. Further explanation on how the enthalpies of reaction and the corresponding activation barriers are calculated can be found in the Supporting Information.

Using the calculated activation barriers for all reactions, it was possible to identify the favored reaction pathway for the dry reforming of methane on LRhZ pyrochlore catalysts. The change in reaction energy for each mechanistic step along this favored reaction pathway is shown in Fig. 6 (a full list of reaction energies used in the making of Fig. 6 can be found in Supporting Information).

Fig. 6. DFT derived total energy change associated with each mechanistic step along the favored reaction pathway for the dry reforming of methane on the (111) surface of Rh doped pyrochlore catalysts. (*) denotes adsorbed species.

It is observed that the dehydrogenation and subsequent oxidation of methane, shown in the top of Fig. 6, involves several endothermic and exothermic reaction steps along the entire pathway. As methane undergoes dehydrogenation, the surface hydride species formed via these reactions can recombine to form molecular hydrogen and desorb from the catalyst surface. The hydrogen-hydrogen addition and desorption processes are endothermic.

To complete the DRM catalytic cycle, methane oxidation processes are complemented by CO_2 reduction reactions to yield CO. The DFT derived energetics associated with the

reduction of CO₂ are shown in the lower part of Fig. 6. Ab initio calculations suggest that two reaction pathways are possible, an indirect route involving hydrogen addition to adsorbed CO₂ and a direct route since both routes present similar energetic barriers.

Inspection of the energy of reaction data in Fig. 6 shows the reaction of O* with CH₂* is the most endothermic step (2.08 eV), suggesting it as a slow step. As discussed later, the assignment of the rate limiting step to the CH₄ dehydrogenation segment of the overall reaction mechanism was confirmed by activation energy calculations as well as experimental observations [17]. Additionally, the overall reaction energy for DRM calculated by DFT methods is 374.4 kJ/mol, whereas the theoretical value calculated from the heats of formation of reactants and products is 247.4 kJ/mol.

3.2.2 Activation energies and the Brønsted-Evans-Polanyi relationship

The proposed reaction network for DRM on pyrochlore surfaces (Fig. 2) includes 130 reactions, considering all forward and reverse reactions occurring on multiple site types on two different catalytic planes. To solve this computationally intensive problem, the coupling of rigorous DFT calculations with proven scaling methods was critical. For activation energies calculated using rigorous DFT methods, the climbing image – nudged elastic band approach was used to identify the minimum energy pathway between reactants and products.

For activation energies not explicitly calculated using DFT, the Brønsted-Evans-Polanyi (BEP) scaling method was used to estimate reaction energy barriers. The BEP relationship ($\Delta E_{\text{act}}' = \beta \Delta H_{\text{rxn}}' + \alpha$) linearly correlates the activation energy of an elementary reaction to the reaction enthalpy for that process, and it has been successfully applied to many catalytic systems for efficiently locating activation barriers.[52-59] However, use of this approach requires that all reactions be defined such that the reactants are non-associated gases adsorbing on pristine catalyst surface sites, see Fig. 7. For a certain set of elementary reactions, e.g., dissociation reactions, the BEP correlation is independent of the adsorbate (reactant) and the metal on the catalytic surface, which enables the development of a universal reaction correlation for a given metal surface geometry. This universality is based on the fact that the transition state structures are independent of the adsorbate and the metal on the surface.

Fig. 7. Potential energy diagram for the dissociative adsorption of a representative diatomic gas. For the BEP relationship, the activation and reaction energies reference the gas phase reactant.

On the pyrochlore catalyst surface, metal adsorption sites are separated by bridging oxygen atoms. As the preferred adsorption sites for species involved in a given reaction step are not necessarily adjacent to each other on the catalyst surface, calculated activation energies implicitly include all necessary energy barriers associated with close proximity diffusion upon the surface. Fig. 8 shows a select case of a reaction path found using the CI-NEB method, the CHO dehydrogenation on the plane (011) of LRhZ, where major displacement of the H-atom is required to reach the preferred adsorption site (bridge Rh-La), which leads to a high activation barrier (3.08 eV). All the reaction barriers calculated by rigorous DFT methods are shown in Fig. 9 for reactions occurring on both the (011) and (111) LRhZ pyrochlore surfaces. Additional structures for reaction paths calculated using the CI-NEB method can be found in the Supporting Information.

Fig. 8 Reaction path for $\text{CHO}^{*+*} \rightleftharpoons \text{CO}^{*+}\text{H}^{*}$ on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to CHO^{*+*} . The Rxn coordinate '4' refers to $\text{CO}^{*+}\text{H}^{*}$. The Rxn coordinates '1', '2' and '3' refer to the three intermediate images considered.

	Dissociation form to be used in the BEP relationship	Surface Reaction	Plane
a	$\text{CO}_{(\text{g})} + 2^* \rightleftharpoons \text{C}^* + \text{O}^*$	$\text{C}^* + \text{O}^* \rightleftharpoons \text{CO}^* + ^*$	011
b	$\text{H}_{2(\text{g})} + 2^* \rightleftharpoons \text{H}^* + \text{H}^*$	$\text{H}^* + \text{H}^* \rightleftharpoons \text{H}_2^* + ^*$	011
c	$\text{H}_{2(\text{g})} + 2^* \rightleftharpoons \text{H}^* + \text{H}^*$	$\text{H}^* + \text{H}^* \rightleftharpoons \text{H}_2^* + ^*$	111
d	$\text{CH}_{3(\text{g})} + 2^* \rightleftharpoons \text{CH}_2^* + \text{H}^*$	$\text{CH}_3^* + ^* \rightleftharpoons \text{CH}_2^* + \text{H}^*$	111
e	$\text{CHO}_{(\text{g})} + 2^* \rightleftharpoons \text{CO}^* + \text{H}^*$	$\text{CHO}^* + ^* \rightleftharpoons \text{CO}^* + \text{H}^*$	011
f	$\text{OH}_{(\text{g})} + 2^* \rightleftharpoons \text{O}^* + \text{H}^*$	$\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + ^*$	111
g	$\text{OH}_{(\text{g})} + 2^* \rightleftharpoons \text{O}^* + \text{H}^*$	$\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + ^*$	011
h	$\text{COH}_{(\text{g})} + 2^* \rightleftharpoons \text{C}^* + \text{OH}^*$	$\text{C}^* + \text{OH}^* \rightleftharpoons \text{COH}^* + ^*$	011
i	$\text{COH}_{(\text{g})} + 2^* \rightleftharpoons \text{CO}^* + \text{H}^*$	$\text{COH}^* + ^* \rightleftharpoons \text{CO}^* + \text{H}^*$	011
j	$\text{CH}_{(\text{g})} + 2^* \rightleftharpoons \text{C}^* + \text{H}^*$	$\text{CH}^* + ^* \rightleftharpoons \text{C}^* + \text{H}^*$	011

Fig. 9. DFT calculated activation energies for selected reactions, as well as the combined BEP correlation for the (011) and (111) LRhZ pyrochlore surfaces.

Despite the heterogeneity of the adsorption sites found on the LRhZ surfaces, the reaction and activation energies for most DRM reactions showed an evident linear correlation. Furthermore, the reactions used to construct the correlation involved the breaking of multiple types of bonds, including C-O, H-H, C-H and O-H, confirming that the linear BEP relationship $\Delta E_{\text{act}}' = 0.8253 \cdot \Delta H_{\text{rxn}}' + 0.6216$ ($R^2=0.88$) could be applied to all elementary reaction steps occurring on the LRhZ surface. Subsequently, the BEP relationship was used to quantify all activation energies not explicitly calculated by CI-NEB/DFT methods using previously calculated heats of reaction data derived using rigorous DFT methods.

3.3 Reaction mechanism

The first steps of the DRM reaction mechanism are by necessity the adsorption of reactants on to the catalyst surface. From prior simulation and experimental data, it is expected that the methane adsorption process is energetically unfavorable because of the low affinity that methane has for metal and oxide surfaces. To elucidate the exact mechanism for the adsorption of DRM reactants on LRhZ catalysts, DFT simulations were used to develop the potential energy diagrams for CH_4 and H_2 adsorption and dissociation that are shown in Fig. 10. Though it is possible for the molecular reactants to adsorb intact on the catalyst surface, these adsorption processes are found to only yield physisorbed species. Recognizing from simulations that low activation barriers exist for dissociation of the physisorbed species, it is more likely that methane and hydrogen undergo dissociative adsorption, compacting then the physisorption and later dissociation into a single step (see Fig. 10).

Fig. 10. Potential energy diagram for CH_4 and H_2 physisorption and subsequent dissociation. Solid lines indicate the dissociation path over the physisorbed species. Dashed lines indicate the dissociative adsorption path.

The activation energies for the forward and reverse reactions of all considered elementary steps are presented in Fig. 11 for the (011) and (111) pyrochlore planes. Based upon the magnitude of the barriers for these reactions, some elementary steps were considered

irreversible reactions, and those reactions are represented by single-ended arrows in the diagram. In contrast, reactions indicated by two-sided arrows are considered reversible.

Fig. 11. Full reaction network for DRM on planes (011) and (111) of LRhZ. The values above, below and next to the arrows are the activation energies in eV, and the small arrows next to these values indicate what direction each activation energy corresponds to.

On both LRhZ planes, the dissociation of CH₃OH into CH₃ and OH, as well as the dissociation of CH₂OH into CH₂ and OH are nearly barrierless reaction steps, inhibiting then methanol formation, as observed experimentally. Water dissociation is also a barrierless reaction in both planes, for this reason, water formation is not expected in significant amounts. Experimentally, RWGS takes place over LRhZ up to approximately 700 °C [9], and therefore, negligible amounts of water are observed at higher reaction temperatures.

CH dissociation into atomic C and atomic H is practically unfeasible with this catalyst according to our simulation results. This observation helps to explain the resistance LRhZ pyrochlore catalysts have to coke formation during reaction. Further, many experimentalists [14-17] have proposed methane cracking to be the rate limiting step for the DRM. These observations corroborate the findings of this work; where the two rate limiting steps for DRM are found in the CH₄ dehydrogenation process. However, the reaction network proposed in this work provides an alternative route for C from CH₄ to oxidize and produce CO, different from what has been reported experimentally on Rh [11, 17, 48, 60, 61] and Ni supported catalysts [47], where full dehydrogenation of CH₄ is a necessary part of the reaction mechanism, and also different from computational findings using Ni surfaces, where CH and C species are generated [49, 62]. Specifically, the formation and subsequent dissociation of a CHO intermediate provides an alternative (minimum energy) pathway for CO generation from methane. By analyzing the activation energies for all possible reaction steps it is possible to discern a most favored reaction pathway for the DRM reactions. This preferred pathway for methane conversion to CO is illustrated in Fig. 12 for both the (011) and (111) LRhZ pyrochlore planes, identified by means of the activation energies presented in the complete reaction network (Fig. 11).

Fig. 12. Main reaction pathway for DRM on planes (011) and (111) of LRhZ. The values above, below and next to the arrows are the activation energies in eV, and the small arrows next to these values indicate what direction each activation energy corresponds to. The stars (☆) represent active sites where Rh is present.

The calculated activation barriers for the (011) plane suggest that it is less active for DRM. More specifically, it is energetically unfavorable for reactive carbon species proceeding from CH₄ to fully dehydrogenate and undergo subsequent oxidation to form adsorbed CO. The oxidant feed gas CO₂ is however able to readily dissociate into CO and O via direct decomposition. These results suggest that the (011) LRhZ plane is partially poisoned by unreacted carbon species resulting from adsorbed CH₄, which severely limits overall H₂ and CO production.

In contrast, the (111) LRhZ pyrochlore plane provides a moderate activation energy route for CH₂ oxygenation ($\Delta E_{\text{act}} = 2.88$ eV) and later CHO dehydrogenation ($\Delta E_{\text{act}} = 2.40$ eV) to produce CO, compared to the higher energy barrier on the (011) plane for the same reaction steps ($\Delta E_{\text{act}} = 3.49$ eV and $\Delta E_{\text{act}} = 3.08$ eV, respectively). Along with this barrier reduction, most of the elementary reactions occurring on (111) plane possess lower activation barriers compared to the (011) plane, and more species (CH₄, CH₂, CH₂O, CHO, CH, C, CO, COOH, H, O) present their most stable configurations on Rh-containing active sites (see Fig. 12) compared to the (011) plane. Additionally, surface energy calculations described in Section 2.3 suggest that the (111) plane is the most thermodynamically stable, which helps to support the conclusion that the (111) plane exhibits greater catalytic activity towards DRM. Finally, rhodium facilitates the indirect decomposition of CO₂ via hydrogenation to form carboxylic species on the plane (111). Yet, both direct and indirect decomposition are of consideration for this plane. The structures of adsorbed species involved in the reaction pathway on the (111) LRhZ pyrochlore plane can be found in the Supporting Information.

From Fig. 12, a simplified main reaction pathway can be discerned, since CH dehydrogenation encounters high activation barriers (3.37 eV or 4.01 eV) and later on, C oxygenation possesses a high activation barrier (3.31 eV) as well. Therefore, the main reaction pathway can be narrowed down to the one shown in Fig. 13. Where CH₂ oxygenation ($\Delta E_{\text{act}} = 2.88$ eV) and CHO dehydrogenation ($\Delta E_{\text{act}} = 2.40$ eV) appear as rate determining steps, taking into account the inherent limitations associated with DFT calculations and the simplifications assumed in this work.

Fig. 13 Simplified main reaction pathway for DRM on the plane (111) of LRhZ. The values above, below and next to the arrows are the activation energies in eV, and the small arrows next to these values indicate what direction each activation energy corresponds to. The stars (★) represent active sites where Rh is present.

The identified main reaction pathway occurring on the (111) LRhZ pyrochlore surface shows remarkable agreement with experimental results. The absence of Rh in the most favorable adsorption sites for the key species on plane (011) goes along with the fact that no catalytic activity for DRM was observed for undoped LZ pyrochlores; whereas, the (111) LRhZ surface readily adsorbs intermediates at Rh containing sites and shows activity for DRM. The reported CH_4 and CO_2 conversions after 200 min at 550 °C, 1 atm and a GHSV = 48,000 mL/g_{cat}/h are 12.3% and 19.7%, respectively. This difference in conversion occurs despite there being a stoichiometric feed to the reactor and results from reverse water gas shift (RWGS, $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) reactions, which also consume CO_2 , occurring simultaneously with the dry reforming of methane. Specifically, the lower conversion for methane (as compared to CO_2) results from the high number of dehydrogenation/oxidation steps and relatively high activation barriers (e.g., $\Delta E_a = 2.88$ eV and 2.40 eV for CH_4 versus 1.26 eV for CO_2) that must be overcome for methane to convert to CO; whereas CO_2 is readily converted to CO via two reactions pathways, DRM and RWGS. The relative rates of the DRM and RWGS reactions are also reflected in the H_2 to CO ratio 44:100 found experimentally [9], which indicate that CO_2 molecules on the surface react with methane derived hydrogen through RWGS reactions.

Apparent activation energies calculated from experimental data for CH_4 and CO_2 conversion using LRhZ catalysts are 1.50 and 1.17 eV, respectively.[17] This difference in activation energies is explained by the DFT simulation results, which show that the RWGS reaction has lower barriers to reaction than the DRM reaction on LRhZ catalysts. Specifically, the highest activation barrier calculated using DFT methods for CH_4 and CO_2 consumption via DRM reactions is 2.88 eV (for CO formation from methane), whereas the highest barrier for CO_2 consumption from RWGS was 2.08 eV (for $\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^*$, see reaction energetics reported in Supporting Information). These data clearly show that the

RWGS reaction has lower activation barriers to conversion than DRM reactions. Thus, the RWGS reaction is likely limited by the DRM reaction, which produces surface bound hydrogen species essential for the RWGS reaction. This qualitative comparison of experimental and DFT derived simulation results further indicates that the reaction mechanism, energetics, and general methodology for computations reported here provide an accurate description of the DRM and RWGS reactions occurring on LRhZ pyrochlore catalysts.

4. Conclusions

Plane wave DFT methods proved effective at modeling the reaction mechanisms for the dry reforming of methane and reverse water gas shift reactions on Rh-substituted lanthanum zirconate pyrochlore catalysts. DFT simulation results were found to accurately describe the bulk crystal properties of LRhZ pyrochlore catalysts as well as the energetics for species adsorption, diffusion and reaction on the catalyst surface. The activation barriers calculated for all elementary steps of the proposed DRM reaction network on the (111) and (011) pyrochlore planes yielded reaction energetics that were consistent with reported experimental data for this system. Further, the computed LRhZ lattice parameters match experimental X-ray diffraction results, and the predicted adsorption behavior for CO and CO₂ agree with infrared absorption data for these species adsorbed on LRhZ pyrochlores and related metal oxide surfaces.

From the computed activation barriers, the (111) plane of LRhZ pyrochlore catalysts was identified as the most reactive surface for DRM, and surface Rh atoms incorporated into the lattice are integral to many of the active sites along the main reaction pathway. This pathway consists of the dehydrogenation of adsorbed CH₄ to form CH₂, which then is oxygenated by atomic oxygen generated from CO₂ dissociation. CH₂O dehydrogenates to create CHO, which undergoes dissociation to release a hydrogen atom and an adsorbed CO that later desorbs to yield product gas. These adsorbed hydrogens can also interact with surface bound species derived from CO₂ to yield additional CO product and water via the reverse water gas shift reaction. The CH₂ oxygenation and CHO dehydrogenation processes exhibit the highest activation energies (2.88 eV and 2.40 eV, respectively) in the proposed DRM reaction mechanism, thus placing the rate limiting step along the CH₄ dehydrogenation segment of the reaction pathway. The highly endothermic reaction of CH₂ with O corroborates that the CH₄ dehydrogenation/oxidation is the rate limiting pathway in the mechanism, whereas CO₂ dissociation presented lower activation barriers and can occur either directly or via a hydrogen-induced route involving COOH species. Finally, experimental results of LRhZ catalyst performance show great agreement with the findings in this work. For example, activation energies calculated in this work indicate that CO₂

undergoes both RWGS and DRM reactions, with CH_4 conversion to yield hydrogen and CO being the rate limiting step for both processes. This observation explains why feeding a stoichiometric ratio of CO_2 and CH_4 to a DRM reactor yields higher CO_2 conversions than observed for CH_4 and why H_2 to CO product ratios obtained experimentally are always less than unity.

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