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## Methane partial oxidation under periodic reaction conditions on Pt/Al<sub>2</sub>O<sub>3</sub><sup>†</sup>

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The increasing interest in utilizing methane, the primary component of natural gas, for chemical production has spurred research into methane partial oxidation (MPO) as an alternative to traditional steam methane reforming (SMR). MPO has lower energy requirements and potential for carbon capture, making it an attractive option for hydrogen production. Challenges remain, however, such as carbon deposition leading to degradation and achieving high hydrogen selectivity. Here, the impact of periodic reactor operation on MPO over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was studied, primarily *via* varying reactor inlet compositions. Experiments were conducted using periodic operation strategies to assess the influence of changing reactant inlet concentrations on hydrogen formation during MPO. The results suggest that cycling between mixtures with low and high oxygen content can lead to transient hydrogen formation rates that surpass those achieved at steady state. Control experiments and density functional theory (DFT) calculations show that enhanced hydrogen formation can be attributed to the reaction between CO with hydroxyl groups at the metal and alumina support interface. This work underscores the critical role of surface coverages at the metal-support interface and suggests avenues for future exploration, including alternative support materials with higher OH mobility and changes in the cycling scheme to enhance catalyst performance under periodic conditions.

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## 1. Introduction

Given the abundance of methane, the main component of natural gas, there is growing interest in the scientific community to utilize methane in chemicals production, and not just combust it to generate heat or electricity.<sup>1,2</sup> Even though C–H activation is feasible on metal-based catalysts, the selective conversion of methane to useful products remains a ‘Holy Grail’ for chemical engineers.<sup>1</sup> Methane can be converted to hydrogen, which is industrially important and can be used as a clean fuel or as feedstock for a variety of reactions. Traditionally, hydrogen is produced through steam methane reforming (SMR) for industrial and energy applications.<sup>3</sup> However SMR is energy-intensive and can generate significant greenhouse gas emissions. Methane partial oxidation (MPO) has emerged as a potential alternative

for hydrogen production due to its lower energy requirements and potential for carbon capture.<sup>4,5</sup> During MPO, methane reacts with oxygen producing H<sub>2</sub> and CO. This reaction can be catalyzed by metals such as platinum, palladium, and rhodium supported on alumina, silica or ceria.<sup>6–10</sup> While MPO has shown promise as a potential route for hydrogen production, there are still several challenges that must be addressed. One major challenge is the potential for carbon deposition, which can lead to catalyst deactivation and reduced efficiency.<sup>4,11</sup> Another challenge is achieving high selectivity to H<sub>2</sub>, as other unwanted by-products such as H<sub>2</sub>O and CO<sub>2</sub> can form *via* methane combustion and are thermodynamically preferred.<sup>12,13</sup> Methane reactivity on a Pd/Pt based catalyst is a strong function of CH<sub>4</sub>/O<sub>2</sub> ratio. Chin *et al.* have shown a high oxygen content poisons the Pt catalyst surface<sup>14</sup> and can lead to Pd oxide formation.<sup>15</sup> Thus, methane conversion to hydrogen is limited by slow kinetics and low selectivity at high oxygen partial pressures, and the tendency for coke formation increases with low oxygen partial pressure.

To address this limitation, periodic reactor operation has been proposed as a promising strategy.<sup>16,17</sup> With periodic reactor operation it is possible to modulate surface coverage and oxidation state by varying the reaction conditions, which can result in significant performance enhancement.<sup>18–20</sup>

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Particularly, for redox reactions it is possible to feed pulses of reactants with different ratios of reactant gases and oxygen, often termed as rich if oxygen is lesser than the stoichiometric amount, or lean if the oxygen content is greater.<sup>20</sup> For example, Stötzel *et al.* have shown that cycling methane and oxygen can improve hydrogen selectivity by inhibiting water formation on a Pd-based catalyst during methane partial oxidation to synthesis gas.<sup>21</sup> Fathi *et al.* demonstrated a highly selective route for synthesis gas production from methane and oxygen in a cyclic reaction using cerium oxide.<sup>22</sup> In this route, cerium oxide acted as an intermediate oxygen carrier. The required temperature for this process was approximately 700 °C, significantly lower than the typical temperature used in conventional synthesis gas production, which is around 900 °C. During methane oxidation on Pd-based catalysts, Franken *et al.* employed a short reducing pulse every 5 minutes.<sup>23</sup> This improved the activity of the catalyst along with the catalyst lifetime by maintaining a mixed metallic and oxide phase. Karinshak *et al.* have shown reduction in  $T_{50}$  during methane combustion light-off with feed modulation over a Pt-Pd/spinel catalyst by varying the ratio of oxidants to reductants in the feed.<sup>20</sup> Creaser *et al.* have demonstrated that cycling between propane and oxygen during propane dehydrogenation over a V-Mg-O catalyst resulted in higher yields than with static conditions.<sup>24</sup> Similarly, Rambeau and Amariglio observed that switching between a feed of nitrogen and hydrogen led to higher ammonia synthesis production than that attained with steady state conditions over a ruthenium powder.<sup>25</sup> Fu *et al.* also demonstrated that periodic pulsing of hydrogen on a PtWO<sub>x</sub>/C catalyst achieved alternate states that led to one order of magnitude higher activity than under constant hydrogen feed during *tert*-butanol dehydration.<sup>18</sup> These studies highlight the potential advantages of periodic reactor operation, including enhanced catalytic efficiency and the ability to achieve higher yields of desired reaction products. Furthermore, periodic reactor operation offers flexible reactor dynamics by allowing for modulation of parameters such as reactor inlet composition, temperature, and pressure, among others.<sup>16</sup>

In this study, we investigated the effect of periodic reactor operation on methane partial oxidation (MPO) over Pt/Al<sub>2</sub>O<sub>3</sub> by modulating the reactor inlet compositions. We conducted experiments that included periodic operation strategies to understand how changing the reactant inlet concentrations impact hydrogen formation during methane partial oxidation over a supported Pt catalyst. Previous research by Carlsson *et al.* found increased catalytic activity of Pt/Al<sub>2</sub>O<sub>3</sub> when switching from CH<sub>4</sub>-rich to CH<sub>4</sub>-lean conditions during methane oxidation, but ultimately poor reactor utilization due to no methane conversion during the CH<sub>4</sub>-lean cycle.<sup>13,26</sup> In our experiments, we also explored strategies that would maintain similar reactor utilization as in static inlet condition experiments. We conducted our experiments primarily under methane-rich conditions, as excess oxygen promotes the formation of combustion products. Our results

show that varying the oxygen content in the feed streams can result in a transient increase in H<sub>2</sub> formation when switching from a higher O<sub>2</sub> content to a lower one. Through control experiments and supporting density functional theory (DFT) calculations, we determined that enhanced hydrogen formation can be attributed to the reaction of CO with hydroxyl groups on the alumina-support at the metal-support interface.

## 2. Methods

### 2.1 Experimental

**2.1.1 Catalyst synthesis.** The Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized using incipient wetness impregnation. Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, a precursor purchased from Sigma-Aldrich, was used to achieve 1% Pt weight loading onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, also purchased from Sigma-Aldrich. The Pt-containing catalysts were then dried in a Thermo Scientific Lindberg muffle furnace at 120 °C for 4 hours in a static air atmosphere. Subsequently, the temperature was gradually increased to 600 °C at a rate of 1 °C min<sup>-1</sup>, and held there for 4 hours to calcine the catalyst. The average Pt particle size of the synthesized catalyst was estimated to be approximately 2 nm with 54% dispersion using a H<sub>2</sub> chemisorption procedure, as described elsewhere.<sup>27</sup> The as-synthesized catalyst was reduced in hydrogen at 500 °C for 4 hours after loading it into the reactor and prior to reaction experiments.

**2.1.2 Reactor setup.** The reactor schematic is shown in Fig. S1.† Switching valves, purchased from VICI, were used to periodically switch between the reactor inlet streams. A back pressure regulator was installed in the bypass line to ensure that there were no fluctuations in concentration due to periodic operation. The catalyst, consisting of 50 mg of Pt/Al<sub>2</sub>O<sub>3</sub>, sieved to 0.25–0.4 mm particle size, mixed with 50 mg inert silica of the same pellet size range, was placed in a quartz tube with an internal diameter of 4 mm. The tube was positioned in the furnace and the outlet temperature was measured using a K-type thermocouple purchased from Omega.

The total flow rate was set to 100 sccm and the flow rates for all the gases were regulated using MKS mass flow controllers. The MKS mass flow controllers and switching valves were controlled using NI LabView software. Prior to the experiments, the catalyst was pre-treated in 5% H<sub>2</sub> in Ar at 500 °C for 30 minutes. All the experiments were performed at 450 °C unless otherwise specified. The periodic reaction experiments were performed by cycling a specified feed and regeneration mixture at an interval of 20 s. The methane concentration was kept at 2% in all experiments and the oxygen concentration was varied between 0.1 and 3%. The outlet concentrations were monitored using a Hiden HPR-20 mass spectrometer. Masses monitored were 2, 15, 18, 28, 32, 36, 44 corresponding to H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, CO, O<sub>2</sub>, Ar, CO<sub>2</sub> respectively, at a frequency of 33.3 Hz. Concentrations were calculated based on calibrations for each of the gases. Gases were purchased from Praxair.

**Caution!** Our experimental methods require the use of methane, hydrogen, carbon monoxide, carbon dioxide and oxygen gases. Methane, hydrogen and carbon monoxide are classified as GHS flammable gas, category 1. Oxygen is classified as GHS oxidizing gas, category 1. Carbon dioxide is classified as asphyxiant. The storage and use of the compressed gas cylinders were handled using UVA Environmental Health and Safety procedures.

## 2.2 Computational

We conducted periodic DFT calculations using the Vienna *ab initio* simulation package (VASP)<sup>28–33</sup> with a plane wave basis set under the Kohn–Sham formulation. We used the Atomic Simulation Environment (ASE)<sup>34</sup> for workflow management, visualization, and post-analysis. The electron exchange–correlation energy was determined using the Perdew–Burke–Ernzerhof (PBE)<sup>35,36</sup> functional, which included DFT-D3 dispersion corrections.<sup>37</sup> We used the projector augmented wave (PAW) method to describe the interaction between ion cores and electrons.<sup>38</sup> The valence electron wavefunction was expanded into a plane wave basis set with an energy cut-off of 400 eV, and spin polarization was enabled. We used Gaussian smearing with a width of  $k_B T = 0.1$  eV and subsequently extrapolated to 0 K. We stopped the self-consistent-field (SCF) cycle when the electronic energies converged to  $10^{-6}$  eV. A similar approach has been used previously for calculations for a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system.<sup>39</sup>

We adopted the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bulk structure from a previous study by Raybaud and co-workers.<sup>40</sup> For  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> we obtained the following unit cell parameters:  $a = 5.548$  Å,  $b = 8.360$  Å,  $c = 8.036$  Å;  $\alpha = \gamma = 90.00^\circ$ ,  $\beta = 90.59^\circ$  which are close to the reported values.<sup>39,41</sup> We further generated the (110) surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a thickness of 8 atomic layers, similar to the setup used by Hoffman *et al.*<sup>41</sup> We then grafted a Pt nanorod on top, ensuring minimal expansive strain in the Pt nanorod of only 0.1%. The open  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sites were fully hydrated as the (110) surface can have close to 3 OH per nm<sup>2</sup> at 450 °C.<sup>42</sup> The nanorod model with full hydration is shown in Fig. 1. Ionic relaxations were performed until the atomic forces were less than  $0.02$  eV Å<sup>-1</sup>, and we applied dipole correction in the direction normal to the surface. The Brillouin zone of the Pt nanorod model was sampled using a  $2 \times 1 \times 1$   $k$ -point mesh.

To compute gas-phase energies, we used the aforementioned parameters, except for a narrower Gaussian smearing width of 0.01 eV. We performed ionic relaxations until the atomic forces were less than  $0.005$  eV Å<sup>-1</sup> and applied dipole corrections in all three Cartesian directions, keeping the gas molecule at a central position in a cell of size  $15$  Å  $\times$   $15$  Å  $\times$   $15$  Å.

For adsorption/desorption steps, we define the adsorption energy as

$$\Delta E = E_{\text{mod/ads}} - E_{\text{mod}} - E_{\text{gas}},$$

where  $E_{\text{mod/ads}}$  is the total energy of the model with adsorbate,  $E_{\text{mod}}$  is the energy of optimized model, and  $E_{\text{gas}}$  is the energy of



Fig. 1 Pt nanorod on alumina model.

the gas phase reference molecule. In our definition, favorable binding is indicated by negative values of  $\Delta E$ .

## 3. Results and discussion

### 3.1 Reaction experiments under periodic inlet conditions

Fig. 2 depicts the schematic for a periodic reaction experiment, wherein a reactor inlet feed-mixture of 2% CH<sub>4</sub> and varying oxygen concentrations (0.05–1%) were periodically cycled with a regeneration mixture containing 1% O<sub>2</sub>, balance Ar mixture. Fig. 2(b–f) illustrate the reactor outlet profile during two phases of the periodic experiment after steady cycle-to-cycle outlet concentrations were obtained. Complete oxygen conversion was observed during the phase containing CH<sub>4</sub> (feed-phase), while the oxygen concentration rapidly attained the inlet value during the half-cycle without CH<sub>4</sub>. This rapid increase in O<sub>2</sub> concentration to the inlet value is attributed to the saturation of oxygen atoms on the Pt surface, as platinum is known not to form bulk platinum oxide under these conditions.<sup>43,44</sup> Methane conversion was observed to be dependent on the oxygen concentration. At lower oxygen concentrations in the feed phase containing CH<sub>4</sub>, enhanced hydrogen formation was initially observed, followed by a decrease to the steady state level of the respective mixture. A similar behavior was observed by Carlsson *et al.* during their periodic reaction experiments on 5% Pt/Al<sub>2</sub>O<sub>3</sub>, with cycling between 0 and 1250 ppm oxygen.<sup>13</sup> We also



**Fig. 2** (a) Schematic of cycling strategy 1. Reactor outlet profile at 450 °C for a periodic reactor inlet mixture containing 2% CH<sub>4</sub> and (b) 0.05% O<sub>2</sub>, (c) 0.1% O<sub>2</sub>, (d) 0.2% O<sub>2</sub>, (e) 0.5% O<sub>2</sub>, (f) 1% O<sub>2</sub>, all balanced in Ar, with the 2nd phase containing 1% O<sub>2</sub> in balance Ar. The shaded areas indicate excess H<sub>2</sub> production above the equivalent steady state condition.

performed experiments where there was a periodic switch between the CH<sub>4</sub>/O<sub>2</sub> phase and a phase with just Ar, *i.e.*, inert, with results shown in Fig. S2,† to verify that the peaks that we observed during the experiments are not because of any artifact from pressure changes during switching.

We compared the amount of hydrogen formed during the feed-phase for all the experiments with the cycling strategy described in Fig. 2(a). The hydrogen formation during this half cycle with this scheme was generally higher than the steady state cases, except for the highest O<sub>2</sub> concentration (Fig. 3). This latter observation is attributed to excess oxygen on the surface and feed, which is consistent with Chin *et al.*'s findings, where they reported methane activation to be dependent on the oxygen concentration with methane activation strongly inhibited by oxygen at O<sub>2</sub>/CH<sub>4</sub> > 1.<sup>14</sup> We did not observe any significant difference in CO formation during cycling as its concentration remained about 0.25% during all experiments (Fig. 2(b–f)). We can attribute the nearly constant CO concentration to favorable CO oxidation or water gas shift reaction on the Pt catalyst and lower CO selectivity as the oxygen content increases. The concentration profiles for CO<sub>2</sub> and H<sub>2</sub>O are shown in Fig. S3.† Overall, this cycling strategy demonstrates how partial oxygen coverage can aid in achieving enhanced hydrogen formation, by avoiding oxygen poisoning which inhibits methane activation. However, this strategy leads to poor utilization of the reactor as there is no methane flow into the reactor for half of the time. Therefore, we investigated periodic

experiments with cycling between a mixture containing the same methane concentration but lower oxygen (feed mixture) and higher (regeneration mixture) concentrations.

Fig. 4(a) depicts a cycling strategy where, similar to the previous experiment, the oxygen concentration in one phase was varied, but here the methane concentration was held constant at 2% through both phases. The reactor outlet



**Fig. 3** Hydrogen produced in the feed phase during the cycling conditions described in Fig. 2, and a comparison with steady state measurements.





**Fig. 4** (a) Schematic of the cycling strategy 2. Reactor outlet profile at 450 °C for feed mixture containing 2% CH<sub>4</sub> and (b) 0.05% O<sub>2</sub>, (c) 0.1% O<sub>2</sub>, (d) 0.2% O<sub>2</sub>, (e) 0.5% O<sub>2</sub>, (f) 1% O<sub>2</sub>, all balanced in Ar. The alternating phase always contained 2% CH<sub>4</sub> and 3% O<sub>2</sub>, all balanced in Ar. The shaded areas indicate excess H<sub>2</sub> production above the equivalent steady state condition.

profiles are shown in Fig. 4(b–f). Complete oxygen conversion was observed in both phases of the cycle, as the reaction mixture was continuously in a CH<sub>4</sub>-rich phase relative to combustion stoichiometry. Methane conversion was again dependent on the O<sub>2</sub> concentration. Although hydrogen formation was initially high with the switch in inlet composition to the lower O<sub>2</sub> phase (feed phase) of the cycle, it eventually decreased. Interestingly, with cycling strategy 2, hydrogen formation was higher than steady state even with the 1% O<sub>2</sub> feed mixture, where we observed inhibition for the same mixture with cycling strategy 1. Fig. 2 shows up to 1% unreacted oxygen leaving the reactor during the regeneration cycle of strategy 1, whereas oxygen is completely consumed in strategy 2. Thus, a possible explanation for the higher hydrogen formation rate at the beginning of the feed cycle of strategy 2 is that continued methane oxidation during the regeneration phase reduces the surface coverage of oxygen. The lower oxygen surface coverage at the beginning of the feed phase of strategy 2 promotes hydrogen desorption over water formation.

We calculated the amount of additional H<sub>2</sub> formation with respect to the steady state during feed phase with variable O<sub>2</sub> and compared this to the amount formed at steady state for each of those mixtures, with the results shown in Fig. 5. The excess H<sub>2</sub> formation decreased with an increase in O<sub>2</sub> concentration due to the higher side reaction to water. The

profiles for water and CO<sub>2</sub> are shown in Fig. S4,<sup>†</sup> describing the more significant water formation with a higher level of overall O<sub>2</sub> and 3% O<sub>2</sub> in the regeneration phase. We also experimented with different durations of the regeneration



**Fig. 5** Amount of additional (compared to respective steady state) hydrogen produced in the feed phase during cycling strategy 2.

phase and discovered that we could increase feed utilization. However, this increase came at the cost of reducing the total hydrogen produced (Fig. S5†).

The excess  $\text{H}_2$  formation was up to 5 times that of the Pt active sites, which indicates that  $\text{H}_2$  originates from a catalytic process that is facilitated by the presence of O-containing surface species that have accumulated on the catalyst during the regeneration phase, or the involvement of species stored on the support. Oxygen or hydroxyl species on Pt reportedly inhibit  $\text{CH}_4$  activation<sup>14,45</sup> and therefore cannot explain the observed increase in  $\text{H}_2$  production. The most commonly implicated support species are hydroxyl or carbonate species. For example, Becker *et al.* attributed the enhanced formation of CO in the rich phase during methane oxidation on Pt/ $\text{Al}_2\text{O}_3$  under cycling phases of net-reducing and net-oxidizing feed to excess O-containing species (hydroxyl or carbonate species on alumina).<sup>46</sup> Sautet's group has calculated that hydroxyls remain stable at temperatures up to 450 °C.<sup>42,47</sup> This is consistent with Kalamaras *et al.*'s observation, where they exposed Pt/ $\text{Al}_2\text{O}_3$  to  $\text{D}_2\text{O}$ , followed by a mixture of CO and  $\text{H}_2\text{O}$ , resulting in the formation of  $\text{H}_2$ , HD, and  $\text{D}_2$ , demonstrating the presence of OD species on the surface.<sup>48</sup>

We chose overall  $\text{CH}_4$ -rich conditions for our study to mitigate oxygen inhibition on  $\text{CH}_4$  activation, but under these reducing conditions the support hydroxyl coverage may be limited under steady state operation. In contrast, the additional oxygen in the regeneration cycle of our periodic operating scheme leads to substantial water formation and presumably high hydroxyl coverages on  $\text{Al}_2\text{O}_3$ . We hypothesize that the transient formation of support hydroxyls favors the water-gas shift (WGS) reaction with CO at the metal-support interface (MSI) and can account for the measured increase in  $\text{H}_2$  formation. To probe the nature of surface species present on the catalyst after the regeneration phase of the cycle, we performed titration experiments where we exposed the catalyst to CO. CO was chosen as titrant, because it is a partial oxidation product that binds strongly to Pt, it has the potential to inhibit  $\text{CH}_4$  conversion,<sup>49,50</sup> can displace other adsorbates, and it can react with hydroxyls or carbonates at the Pt/ $\text{Al}_2\text{O}_3$  interface.

### 3.2 CO titration experiment

For the CO titration experiments we exposed the catalyst to a mixture of 2%  $\text{CH}_4$  and 3%  $\text{O}_2$  and subsequently purged the reactor system with Ar to remove residual gases. During the purging step we did not observe any  $\text{H}_2$  desorption. We then introduced 1.5% CO into the system and cycled it with Ar, as shown in Fig. S6†. The observed formation of  $\text{H}_2$  and  $\text{CO}_2$  are depicted in Fig. 6. The  $\text{H}_2$  and  $\text{CO}_2$  formation decreased over multiple cycles and ultimately stabilized. Although we used moisture and hydrocarbon traps, we suspect in the last few cycles  $\text{CO}_2$  and  $\text{H}_2$  formation is due to impurities ( $\text{CO}_2$  and  $\text{H}_2$  formation without using traps is shown in Fig. S7†). Even after removing the contribution from impurities, we observed

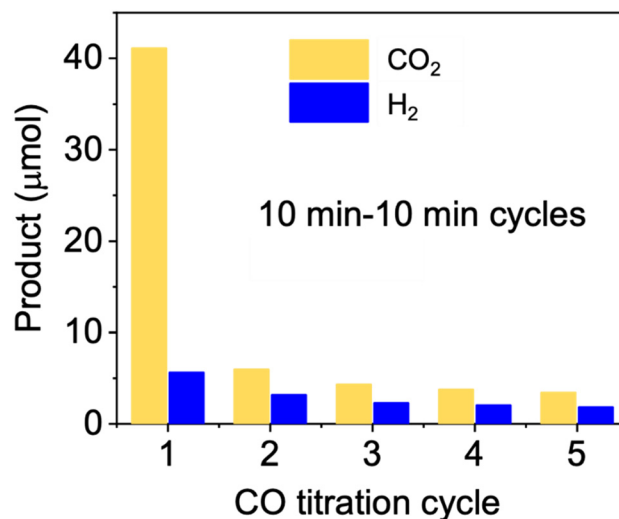


Fig. 6 Amount of  $\text{CO}_2$  and  $\text{H}_2$  produced during CO titration experiments at 450 °C. A schematic of the CO titration experiment and respective reactor outlet profiles are shown in Fig. S6†.

$\text{CO}_2$  formation of around 37 μmol and  $\text{H}_2$  formation of 2.5 μmol. Both the amount of  $\text{CO}_2$  and  $\text{H}_2$  are higher than the number of active Pt sites (1.4 μmol). A plausible source of  $\text{H}_2$  is water-gas shift chemistry involving support hydroxyls. The higher content of  $\text{CO}_2$  is also consistent with water-gas shift, or could originate from CO oxidation with residual O atoms on Pt, or from carbonate decomposition from alumina.

Considering the large amounts of excess  $\text{H}_2$  relative to the number of Pt sites and the absence of  $\text{H}_2$  during Ar purging, hydrogen storage in the form of a Pt-surface intermediate cannot account for all excess hydrogen formed during partial oxidation. Thus, the modified catalyst surface must alter reactivity or selectivity. We can eliminate O-assisted C–H bond activation on Pt, because in our experiments we routinely see lower  $\text{CH}_4$  conversion with increasing  $\text{O}_2$  concentration. Carbonate on  $\text{Al}_2\text{O}_3$  can form from CO or  $\text{CO}_2$  exposure, but it is frequently implicated as poison of metal-support interface (MSI) sites and unlikely to co-catalyze the partial oxidation of  $\text{CH}_4$  to  $\text{H}_2$  as surface carbonates have been found to inhibit methane activation as well as CO oxidation on various supported catalysts.<sup>51–54</sup> That leaves hydroxyls on the alumina support, which can readily form during the regeneration phase where we observe significant water formation. During the feed phase, these hydroxyls may co-catalyze  $\text{CH}_4$  partial oxidation, enable steam-reforming chemistry, or react with the partial oxidation product CO to form  $\text{CO}_2$  and  $\text{H}_2$ .<sup>20,55–58</sup> The formation of  $\text{CO}_2$  and  $\text{H}_2$  from CO is confirmed in our titration experiments. Moreover, since the measured amount of  $\text{H}_2$  exceeds the total amount of Pt sites including the perimeter sites, support hydroxyls must be mobile to replenish the reactive hydroxyl groups at the interface. To provide a molecular interpretation for these observations, we have used DFT to propose a possible WGS pathway at the Pt/alumina interface.

### 3.3 WGS reaction mechanism at the Pt/alumina interface

The WGS reaction is a well-studied process that occurs on supported Pt catalysts.<sup>48,56,57,59–64</sup> During this reaction, OH groups, formed by the dissociation of water, react with CO to form H<sub>2</sub> and CO<sub>2</sub>. Several studies<sup>48,61,65–68</sup> have been conducted to understand the H<sub>2</sub> and CO<sub>2</sub> formation mechanism *via* CO reacting with OH, and many suggest that there is some reactivity at the MSI. Interfacial activity has been supported through mechanistic DFT studies on Pt/TiO<sub>2</sub> and Pt/ceria among others where the support is more reducible.<sup>59,60,69</sup> Previously, our group has studied H<sub>2</sub> activation at the Au/TiO<sub>2</sub> interface using a nanorod model and assigned pivotal roles to support hydroxyls during CO and H<sub>2</sub> oxidation.<sup>70,71</sup>

However, despite the importance and widespread use of Pt/alumina as a catalyst, there have been no DFT studies to identify the elementary steps for the CO and OH reaction at the Pt–alumina interface. To fill this knowledge gap, we have calculated the thermodynamic potential energy diagram for WGS on extended Pt nanorods on alumina. Activation energy barrier calculations using the climbing image nudged elastic band (CI-NEB) method were attempted, but intermediate images repeatedly failed to reach electronic convergence and transition states could not be located.

To probe the reaction between CO and support hydroxyls, we considered the periodic Pt nanorod model on fully hydrated alumina support depicted in Fig. 1 and explored the mechanism illustrated in Fig. 7. The respective energy profile is shown in Fig. 8. The fully hydrated alumina surface is expected to approximate the state of the catalyst after the regeneration phase. CO adsorbs to the Pt nanorod near the MSI (Fig. S8†) with a binding energy of  $-2.10$  eV. To initiate the interfacial reaction, we calculated the formation of a carboxyl and the reverse spillover step of H atom migration from alumina to Pt. The formation of carboxyl was strongly endothermic with  $1.53$  eV, which we attribute to an unstable electronic defect on alumina. Alumina is an insulator with a band gap of  $8.7$  eV and cannot easily accommodate the excess electron that remains after OH is removed from the support.<sup>72–74</sup> However, the electronic surface structure of alumina can strongly deviate from its bulk properties. For example, the (100) and (110) surfaces of crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>



Fig. 8 Energy profile for the reaction pathway shown in Fig. 7. The labels in the profile correspond to the structures in the Fig. 7.

are predicted to have valence bands near the Fermi level and band gaps of only  $\sim 3$  eV.<sup>75</sup> Similarly, the band gap for ultrathin (7–10 nm) films of amorphous alumina has been measured to be  $2.5$  eV, which is in the semiconductor range.<sup>76</sup>

We performed a projected density of states (PDOS) analysis of the interface Al and O atoms with the Pt nanorod model and compared this with the bare alumina surface as shown in Fig. 9. Surface hydration was not considered, to simplify the interpretation of the PDOS analysis. Interestingly we observed new O-2p and Al-2p bands, which appeared near the Fermi level and were continuous, implying alumina near the MSI becomes more metallic in character. Because of the additional electronic states near the Fermi level, the H transfer step (Fig. 7C) and carboxyl formation (Fig. 7D) were found to be only mildly endothermic. This system constitutes an example where electronic interactions between a metal particle and the support atoms near the MSI can further help in stabilizing intermediates that require electron transfer at the interface. Higher hydroxyl mobility can further increase the reactivity at the MSI.<sup>74,77</sup>

In contrast to carboxyl formation, the transfer of H from alumina to Pt is endothermic by only  $0.38$  eV. Once the H atom, including its associated electron, has been transferred, carboxyl formation becomes mildly endothermic by  $0.22$  eV. Dehydrogenation of the carboxyl group being close to thermoneutral results in linear CO<sub>2</sub>. The recombination of H atoms to form a weakly adsorbed H<sub>2</sub> molecule on Pt was endothermic by  $0.75$  eV, which is similar to calculated values on the extended Pt(111) surface.<sup>62</sup> To close the catalytic cycle for WGS, after H<sub>2</sub> desorption we regenerate the interfacial hydroxyl groups through water adsorption. The overall calculated WGS reaction energy is exothermic by  $-0.73$  eV, which is in reasonable agreement with the value obtained from the NIST database ( $-0.43$  eV).<sup>78</sup> Overall our thermodynamic evaluation suggests that the potential energy diagram for CO oxidation by hydroxyls at the Pt/alumina interface is comparable to that of WGS on Pt(111).<sup>62</sup> Thus, WGS involving transiently formed hydroxyls at the MSI is a plausible explanation for the excess H<sub>2</sub> (and CO<sub>2</sub>) observed in

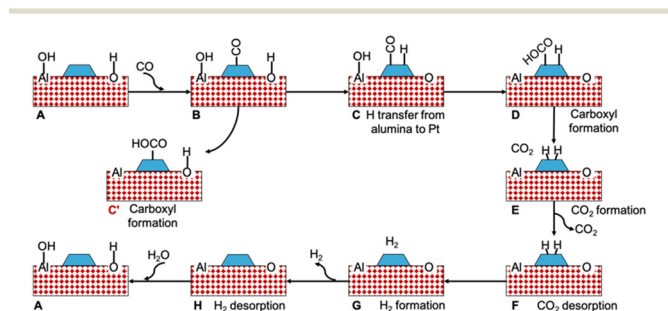


Fig. 7 Schematic reaction pathway for CO oxidation by OH groups on Pt (nanorod)/alumina. The simplified representation shows only one water molecule in the mechanism.

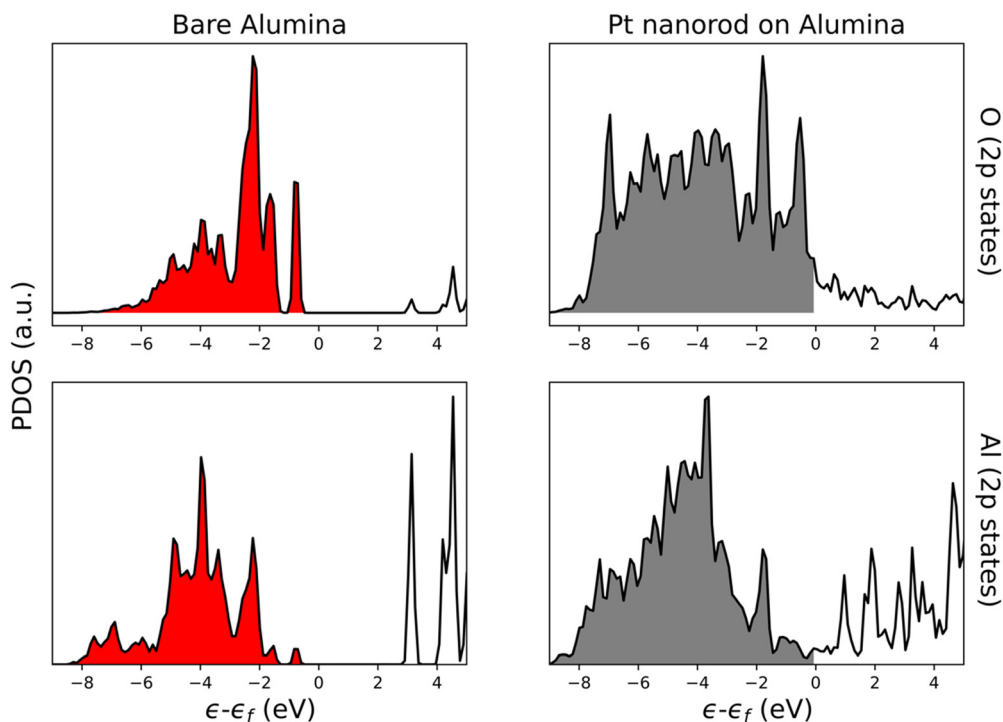


Fig. 9 PDOS analysis for interface Al (2p states) and O (2p states) atoms on Pt/alumina (Pt nanorod on alumina) and only alumina (bare alumina).

our periodic experiments. To further improve the  $H_2$  yield of  $Pt/Al_2O_3$  under periodic operating conditions it appears prudent to increase the number of accessible hydroxyls at the MSI. This may be achieved by selecting supports with high hydroxyl storage capacity and hydroxyl mobility. Alternatively, catalyst architectures that mirror the dual-layer design of  $CH_4$  oxidation catalysts integrated with  $CeO_2$  or spinel-oxides as dynamic oxygen storage materials could be explored.<sup>79,80</sup> Possible candidates for dynamic hydroxyl storage materials are bulk metal hydroxides or oxyhydroxides.

## 4. Conclusions

Experimental and computational approaches were used to investigate periodic reactor operation for methane partial oxidation on a model  $Pt/Al_2O_3$  catalyst. Our findings indicate that alternating between low and high oxygen content mixtures can result in transient hydrogen formation rates that exceed those obtained at steady state. While this cycling approach shows potential for attaining higher  $H_2$  levels, under the conditions used in this study, there was no overall enhancement in  $H_2$  formation when integrating the amounts formed over the entire cycle due to some portion of the cycle being less active. We attribute the higher  $H_2$  (and  $CO_2$ ) levels under cyclic operation to increased hydroxyl availability and WGS activity at the  $Pt/Al_2O_3$  interface compared to steady state operation, with evidence for the reaction between CO and support hydroxyls provided by CO titration experiments and DFT calculations.

Our study highlights the importance of surface coverages at the metal-support interface, which can play a crucial role during periodic conditions. The selective formation of hydrogen from OH groups at the interface could be exploited by supporting Pt on a different oxide with higher OH mobility and storage capacity. In this context, it is worth exploring multi-layer architectures involving stable metal hydroxides or oxyhydroxides. Additionally, changes in the cycling scheme, such as including water in the regeneration period, could further improve the catalyst's performance under periodic conditions.

## Conflicts of interest

There are no conflicts to declare.

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