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Unraveling the Methanol Oxidation Mechanism over a Titania-Supported Platinum Catalyst

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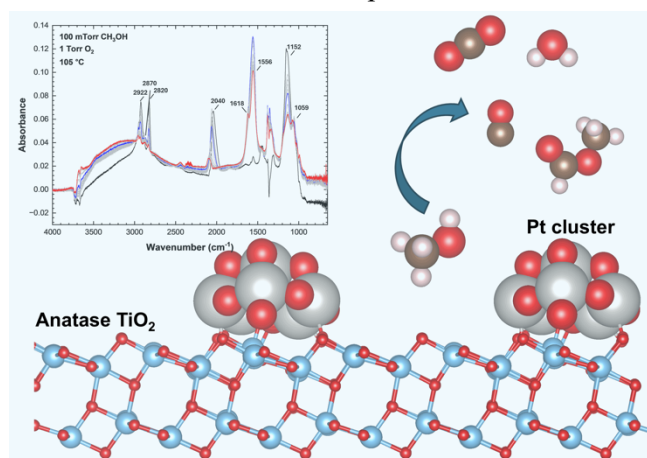
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Abstract

The development of noble metal catalysts with sustained high activity for methanol oxidation is essential for chemical production and for energy transformation with methanol fuel cells. Here, we report Pt oxide clusters supported on anatase TiO₂, exhibiting enhanced methanol oxidation performance. Interfacial interactions between oxidized Pt clusters and TiO₂ strongly influence electronic states and adsorption of intermediates, thereby shaping catalytic performance. Density functional theory (DFT) combined with Fourier-transform infrared spectroscopy (FTIR) revealed methanol adsorption and oxidation mechanisms. Using grand canonical basin hopping (GCBH), we identified stable and metastable model Pt₆O_x clusters on TiO₂(101), with Pt₆ partially oxidized to Pt₆O₁₀ under ambient conditions. Three methanol oxidation pathways were examined: partial oxidation to CO, formation of methyl formate (HCOOCH₃) by C-O coupling, and complete oxidation to CO₂, proceeding via the *OCH₂O (dioxymethylene DOM) intermediate. The formation of DOM enables an alternative pathway in which the C-O bond forms at an early stage, thus offering a CO-free mechanism that prevents CO poisoning. The Pt oxide cluster exhibits dynamic redox behavior, undergoing initial partial reduction followed by reoxidation, highlighting the adaptive nature of the catalytic system. Notably, the catalytic activity is further enhanced when water formation accompanies the reaction pathway. Overall, this work provides insight into how the Pt/TiO₂ interface is the origin of a high methanol oxidation activity, consistent with experimental observations. These insights bring a rational framework for designing efficient and durable catalysts for selective oxidation reactions.

Keywords

Pt oxide cluster, Titanium oxide, Metal-Support interaction, Methanol oxidation, Reaction mechanism, Infrared spectroscopy



1. Introduction

Methanol is increasingly recognized as a valuable chemical feedstock and sustainable energy carrier, offering a promising alternative to conventional fossil fuels. One key application in the domain of energy is the direct methanol fuel cell (DMFC), which is appealing due to its high energy density, ease of operation, and the practicality of methanol storage and transport. These qualities make DMFCs well-suited for both portable and stationary energy systems.¹ Beyond its use as a fuel and fuel additive, methanol holds a pivotal position in the chemical industry, acting as a starting material for the synthesis of a wide range of high-value chemicals, such as formaldehyde (CH_2O),² dimethyl ether (CH_3OCH_3 , DME),³ and light olefins like ethylene and propylene.⁴ Additional notable oxidation products include methyl formate (HCOOCH_3 , MF)⁵ and dimethoxymethane ($\text{CH}_3\text{OCH}_2\text{OCH}_3$, DMM),⁶ with methyl formate gaining attention as a fundamental intermediate in C_1 chemistry. Traditionally, methyl formate is industrially synthesized through the carbonylation of methanol using sodium methoxide and carbon monoxide, but there is growing momentum toward the development of more sustainable and efficient catalytic methods that enable its direct production from methanol.⁷ Furthermore, understanding the catalytic pathways of methanol oxidation is a major research focus. While the conversion of methanol to formaldehyde is well-documented,⁸ the specific mechanisms that lead to the formation of methyl formate are still not fully understood. Studies also highlight that carbon monoxide (CO), formed during methanol decomposition, can deactivate catalysts through poisoning,⁹ prompting ongoing efforts to design catalysts with enhanced resistance to CO poisoning, or promoting CO-free reaction pathways.^{10, 11}

Over the past 20 years, a wide range of studies have investigated methanol activation and decomposition on various catalytic surfaces, including metals,¹² metal alloys,^{13, 14} metal clusters,¹⁵ metal oxides,^{5, 16} mixed metal oxides,¹⁷ and zeolites.¹⁸ Mavrikakis and co-workers conducted a comprehensive DFT study on methanol oxidation to CO_2 across extended surfaces of eight face-centered cubic (fcc) metals: Au, Ag, Cu, Pt, Pd, Ni, Ir, and Rh, examining two different crystal facets.¹² Their results highlighted platinum as the most effective catalyst for CO_2 formation. Furthermore, they demonstrated that the adsorption free energies of OH^* and CO^* are key descriptors in predicting the onset potential for methanol electrooxidation on generic fcc(100) and fcc(111) surfaces. Doped transition metal oxide surfaces have emerged as excellent candidate materials for methanol oxidation and coupling reactions. For instance, López et al. have investigated the activity and selectivity of molybdenum-based oxides in converting methanol to formaldehyde.¹⁹ Their work showed that doping $\alpha\text{-MoO}_3(010)$ with iron at subsurface sites enhances activity while preserving selectivity by tuning the vacancy formation energy in the right window for activity, thus improving thermodynamic favorability toward formaldehyde production. In general, metal oxides are found to be superior catalysts for methanol activation due to the presence of surface oxygen atoms, which provide active sites for the reaction. Oxide-supported metal catalysts such as Au/ TiO_2 and Pt/ TiO_2 have also proven highly effective in oxidizing small organics like CO,²⁰ formaldehyde,²¹ and methanol.²² Pt/ TiO_2 , in particular, shows notable activity for coupling reactions that produce compounds such as methyl formate.^{22, 23} Furthermore, Morris et al. combined packed-bed reactor studies with high-vacuum surface science experiments to investigate the methanol oxidation mechanism over a Pt/ TiO_2 catalyst.²⁴ They identified formation of dioxymethylene (DOM) as a surface intermediate, than can undergo coupling to yield methyl formate (MF). They also suggested that incorporating co-reactive sites capable of removing water produced during the reaction could enhance methyl formate selectivity. Despite these insights, there remains a lack of computational studies to comprehensively map out competing

reaction pathways. Studying methanol oxidation on such Pt-modified TiO_2 surfaces offers a valuable approach for unraveling the role of platinum and of the support under oxidative conditions.

The oxidation of methanol (CH_3OH) can yield a range of products depending on the extent of oxidation and the specific reaction conditions. Under partial oxidation conditions, methanol is typically converted into valuable intermediates such as formaldehyde (HCHO), formic acid (HCOOH), methyl formate (HCOOCH_3), or dimethyl ether (CH_3OCH_3), depending on the catalyst used and the reaction temperature. These products are industrially significant and are often the focus of selective oxidation strategies. Formaldehyde is a primary product in mild oxidation, while further oxidation can yield formic acid or even carbon monoxide (CO). On the other hand, complete oxidation or total combustion converts methanol into carbon dioxide (CO_2) and water (H_2O), maximizing energy output and typically requiring elevated temperatures and an ample oxygen supply. The diversity of possible oxidation products emphasizes the importance of reaction control to steer methanol oxidation toward either value-added chemicals or full energy release, depending on the desired application. The outcome of methanol oxidation is highly dependent on factors such as the catalyst's composition and surface structure, as well as the reaction conditions. As a result, achieving selective partial oxidation over complete combustion requires precise manipulation of these variables. Gaining insight into the elementary reaction steps, active catalytic sites, and both thermodynamic and kinetic influences are essential for the rational design of catalysts and optimization of reaction processes.

This paper is centered on providing a detailed mechanistic understanding of methanol oxidation over a titania-supported platinum oxide catalyst. Our findings reveal three main reaction pathways under specific conditions: partial oxidation leading to CO , formation of methyl formate, and complete combustion producing CO_2 . This study aims to map out the mechanistic landscape of methanol oxidation and identify the key factors that govern product selectivity and catalytic performance at the atomic level. We underline a possible pathway through the DOM intermediate that does not involve CO species and therefore could alleviate poisoning from strong CO adsorption on the catalyst. We observed the redox fluxionality and dynamics of the catalyst system throughout the reaction. By employing a high-vacuum FTIR transmission cell, we have been able to monitor the surface-bound intermediates that form during the reaction.

2. Methods

2.1. Computational Model

All spin polarized plane-wave DFT calculations were conducted using the Vienna Ab Initio Simulation Package (VASP).²⁶ The exchange–correlation interactions were treated using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) framework,²⁷ and a kinetic energy cutoff of 400 eV was employed for the plane-wave basis set. The projector augmented wave (PAW) method,²⁵ was used to describe the effect of core electrons on the valence density. To accurately describe the localized Ti 3d states, the DFT+U method was adopted with Dudarev's formulation, using an effective U value of 4.2 eV.²⁸ To incorporate van der Waals interactions, the dDsC dispersion correction scheme was applied.²⁹ We chose dDsC because it incorporates dispersion effects self-consistently and adapts to changes in the electronic environment, which is essential for metal–oxide systems. It provides a more reliable balance of accuracy and robustness than empirical D3 or MBD approaches.

Highly dispersed Pt clusters with formulae Pt_6O_x deposited on the thermodynamically stable anatase TiO_2 (101) surface were used as catalyst models in this study. For ideal bulk simulations, both atomic positions and lattice parameters were fully relaxed without imposing symmetry constraints. The optimized lattice constants ($a = b = 3.81 \text{ \AA}$, $c = 9.73 \text{ \AA}$) with PBE+U calculations, closely matched experimental

values³⁰. The anatase TiO₂ (101) surface was modeled using a four-layer slab approximately 12 Å thick, separated by a 15 Å vacuum gap to avoid artificial interactions along the surface normal.³¹ The surface lattice vectors were $a = 19.35$ Å and $b = 16.76$ Å. The TiO₂ slab, consisting of 60 Ti atoms, is denoted as (TiO₂) in the reaction pathway. During geometry optimization, the bottom two atomic layers were fixed to their bulk positions, while the upper two layers were allowed to relax. To explore the most favorable stoichiometry and structure of Pt₆O_x clusters under realistic conditions, we used the grand canonical basin hopping (GCBH) algorithm for global optimization. Further computational specifics are included in the Supporting Information.

The modelled cluster diameter is found to be around 0.75 nm which is smaller than the experimental diameter (~1.5 nm), although we believe our model catalyst system can correctly represent the interface sites between Pt and TiO₂ and the corresponding surface chemistry of the catalyst. The restriction to small size clusters for the modelling is motivated by our wish to correctly sample catalyst configurations in reaction conditions, potential active sites and evaluate vibrational contributions to the free energy. Such a detailed treatment is not accessible on a larger supported cluster. Single-atom catalysts were not considered since they have low probability in the considered preparation conditions. In addition, methanol oxidation pathways examined here involve hydrogen transfer, changes in Pt oxidation state, and rearrangements at the Pt-TiO₂ perimeter that require an ensemble of Pt atoms and a fluxional Pt-O-Ti interface that would not occur on single atom models.

Adsorption of the cluster was restricted to one face of the TiO₂ slab, and dipole corrections were applied accordingly. From the large size of the unit cell, calculations were performed at the gamma point. Convergence criteria were set to 10⁻⁵ eV for electronic energy and 0.02 eV/Å for atomic forces. Transition states were identified using the climbing image nudged elastic band (CI-NEB) method³² and the dimer method.³³ Each transition state was confirmed by vibrational frequency analysis, exhibiting a single imaginary mode. The adsorption energy (E_{ads}) is defined as:

$$E_{ads} = E_{mol/surf} - (E_{mol} + E_{surf})$$

where $E_{mol/surf}$ is the total energy of the bound system and E_{mol} and E_{surf} are the respective energies of the adsorbed molecule in gas phase and the clean surface. A negative value of the adsorption energy signifies exothermic adsorption on the Pt cluster surface, indicating that the adsorbed species is thermodynamically stable. To incorporate zero-point energy (ZPE) corrections, vibrational frequencies were computed for both gas-phase molecules and surface-bound species using numerical differentiation of forces via a second-order finite difference method, with a displacement step size of 0.015 Å.³⁴ The mass-weighted Hessian matrix was diagonalized to obtain the vibrational frequencies and normal modes of the adsorbed species. Entropic contributions were also included: for gas- and liquid-phase molecules, standard entropy values were taken from the literature,³⁵ while for surface-adsorbed species, vibrational entropy was estimated using the quantum harmonic oscillator model based on the same frequencies used for ZPE correction.³⁵ Additional details are given in SI (Section 1). Additionally, Bader charge analysis was performed to examine the charge distribution of intermediates along the reaction pathway.³⁶

2.2. Experimental procedure

2.2.1 Synthesis and characterization

Catalyst Preparation (10% Pt/TiO₂ via Wet Impregnation)

The Pt/anatase TiO₂ catalyst used in this study was synthesized by wet impregnation (WI) method with a nominal Pt loading of 10%. The anatase TiO₂ support used for synthesis was purchased from the U.S.

Research Nanomaterials (99.5%, stock #US3838). 2 g of 10% Pt/TiO₂ was prepared in one batch. First, TiO₂ support was dried in a vacuum oven at 120 °C overnight before use. Then, 1.8 g of the dried support was weighed, and dispersed in 250 ml of ammonium hydroxide solution (NH₄OH with pH of 13.7; ACS reagent, 29.8% NH₃ basis, Sigma-Aldrich 221228, lot #SHBJ4683) in a glass bottle by stirring at 700 rpm on a stirrer hotplate at 25 °C. An appropriate amount (0.3976 g) of tetraammineplatinum(II) nitrate precursor ([Pt(NH₃)₄](NO₃)₂; 50.3% Pt basis, Aldrich 278726, lot #MKBN9761V), according to the nominal Pt loading, was weighed and dissolved in ~30 ml of the same ammonium hydroxide solution mentioned before. The Pt precursor solution was then slowly added into the 250 ml support dispersion, while constantly being stirred at 700 rpm, using a syringe pump at a rate of 2 ml/hr. Following the deposition of Pt, the catalyst solution was left on the hotplate for ~12 hr at 50 °C to evaporate the solvent. The solid catalyst sample was then dried in a muffle furnace at 120 °C (ramp rate of 1 °C/min) for 12 hr and calcined at 450 °C (ramp rate of 5 °C/min) for 4 hr. The calcination temperature was limited to 450 °C to maintain the anatase phase which transforms to rutile at ~500 °C.^{37, 38} Moreover, this temperature was reported to be sufficient to completely remove the amine and nitrate ligands from the tetraammineplatinum(II) nitrate precursor.³⁹

Catalyst Characterization

Aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) images were taken *ex-situ* after the reduction pretreatment of the 10% Pt/TiO₂. The images were taken on a JEOL JEM-ARM200F atomic resolution electron microscope at an acceleration voltage of 200 kV equipped with EDS detector EX-24221M1G5T. To obtain the particle size distribution (PSD), as shown in the form of area distribution in **Figure 1a** and atomic percentage distribution in **Figure 1b**, and average particle size for the 10% Pt/TiO₂ sample, we measured ~ 550-650 Pt particles for each sample from multiple STEM images. Single atoms present on the sample were counted separately and included in the PSD.

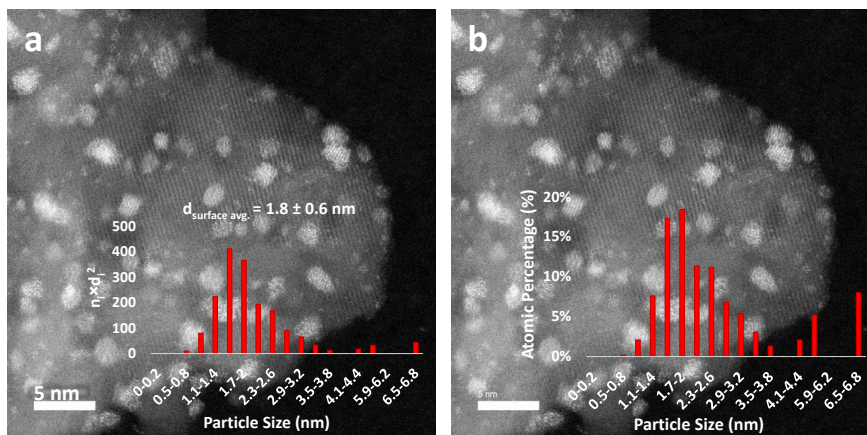


Figure 1: Representative AC-HAADF-STEM image of 10% Pt/TiO₂ catalyst after H₂ reduction pretreatment with particle size distribution in terms of (a) area distribution (weighted by d²) and (b) atomic percentage distribution (included in the inset).

2.2.2 Surface-Sensitive Infrared Spectroscopic Measurements

Surface bound species were monitored during the methanol oxidation reaction with a high-vacuum transmission FTIR cell described previously.^{40, 41} The catalyst samples were pressed as 7 mm spots at 8,000

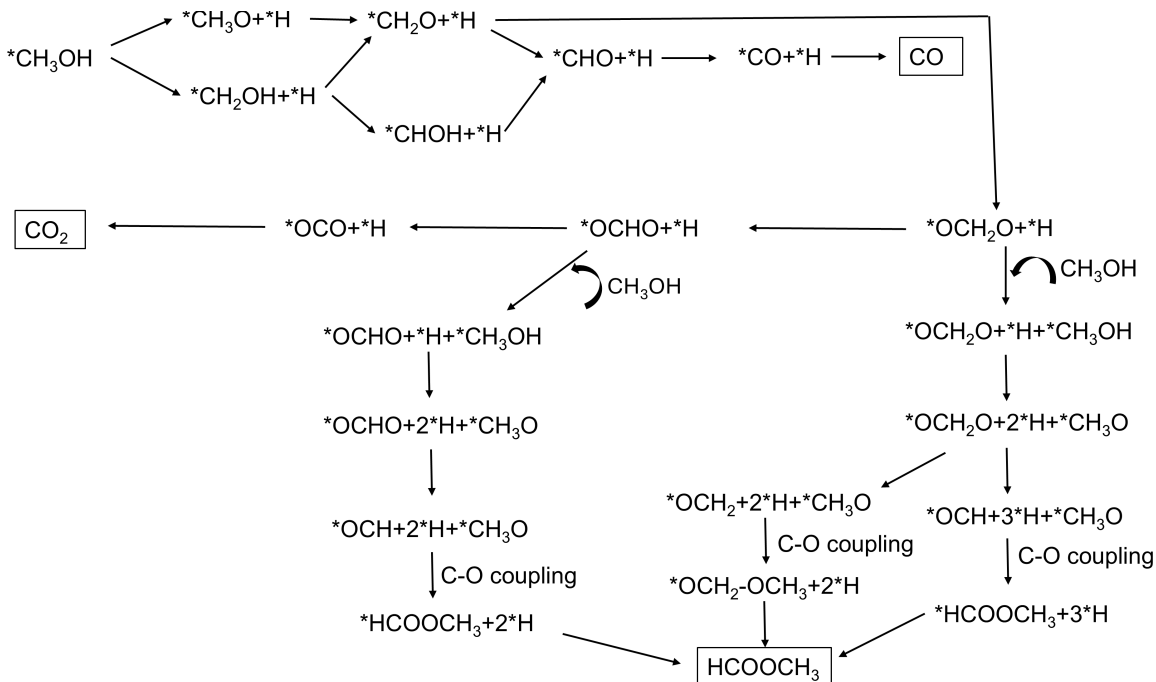
psi into the void spaces of a tungsten mesh (~70% optical transmittance) and secured in a nickel sample holder suspended within a stainless-steel chamber. A K-type thermocouple was spot welded to the top center of the mesh to monitor temperature throughout the reaction. The samples were heated by resistively heating the sample holder with a DC power supply (BK precision 1900B). Infrared spectra were collected with a Thermo Nicolet Nexus 670 spectrometer equipped with a liquid nitrogen cooled MCT-A detector. Each spectrum was an average of 64 scans with a resolution of 1 cm^{-1} .

Prior to each experiment, the samples were pretreated with the following routine. First, the chamber was backfilled with 10 Torr oxygen at room temperature. The samples were heated to $300\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$ and then held at this temperature for 1 hr. The chamber was evacuated while the samples were at still at the high temperature and then the samples were allowed to cool naturally back to room temperature. Then, the chamber was backfilled with 20 Torr of hydrogen. The samples were heated to $350\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$ and then held for 2 hr. The chamber was evacuated, and the samples were allowed to cool naturally.

3. Results & Discussions

3.1. Methanol Oxidation pathways

Let us start by general aspects of potential mechanisms for methanol oxidation. Chemisorbed methanol (CH_3OH^*) can be activated through cleavage of either the O-H or C-H bond, leading to the formation of methoxy ($^*\text{CH}_3\text{O}$) or hydroxymethyl ($^*\text{CH}_2\text{OH}$), respectively. The $^*\text{CH}_2\text{OH}$ intermediate can then undergo stepwise dehydrogenation to form $^*\text{CHOH}$ and subsequently $^*\text{CHO}$, which may also be generated directly from $^*\text{CH}_2\text{O}$ through dehydrogenation.⁴² The $^*\text{CHO}$ species can further dehydrogenate to produce adsorbed CO ($^*\text{CO}$), which may either desorb or be oxidized to CO_2 through intermediates such as $^*\text{OCHO}$ and $^*\text{OCO}$.⁴³ Among the various proposed oxidation pathways, those involving interactions of formaldehyde (CH_2O) with other adsorbed species appear to be especially favorable, featuring lower energy barriers and efficient conversion to final products. While the early dehydrogenation steps are relatively well characterized, the subsequent reactions leading to CO_2 remain less well understood, with multiple mechanisms being proposed. One such mechanism involves $^*\text{CH}_2\text{O}$ reacting with surface-bound hydroxyl ($^*\text{OH}$) or oxygen ($^*\text{O}$) to form dioxymethylene ($^*\text{OCH}_2\text{O}$),⁴⁴ which can then dehydrogenate to form formate ($^*\text{OCHO}$), ultimately yielding CO_2 .



Scheme 1: Possible reaction route to produce CO, CO₂, or methyl formate from CH₃OH oxidation.

Another hypothesis involves the formation of methyl formate (HCOOCH₃), which has been experimentally observed under specific conditions, such as methanol decomposition on copper surfaces in low-water environments and during methanol oxidation on Pt/TiO₂ under mild heating conditions.²⁴ Though reports of methyl formate formation are limited, it is thought to arise from coupling reactions between *CHO and *CH₃O, or between *CH₂O and *CH₃O, followed by hydrogen transfer steps (as illustrated in **Scheme 1**). Therefore, methanol oxidation can proceed via multiple pathways, resulting in various end products such as formaldehyde, CO, CO₂, and methyl formate. We will show now that experimental measurements provide direct evidence for many of the products and intermediates that appear in Scheme 1.

3.2. Uptake and decomposition of methanol: experimental observations

The initial stages of methanol uptake on both TiO₂ and Pt/TiO₂ were investigated via *in situ* infrared spectroscopic measurements within the highly controlled environment of a high-vacuum gas cell starting with a reduced Pt catalyst (**Figure 2**). At the reaction temperature 105°C in the absence of oxygen, methanol was found to adsorb both molecularly and dissociatively onto both surfaces. The broad feature between 3500-3000 cm⁻¹ is indicative of hydrogen bound intact methanol on the titania support.⁴⁵ The infrared bands at 2922 and 2820 cm⁻¹ are associated with the asymmetric and symmetric stretches for Ti-OCH₃ species.⁴⁶ The negative-going features in the 3700-3600 cm⁻¹ region of the spectra are associated with free hydroxyl groups, present on the as-prepared titania support, that convert to hydrogen-bound hydroxyl groups upon interactions with methanol. Evidence for dissociative adsorption also comes from the development of multiple bands in the region of 1100 cm⁻¹, which are known to be associated with the C-O stretch of bound methoxy groups and dioxymethylene.^{24, 47} Remarkably, methanol exposure to the Pt/TiO₂ sample (again in the absence of oxygen), produces carbon monoxide as indicated by the CO-Pt feature at 2040 cm⁻¹.^{48, 49}

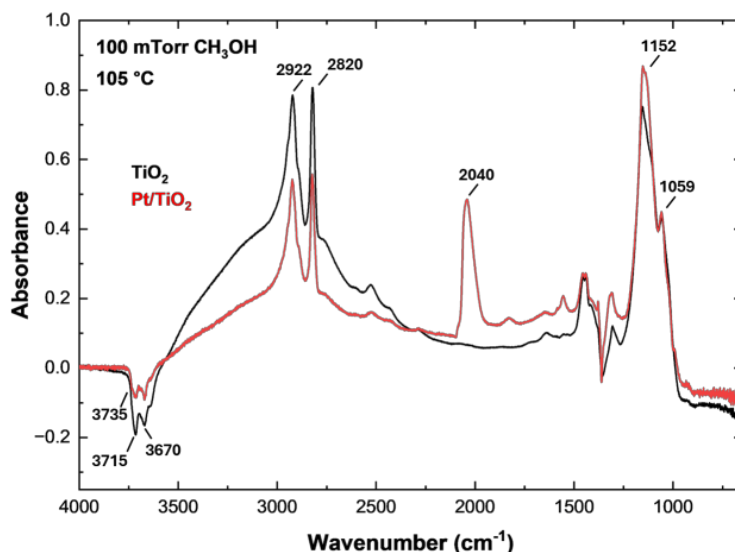


Figure 2. FTIR spectrum of methanol adsorbed on TiO_2 (black) and 10% Pt/TiO_2 (red) at 105 °C immediately prior to oxygen exposure. IR bands suggest the presence of molecular and dissociative adsorption on both samples. The influence of the Pt particles on reactivity is evident by CO formation on the Pt containing sample.

Using CO as a probe of the Pt cluster oxidation state, a significant red shift of the CO-Pt from 2077 cm^{-1} to 2046 cm^{-1} is found after methanol has been adsorbed to the surface (**Figure S1**), suggesting charge accumulation on the Pt particle, which is a key aspect of the mechanism revealed in the computational work described below.^{50, 51} This CO-Pt red shift indicates that Pt has a higher electron density after methanol adsorbs to the surface, suggesting that the cluster acts as an electron acceptor and the hydrogen that is removed to form the methoxy group is a proton. This process closely resembles a proton-coupled electron transfer (PCET) mechanism, through which methanol undergoes oxidation. In short, in the absence of O_2 , the experimental observations suggest a pathway that leads to methoxy, DOM and CO. It is important to note that previously published work, involving smaller 0.9 nm Pt oxide clusters on the same support, shows very similar reactivity.²⁴ That is, we find the surface-bound species to be nearly identical for 0.9 nm particles and the 1.5 nm Pt particles employed here. The only significant difference in the reaction characteristics is the temperature required for the species to form.²⁴

3.3. Methanol Oxidation Products Monitored Spectroscopically

While methanol shows some reactivity upon initial adsorption (i.e., methoxy, dioxymethylene, and CO formation), the chemistry halts until gas-phase oxygen is introduced into the system. In the presence of O_2 , IR bands assigned to methoxy groups on the Pt/TiO_2 surface decrease over time (**Figure 3**). The reduction in IR absorbance for the methoxy bands (see the CH and CO spectral region) and the overlapping dioxymethylene bands is compensated by an increase in bands associated with formate at 1556 cm^{-1} and 1355 cm^{-1} . Once created, the formates convert to more oxidized products. The CO coverage is low on Pt sites during MeOH oxidation and some platinum sites remain open, free from CO which supports occurrence of other parallel CO-free pathways on the CO-free Pt sites (**Figure S2**). Gas-phase CO_2 appears during the reaction as indicated by the asymmetric O-C-O stretch at 2349 cm^{-1} . The IR signature for gas-

phase CO₂ formation is accompanied by the development of a band at 1618 cm⁻¹, which is associated with the bending motion of surface-bound water.

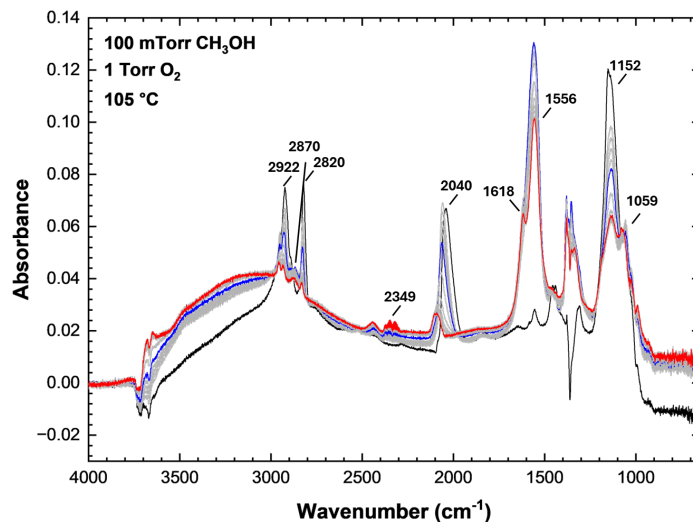


Figure 3. Methanol oxidation over a Pt/TiO₂ sample. Both methanol (initially) and oxygen (afterwards) were co-dosed on the catalyst at 105 °C and surface bound species were tracked over time using infrared spectroscopy. Initial spectrum without any oxygen (black), intermediate spectrum where formate concentration is at its maximum (blue), and the final spectrum (red).

In addition to the formation of CO₂ and H₂O, we observe experimentally that the IR band associated with Pt-CO decreases in intensity and blueshifts as the reaction proceeds, from 2040 to 2104 cm⁻¹ (**Figure 3 and S3**), indicating that, under oxidative conditions, the Pt cluster readily oxidizes and the bound Pt-CO reacts with O₂ to form CO₂.^{48, 49} Although the empirical observations reveal several reaction intermediates, the atomic scale mechanistic, energetic, and electronic details that describe the overall process remains open and will be addressed in our paper from computational modeling of each step along the possible reaction paths.

3.4. Nature of Catalyst and CH₃OH adsorption

From a modelling perspective, it is key to determine the nature and structure of the Pt catalyst on TiO₂ in reaction conditions, such as the overall oxidation state and the interaction with the support. Our modelling is focused on the reactive conditions where oxygen is present. However, as cluster size increases, the number of potential structural configurations and modes for the support surface interaction grows rapidly, especially under reactive conditions.⁵² For that purpose, we examined the structural stability and reactivity of Pt clusters supported on anatase TiO₂ (101), along with their accessible metastable configurations under reaction conditions (105°C, 1 torr O₂), employing the grand canonical basin hopping (GCBH) algorithm.^{53, 54} The details for GCBH simulations are provided in the SI (**Section 3**). We selected Pt₆ for the model cluster size (ca 0.75 nm), which as indicated in the method section, is smaller than the average Pt particle size (1.5 nm) in the experiment. Our selection of Pt₆ is guided by computational practicality, as it is small enough for extensive sampling of configurations in reaction conditions and for detailed mechanistic study while still capturing key structural features of the Pt-TiO₂ interface.

To explore the stoichiometric and structural diversity of Pt₆ clusters, we employed the Grand Canonical Basin Hopping (GCBH) algorithm to globally optimize the potential energy surface. Oxidation conditions were modeled by varying only the number of oxygen atoms, provided from the reservoir of O₂ in gas phase. GCBH samples both configurations and compositions by minimizing the grand potential,

$$G(\text{Pt}_6\text{O}_x@\text{TiO}_2) = E(\text{Pt}_6\text{O}_x@\text{TiO}_2) - \sum_j \mu_j N_j,$$

where E is the DFT electronic energy, μ_j the chemical potential, and N_j the number of species j . Vibrational contributions were neglected, as commonly assumed for slab systems. The relative stability of Pt₆O_x clusters ($x = 0-14$) is shown in **Figure 4a**, fixing the oxygen chemical potential corresponding to experimental conditions $T=105^\circ\text{C}$ and $P(\text{O}_2) = 1$ torr. **Figure 4b** presents the calculated Gibbs free energies of formation for the lowest-energy isomers of Pt₆O_x ($x = 0-14$) identified through the GCBH search, as a function of oxygen chemical potential. Under reaction conditions, Pt₆O₁₀ (represented by the magenta line) emerges as the thermodynamically most stable composition.

The oxidation of the Pt clusters seen from simulations is consistent with our IR spectroscopy data showing a marked blueshift of the CO frequency under O₂ pressure, and with our XANES experiments (detail in **Figure S4**). We note that TiO₂ may also be partially hydroxylated under reaction conditions since methanol oxidation produces water. Our calculations include OH groups produced along the reaction pathway, but we did not consider the influence of additional OH groups on the surface. Although the experimental catalyst contains 1.5 nm Pt particles, the Pt₆O₁₀ cluster serves as a representative model of the low-coordination, oxidized Pt–TiO₂ interfacial sites present at the perimeters of larger nanoparticles. These sites are widely regarded as the most catalytically active regions, making the Pt₆O₁₀ motif appropriate for mechanistic analysis.

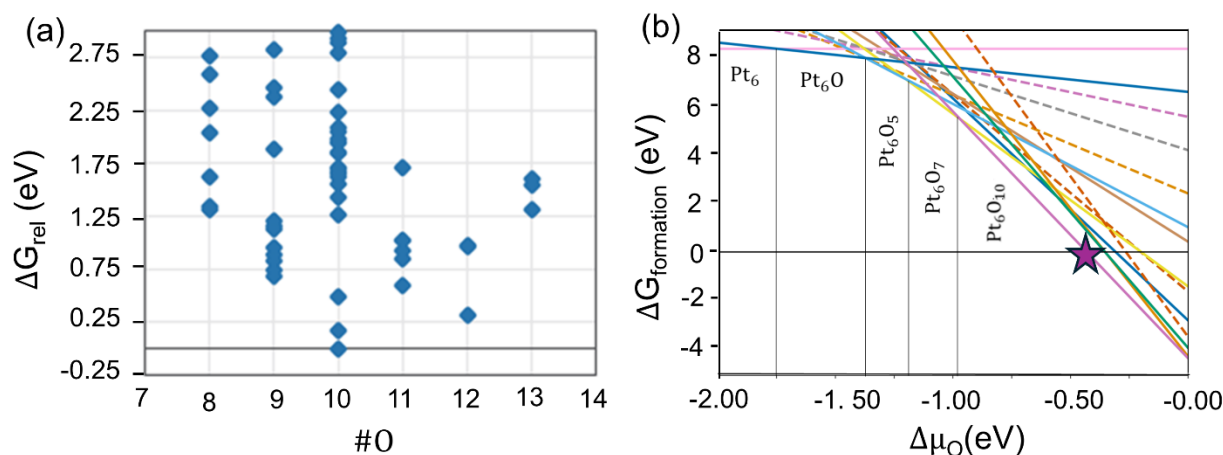


Figure 4. (a) The relative stability of Pt₆O_x found as function of chemical formula at experimental reaction conditions $T=105^\circ\text{C}$ and $P(\text{O}_2) = 1$ torr ($\Delta\mu_{\text{O}}=-0.47$ eV), (b) Stability diagram of Pt₆O_x as a function of oxygen chemical potential (left). The star-marked region indicates the accessible region in experimental reaction condition.

Structurally, the most stable Pt₆O₁₀ cluster forms a bilayer arrangement composed of planar PtO₄-like subunits: five Pt atoms reside in the first layer and one in the second (**Figure S5a**). Each Pt atom is tetrahedrally coordinated with oxygen, and oxygen atoms are two-fold coordinated within the cluster. This

structure with bonded PtO_4 units is significantly more stable than any other and should extend to the surface of larger Pt particles in oxidation conditions, providing more generality for our small size model. There are two types of Ti present in the support. One is low coordinated Ti, which is indicated as Ti_{5c} and other is Ti_{6c} where all the coordination is filled for those particular Ti (**Figure S5b**). Ti_{5c} sites can host CH_3OH molecules and fulfil their coordination.

Methanol can adsorb onto the surface through various configurations. It may chemisorb by forming a bond between its oxygen atom and a Ti or Pt site, or physisorb via hydrogen bonding (as illustrated in **Figure S5c**). The chemisorption on the TiO_2 support, in the proximity of the Pt oxide cluster, is clearly preferred versus adsorption on the cluster itself. CH_3OH forms a $\text{Ti} - \text{O}_{\text{CH}_3\text{OH}}$ bond with a bond length of 2.19 Å and the adsorption internal energy is -1.36 eV. Tests with a thicker slab containing 8 layers show a change of methanol adsorption energy of only 0.03 eV, therefore validating the model. Calculations performed in an enlarged surface cell yield the same CH_3OH adsorption energy, confirming that lateral interactions between neighboring Pt oxide clusters are negligible. It is important to note that on bare TiO_2 the methanol adsorption internal energy is -1.11 eV with $\text{Ti} - \text{O}_{\text{CH}_3\text{OH}}$ bond with a length of 2.21 Å, showing that the presence of the Pt oxide cluster markedly enhances the adsorption strength of methanol on the support in the interfacial area. Bader charge analysis reveals a net electron transfer of approximately 0.24 electrons from the TiO_2 surface to the Pt_6O_{10} cluster. This charge redistribution enhances the ability of the TiO_2 support to adsorb methanol more effectively than the Pt oxide cluster and than the bare TiO_2 surface as discussed above. Once adsorbed, subsequent O–H and C–H bond rupture to form CO, coupling to yield methyl formate, and full oxidation to CO_2 and H_2O have been observed experimentally.

3.5. Modelling Methanol oxidation

In the most stable calculated adsorption structures of methanol on the model catalyst, the oxygen atoms of methanol molecules are adsorbed at the Ti_{5c} sites, and the hydrogen atoms are oriented toward adjacent bridging oxygen atoms (O_b) of the Pt oxide cluster (**Figure S5**). When a single CH_3OH molecule is adsorbed on the $\text{Pt}_6\text{O}_{10}@\text{TiO}_2$ surface, the corresponding Gibbs free energy of adsorption is calculated to be -0.80 eV (structure B in **Figure 5**). Note that the value is different from that given above because entropy effects are included, with Gibbs free energy instead of internal energy.

Pathway for methanol oxidative dehydrogenation to CO

Upon transferring the hydrogen atom from the hydroxyl group of methanol to a neighboring bridging oxygen atom (O_b) of the Pt oxide cluster, a methoxy intermediate ($^*\text{CH}_3\text{O}$) is formed. This configuration (C) has a Gibbs free energy of -0.68 eV. Therefore, the O-H bond cleavage step, leading to methoxy formation, is endergonic by 0.12 eV, as indicated in **Figure 5**. The kinetic barrier associated with this step is 0.60 eV (transition state $1a^\ddagger$) which is easily accessible under reaction conditions (105 °C). It is important to note that in the first step the hydrogen from the hydroxyl group of methanol can also transfer to the oxygen of TiO_2 with a similar barrier (**Figure S6**). However, as the reaction progresses, oxygen atoms of the Pt oxide cluster becomes increasingly favorable for accepting hydrogen, which will be clear later.

The optimized structures of the relevant intermediates and transition states leading to CO formation are presented in **Figure 5** and **Figure S7**. An alternative pathway for CH_3OH activation involves C-H bond cleavage, leading to the formation of $^*\text{CH}_2\text{OH}$. This intermediate is thermodynamically more stable, with a Gibbs free energy gain of -0.90 eV (structure D in **Figure S7**). However, the activation energy for this transformation is significantly higher (1.13 eV, $1b^\ddagger$) compared to that for $^*\text{CH}_3\text{O}$ formation. Therefore,

despite the greater thermodynamic favorability of $^*\text{CH}_2\text{OH}$ formation, the relatively low kinetic barrier associated with O-H bond cleavage suggests that CH_3OH is more likely to dissociate first into $^*\text{CH}_3\text{O}$ under ambient thermal conditions.

To further understand why O-H bond cleavage is preferred over C-H bond scission in CH_3OH activation, a Bader charge analysis was conducted for each species involved (**Figure S8**). We notice that in intermediate B, the adsorbed CH_3OH shows almost no net charge. At this stage, the cluster Pt_6O_{10} bears a negative charge of $-0.4|e|$, while the TiO_2 support is positively charged by $+0.33|e|$. When the hydrogen atom bonded to the oxygen in CH_3OH transfers to a bridging oxygen atom on the cluster, forming $^*\text{CH}_3\text{O}$, the resulting methoxy intermediate carries a net charge of $-0.49|e|$. So, the hydrogen shifted from the $^*\text{CH}_3\text{OH}$ to the cluster, acts like a proton which is expected and can also be seen from the charges on the shifted H ($+0.69|e|$). In this process the cluster containing Pt and O undergoes a slight reduction by $-0.1|e|$. In contrast, during $^*\text{CH}_2\text{OH}$ formation, the hydrogen bonded to the carbon atom in CH_3OH transfers to the bridging oxygen of the cluster. The resulting $^*\text{CH}_2\text{OH}$ intermediate carries a net positive charge of $+0.17|e|$, suggesting that the migrating hydrogen behaves like a hydride, donating electron density to the Pt cluster. Consequently, the cluster becomes significantly reduced by $-1.17|e|$. The activation of the C-H bond and this substantial electron transfer likely contributes to the much higher kinetic barrier observed for $^*\text{CH}_2\text{OH}$ formation, making this pathway less favorable under standard reaction conditions. Additionally, in the transition state $1b^\ddagger$, the oxygen atom on the cluster accepting the hydrogen becomes monodentate, resulting in a local PtO_3 environment for one Pt atom. This deviates from the more stable PtO_4 geometry typically preferred, as identified in the GCBH global optimization. This structural distortion further destabilizes the transition state, contributing to the overall difficulty of CH_2OH formation.

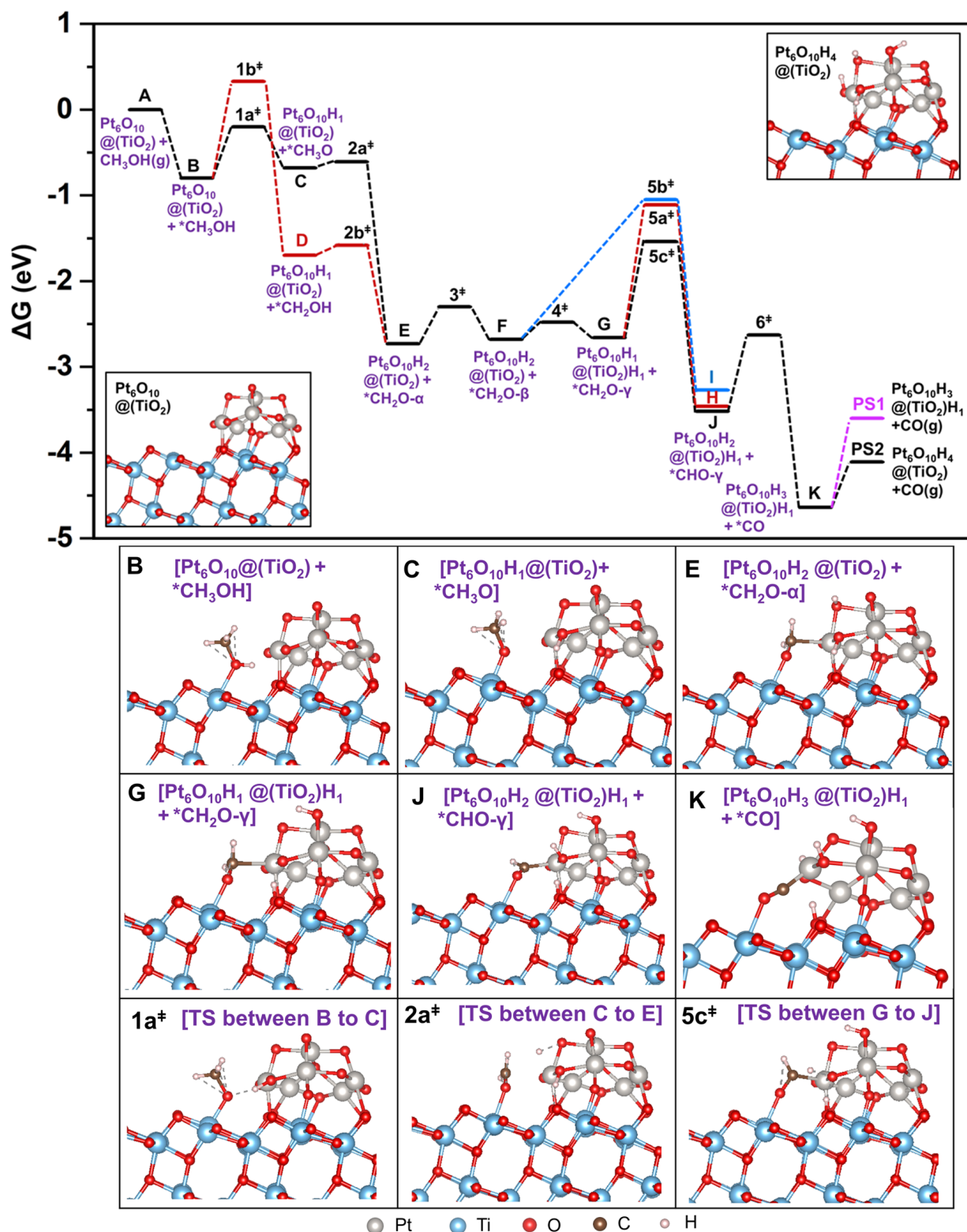


Figure 5. Reaction Gibbs free energy profile for CH_3OH oxidation to produce CO at 105°C and 1 torr of O_2 . The black pathway is the most favorable one. The symbol $\ddagger$ denotes the transition states. The optimized geometries of the intermediates and the transition states along the reaction pathway from methanol to CO .

In the $^*\text{CH}_3\text{O}$ intermediate, the methoxy group forms a covalent bond to the surface titanium atom with a Ti-O bond length of 1.87 Å (structure C). In the subsequent dissociation step, a hydrogen from the methyl group of $^*\text{CH}_3\text{O}$ transfers to a neighboring oxygen atom on the cluster, which results in formation of a second hydroxy group (E). This transformation results in the formation of a hydroxylated cluster with $\text{Pt}_6\text{O}_{10}\text{H}_2$ stoichiometry. The formaldehyde ($^*\text{CH}_2\text{O}$) intermediate has a Gibbs free energy of -2.73 eV (**Figure 5**), which is 1.05 eV lower than that of $^*\text{CH}_3\text{O}$, indicating that this dissociation step is highly favorable energetically. Additionally, the activation barrier for this step is very low, only 0.07 eV ($2\text{a}^\ddagger$), which is remarkable for a C-H cleavage step and contrast with the higher barrier for CH_3OH to CH_2OH ($1\text{b}^\ddagger$). The atomic configuration of the transition state ($2\text{a}^\ddagger$) with the hydrogen atom positioned between the CH_2 group and O_b of the cluster near a Pt atom bound to O_b is relatively stable which results in a low barrier.

A similar phenomenon is observed for the formation of $^*\text{CH}_2\text{O}$ from CH_2OH via transition state $2\text{b}^\ddagger$. $^*\text{CH}_2\text{O}$ adopts a structure (E) at the interface between the cluster and the support, with the O atom bound to Ti and the C atom bound to Pt, with a Pt-C bond length of 2.27 Å. In this configuration the Ti-O bond elongates to 2.06 Å, showing a noticeable increase compared to the Ti-O bond in $^*\text{CH}_3\text{O}$, corresponding to the change between a covalent bond and a dative bond of an oxygen lone pair. Alternatively, the hydrogen atom can transfer to the already formed bridging hydroxyl group (O_bH) in structure C, meaning the entire reaction occurs at a single site on the surface and results in the formation of water. However, the resulting configuration is 1.05 eV less stable than the structure $\text{Pt}_6\text{O}_{10}\text{H}_2@(\text{TiO}_2)+^*\text{CH}_2\text{O}-\alpha$ (E), indicating that the water formation is energetically less favorable compared to the generation of two hydroxy groups on the Pt oxide cluster (**Figure S9**). Indeed, forming a water molecule from a bridging hydroxyl (O_bH) group would imply the creation of an oxygen vacancy, which is energetically unfavorable.

The adsorption internal energy of formaldehyde on the catalyst is calculated to be -1.33 eV, which suggests that CH_2O is strongly bound, and desorption is unlikely to occur. In the $^*\text{CH}_2\text{O}-\alpha$ configuration (E), both adjacent bridging oxygen atoms have already accepted hydrogen during methanol dissociation, preventing further dehydrogenation of CH_2O , as it would require energetically unfavorable water formation (see **Figure S10**). To overcome this limitation, one of the hydrogen atoms bonded to the bridging oxygen (O_b) migrates to a neighboring O_b site within the Pt_6O_{10} cluster. This results in the formation of intermediate F, which is nearly isoenergetic with E. The hydrogen migration step has a low kinetic barrier of 0.50 eV ($3^\ddagger$), making it feasible under reaction conditions. In this new configuration, referred to as $^*\text{CH}_2\text{O}-\beta$ (F), the system is now ready for further dehydrogenation to form a $^*\text{CHO}$ intermediate (H). The CHO group is attached to the Pt center via the carbon atom and three hydroxy groups are generated on the Pt oxide cluster. However, this process faces a substantial kinetic barrier of 1.57 eV ($5\text{a}^\ddagger$), making it unlikely to proceed readily. Therefore, alternative pathways with lower energy barriers are worth exploring. One such alternative involves transferring a hydrogen atom from a bridging oxygen of the Pt oxide cluster to an adjacent oxygen atom on the TiO_2 surface. Only one hydrogen is suitably positioned near the TiO_2 interface, allowing a single possibility for this migration. The resulting configuration, $^*\text{CH}_2\text{O}-\gamma$ (G), features one hydrogen on the cluster's bridging oxygen and another on an interfacial TiO_2 oxygen atom. This intermediate, formed with a low barrier, plays a critical role by setting up two possible pathways for the subsequent hydrogen abstraction step. In the first pathway, CHO is formed in configuration I (**Figure 5**), where two hydrogen atoms are accommodated by the Pt oxide cluster and one by TiO_2 . This transformation is thermodynamically favorable, releasing 0.59 eV (formation of I from G) but requires a high kinetic barrier of 1.58 eV ($5\text{b}^\ddagger$) similar to the previous case ($5\text{a}^\ddagger$). In the second, more favorable pathway, $\text{CHO}-\gamma$ (J) is formed. This structure is analogous to I but involves a different oxygen atom participating in hydrogen

uptake. It is more stable than I by 0.22 eV. Moreover, the formation of CHO- γ (J) from *CH₂O- γ (G) requires a barrier of 1.12 eV (5c[‡]), which is significantly lower compared to the previous two cases (5a[‡] and 5b[‡]), making it more accessible under reaction conditions.

Finally, we obtain the intermediate *CHO (J) which is favorable both thermodynamically and kinetically, with an effective activation barrier of 1.19 eV from CH₂O- α (E). In this favorable *CHO- γ (J) configuration, the *CHO group bridges between a five-fold coordinated Ti atom (Ti_{5c}) of TiO₂ and a Pt atom of the cluster forming Ti-O (2.35 Å) and Pt-C (1.96 Å). Further dissociation of *CHO proceeds via hydrogen transfer to a nearby bridging oxygen (barrier 0.89 eV), resulting in the formation of surface-bound CO (*CO). In this final intermediate (K), the Pt oxide cluster hosts three hydrogen atoms, and one hydrogen remains bonded to an interfacial TiO₂ oxygen. The *CO fragment is bound to a Pt atom with a Pt-C bond length of 2.00 Å. The C-O bond length becomes 1.18 Å which resembles triple bond characteristics of CO.

IR frequency of CO and desorption:

We also calculated the IR frequency of CO adsorbed on the catalyst using DFT. In the most stable configuration (i, **Figure S11**), where CO sits at the interface of Pt oxide cluster and TiO₂, the computed IR frequency is 1937 cm⁻¹. Another configuration where the C atom of CO binds both Pt and Ti atoms at the interface, give an IR frequency of 1901 cm⁻¹. These two interface-bridged modes show lower IR frequencies than the experimental value. To investigate further, we considered CO bound directly to a Pt center. These configurations (iii and iv) show IR frequencies of 2077 cm⁻¹ and 2041 cm⁻¹, which align well with the experimental IR values (**Figure 3 and S3**). From intermediate K, the CO molecule can desorb, forming the reduced catalyst Pt₆O₁₀H₃@(TiO₂)H₁ (PS1). This desorption step is found to be thermodynamically uphill by more than 1 eV. Alternatively, the hydrogen atom on the TiO₂ surface can migrate to a bridging oxygen atom on the Pt oxide cluster, allowing the cluster to accommodate a fourth hydrogen and forming the configuration Pt₆O₁₀H₄@(TiO₂) (PS2). This step is thermodynamically endergonic by 0.53 eV, implying that the configuration Pt₆O₁₀H₄@(TiO₂) is markedly more stable than Pt₆O₁₀H₃@(TiO₂)H₁. Its formation from K involves the migration of two hydrogen atoms, and since earlier hydrogen transfers have shown to proceed with low energy barriers, no further kinetic analysis was conducted here. This observation also supports our previous claim and explained why we focused on hydrogen transfer to the Pt oxide cluster and the interfacial region. We found that the configuration with all four hydrogens adsorbed on the Pt oxide cluster (Pt₆O₁₀H₄) is more stable than geometries where one or more hydrogens reside on the TiO₂ surface (**Figure S12**). Overall, this reaction pathway demonstrates the conversion of CH₃OH to adsorbed CO via a sequence of intermediates from *CH₃OH→*CH₃O→*CH₂O→*CHO→*CO→CO(g) with strategic hydrogen migrations to facilitate a feasible reaction profile under reaction conditions. CO is strongly bound to the catalyst but CO desorption combined with methanol adsorption is favorable by 0.18 eV.

Bader charge analysis during CO formation:

We performed a detailed Bader charge analysis across all the intermediates involved in the reaction pathway leading to CO formation, to track how charge distribution evolves throughout the process (**Figure 6**). As observed earlier, during the O-H bond cleavage of CH₃OH to form CH₃O, the departing hydrogen behaves like a proton, resulting in CH₃O carrying a more negative charge compared to CH₃OH. The electronic redistribution that results in a net increase of charge in the Pt oxide clusters is consistent with experimental observations. That is, following methanol exposure to the Pt/TiO₂ catalyst, we find the vibrational frequency of the CO stretch for carbon monoxide bound to the Pt oxide clusters to be

significantly red-shifted relative to the spectra at highly oxidized Pt. This red-shift is indicative of a slight negative charge on the Pt oxide clusters driven by methanol adsorption (*vide infra*).

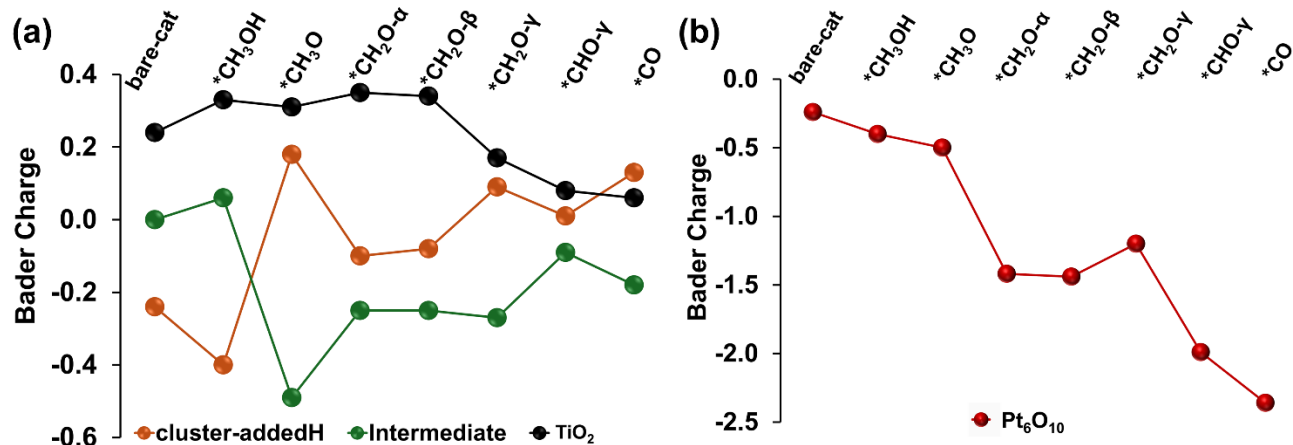


Figure 6. Bader charge analysis of the intermediates involved in CO formation (a) and the Pt oxide cluster (b).

In the next step, one methyl hydrogen gets transferred to the bridging oxygen in the cluster forming $\text{CH}_2\text{O-}\alpha$. This hydrogen transfer behaves more like a hydride transfer since the intermediate contains less negative charge in $\text{CH}_2\text{O-}\alpha$ compared to CH_3O . In this step, two hydrogen atoms are now coordinated to two separate oxygen atoms in the cluster and as a result of this the cluster gets reduced partially. Further hydrogen migration within the cluster, from one oxygen atom to another, results in the formation of $^*\text{CH}_2\text{O-}\beta$, which displays a similar charge pattern to $^*\text{CH}_2\text{O-}\alpha$. Following this, a hydrogen atom transfers from the Pt oxide cluster to an interfacial oxygen atom on the TiO_2 surface, causing a slight reduction of the surface by $+0.17 |e|$. The overall charge of CH_2O fragment remains almost the same across all conformations of $^*\text{CH}_2\text{O-}\alpha/\beta/\gamma$. The next C-H dissociation results in $^*\text{CHO}$ formation where the intermediate becomes less negatively charged. This suggests a hydride transfer during $^*\text{CHO}$ formation similar to the earlier C-H dissociation step. In the final step, a proton-like hydrogen is removed from $^*\text{CHO}$ to form $^*\text{CO}$, and CO is bound in the interface region between the TiO_2 and Pt oxide cluster. There is σ donation and π^* backdonation involved between CO, Ti center and the Pt oxide cluster, as a result CO contains a charge of $-0.17 |e|$.

Throughout the overall reaction progress towards CO formation, we see the cluster becomes more and more reduced since it accumulates more hydrogen atoms shifted from the intermediates. The oxygen atoms within the cluster effectively act as proton acceptors during methanol activation. Meanwhile the Pt_6O_{10} cluster captures more electron density during the reaction progress. The cluster acts like an electron reservoir which in turn increases catalytic activity of the system. All C-H bond cleavage steps can be therefore seen as proton-coupled electron transfers, with the formation of one proton at an O atom of the cluster and the transfer of one electron to the cluster that gain negative charge (Figure 6b).

The charge evolution observed during CO formation aligns well with the changes in bond lengths recorded throughout the reaction pathway (Figure S13, Table S1). Initially methanol is adsorbed onto the TiO_2 surface with a Ti-O bond length of 2.19 Å, with no direct bonding interaction between the molecule and the Pt oxide cluster. As the reaction proceeds through the formation of $^*\text{CH}_3\text{O}$ and $^*\text{CH}_2\text{O}$, the Ti-O bond length progressively increases, and the oxygen atom of the methoxy group shifts closer to the Pt oxide cluster. In the $^*\text{CH}_2\text{O}$ intermediate, the group binds with both the TiO_2 surface and the Pt_6O_{10} cluster with Ti-O bond length of 2.06 Å and Pt-C distance of 2.28 Å. Upon further dehydrogenation to form $^*\text{CHO}$, the

group moves even closer to the Pt oxide cluster with Pt-C bond contracting to 1.96 Å, while the distance from the TiO₂ surface increases (Ti-C = 2.35 Å). In the final adsorbed CO species, the Pt-C bond remains nearly unchanged, and the molecule is bound solely to the Pt oxide cluster. Overall, this trend reflects a weakening interaction with the TiO₂ surface, evidenced by increasing Ti-O bond lengths and a strengthening interaction with the Pt oxide cluster, as shown by the decreasing Pt-C bond distances during CO formation.

3.6. CO₂ formation from Methanol

We will now address pathways that explicitly involve the transfer of an oxygen atom, forming surface bound DOM, formates, and eventually CO₂. The formation of adsorbed formaldehyde *CH₂O (G) has already been discussed in the previous section. In addition to participating in further dehydrogenation steps towards CO, *CH₂O can also undergo structural rearrangement to form dioxymethylene (*OCH₂O, intermediate L, **Figure S14**). In this process, the CH₂ group initially bonded to the Pt center forms a new bond with a bridging oxygen atom in the Pt cluster, resulting in the *OCH₂O intermediate. In this pathway, the C-O bond is formed at an early stage, opening a route that does not pass through CO. This is of high importance to avoid CO poisoning of the catalyst. The OCH₂O group is attached to the interfacial region by making two bonds simultaneously, one with a Ti on the TiO₂ support (Ti-O=1.93 Å) and the other with a Pt of the cluster (Pt-O=2.06 Å), as shown in Table S1. Although this transformation is not thermodynamically favorable, the energy cost is not too high (0.8 eV), making OCH₂O a potential reactive intermediate if it can further transform with a low barrier (**Figure 7a**). Once formed, *OCH₂O can undergo the next dehydrogenation by transferring a hydrogen atom to the nearby O_b on the cluster, producing a formate *OCHO intermediate (M in Figure 7a)). In this structure, the CH group binds to two oxygen atoms. The Ti-O bond is elongated up to 2.26 Å here and Pt-O bond length becomes 2.10 Å (similar to *OCH₂O). This process requires a barrier of 0.55 eV or an effective barrier of 1.21 eV if starting from *CH₂O. This path is therefore kinetically competitive with CHO formation which has a 1.19 eV effective barrier. Two alternative hydrogen migration pathways from *OCH₂O can lead to formic acid-like species (intermediates N and O), but both involve higher kinetic barriers and are thermodynamically less favorable than *OCHO formation.

In *OCHO-α(M) the last hydrogen in the reaction intermediate is not pointed towards the cluster which is necessary for the next dehydrogenation. A slight rotation of the molecule yields a new configuration, P, which is nearly isoenergetic with M. Coupled with the ease of hydrogen migration within the cluster to create available active oxygen adatoms, this opens the possibility for a final C-H cleavage and full oxidation towards CO₂, more readily than CO formation. From P we finally form *OCO (intermediate R in Figure 7a) via the intermediate Q, which is another conformation of the formate. This *OCO formation requires a low barrier of 0.48 eV (from Q) and an effective barrier of 0.82 eV from the most stable configuration of formate (M). In this final structure, the <O-C-O bond angle is 122°, indicating that the CO₂ is activated by the interaction with the cluster. At this stage, three hydrogen atoms are bound to the Pt oxide cluster and one to the TiO₂ surface. CO₂ is coordinated to Pt via the carbon atom, with a Pt-C bond length of 1.98 Å. The adsorption energy of CO₂ in this intermediate is -1.31 eV, which results in a free energy change (ΔG) of 0.76 eV for the CO₂ desorption (PS3). A more favorable desorption pathway involves CO₂ desorption combined with stabilization of the remaining part of the catalyst. A closer look at the configuration PS3 shows that the cluster has one oxygen deficiency which makes the structure unstable. At this point, O₂(g) can re-oxidize the platinum oxide cluster to stabilize it, converting it into a Pt₆O₁₁H₄ stoichiometry (PS4), where one oxygen molecule is adsorbed in a peroxo form between Pt atoms (PS4). Given the abundance

of oxygen in the reaction environment, we finally observe the bound CO_2 to readily desorb from the surface, and the catalyst returns into a stable configuration with $\text{Pt}_6\text{O}_{11}\text{H}_4$ stoichiometry upon addition of one oxygen molecule. This step is an exothermic process with $\Delta G = -1.17$ eV. This correlates with experimental findings where CO_2 production is not observed until oxygen is dosed in the chamber. The optimized geometries of the intermediates as well as the transition states are illustrated in **Figure S14**. The simulated IR spectrum of CO_2 shows a peak at approximately 2377 cm^{-1} (**Figure S15**), which is close to the experimental value of 2349 cm^{-1} .

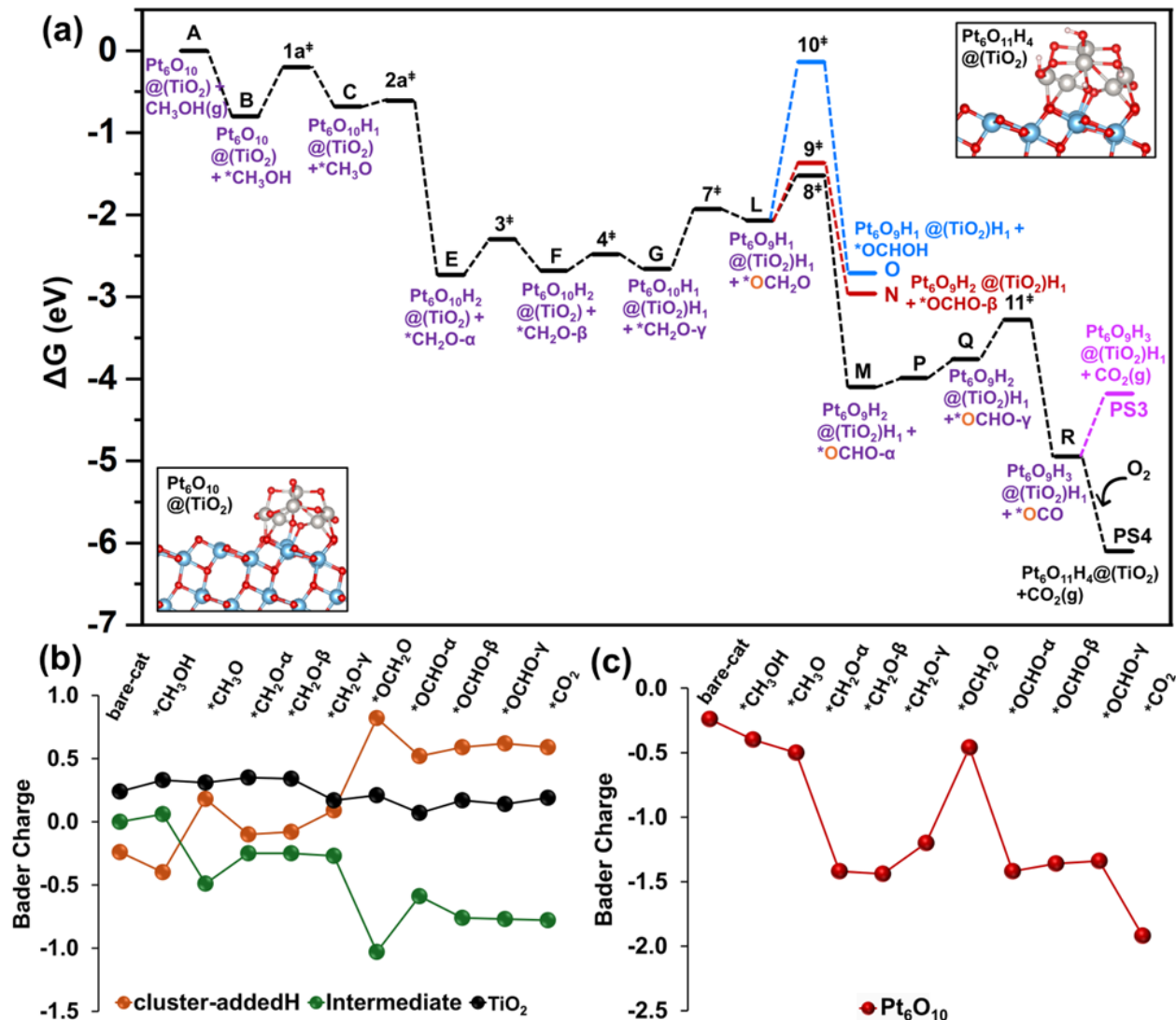


Figure 7. Reaction Energy profile for CH_3OH oxidation to produce CO_2 at 105°C (a). The symbol ‡ denotes the transition states. The black pathway is the most favorable one. Bader charge analysis of the intermediates involved in CO_2 formation (b, c).

Bader charge analysis during CO_2 formation:

To gain theoretical insight into the electronic structure change, we analyzed the Bader charges of all species involved in the conversion of adsorbed CH_3OH to CO_2 (**Figure 7b, 7c**). The charge evolution up to the formation of formaldehyde was discussed in the previous section. Upon formation of the dioxymethylene intermediate ($^*\text{OCH}_2\text{O}$), where the CH_2 group is sandwiched between two oxygen atoms,

a significant increase in electron density is observed on the intermediate (-1.03 |e|), as evidenced by the sharp rise in charge from $^*\text{CH}_2\text{O}-\gamma$ to $^*\text{OCH}_2\text{O}$ (Figure 7b). Subsequent dehydrogenation leads to the formate intermediate ($^*\text{OCHO}$), where a decrease in negative charge is noted compared to $^*\text{OCH}_2\text{O}$. This suggests that the transferred hydrogen behaves like a hydride, resulting in increased electron density being transferred to the Pt oxide cluster. In the final stage, the adsorbed CO_2 molecule carries a charge of -0.78 |e|. This correlates with the observed C-O bond lengths of 1.25 Å and 1.31 Å in $^*\text{CO}_2$, indicating its activation compared to gas-phase CO_2 , which has a C-O bond length of 1.16 Å. Furthermore, as the reaction progresses toward CO_2 formation, the Pt oxide cluster becomes increasingly reduced, reinforcing its role as an electron reservoir. This electron-accepting capability is beneficial for driving the oxidation of CH_3OH and can explain why complete oxidation is not seen on pure TiO_2 in the absence of metal oxide clusters.

3.7. Methyl Formate formation from Methanol

Surface Fourier transform infrared (FTIR) spectra confirm the presence of intermediates such as dioxymethylene (DOM), formate, and CO during the ongoing reaction. On the $\text{Pt}_6\text{O}_{10}@/\text{TiO}_2$ catalyst surface, the species generated from CH_3OH decomposition can potentially recombine to produce methyl formate (HCOOCH_3), which is observed experimentally too. The reaction mechanisms for methyl formate (MF) formation have been explored, either from dioxymethylene (DOM) or from formate intermediate (Figure S16, S17, Section 5 in SI). Three mechanisms have been considered from DOM, and three from the formate intermediate. This comparative analysis helps identify the most favorable pathway for MF production (Figure S18). Considering both kinetic and thermodynamic factors, a pathway from formate emerges as the most favorable route for MF formation. This reaction pathway highlights that the groups formed by CH_3OH decomposition can recombine efficiently to form MF, without poisoning the catalyst. We further calculated frequency corrections for this pathway to calculate Gibbs free energy. The resulting free energy profile and the corresponding optimized structures involved in MF production are displayed in Figure 8 and the calculated Gibbs energy values are provided in Table S2.

The main rate limiting process consists in the dehydrogenation of $^*\text{OCH}_2\text{O}$, forming the reactive $^*\text{OCHO}$, with an effective barrier from CH_2O (E) of 1.21 eV. This is exactly the same rate limiting process as the one for CO_2 formation via $^*\text{OCH}_2\text{O}$ ($8^\ddagger$, Figure 7). Further coupling steps are associated with a lower effective barrier of 0.92 eV from $^*\text{OCHO}+^*\text{CH}_3\text{O}$ to transition state $13^\ddagger$. This coupling reaction is therefore kinetically competitive with the two previously studied ones, CO formation and CO_2 via $^*\text{OCH}_2\text{O}$.

MF desorption is favorable when a methanol molecule is adsorbed (PS8 in Figure 8) but the initial state of the catalyst is not restored. Instead, a partially reduced Pt oxide cluster is formed with 4 OH and 6O, instead of 10 O initially (noted PRC, $\text{Pt}_6\text{O}_{10}\text{H}_4@(\text{TiO}_2)$).

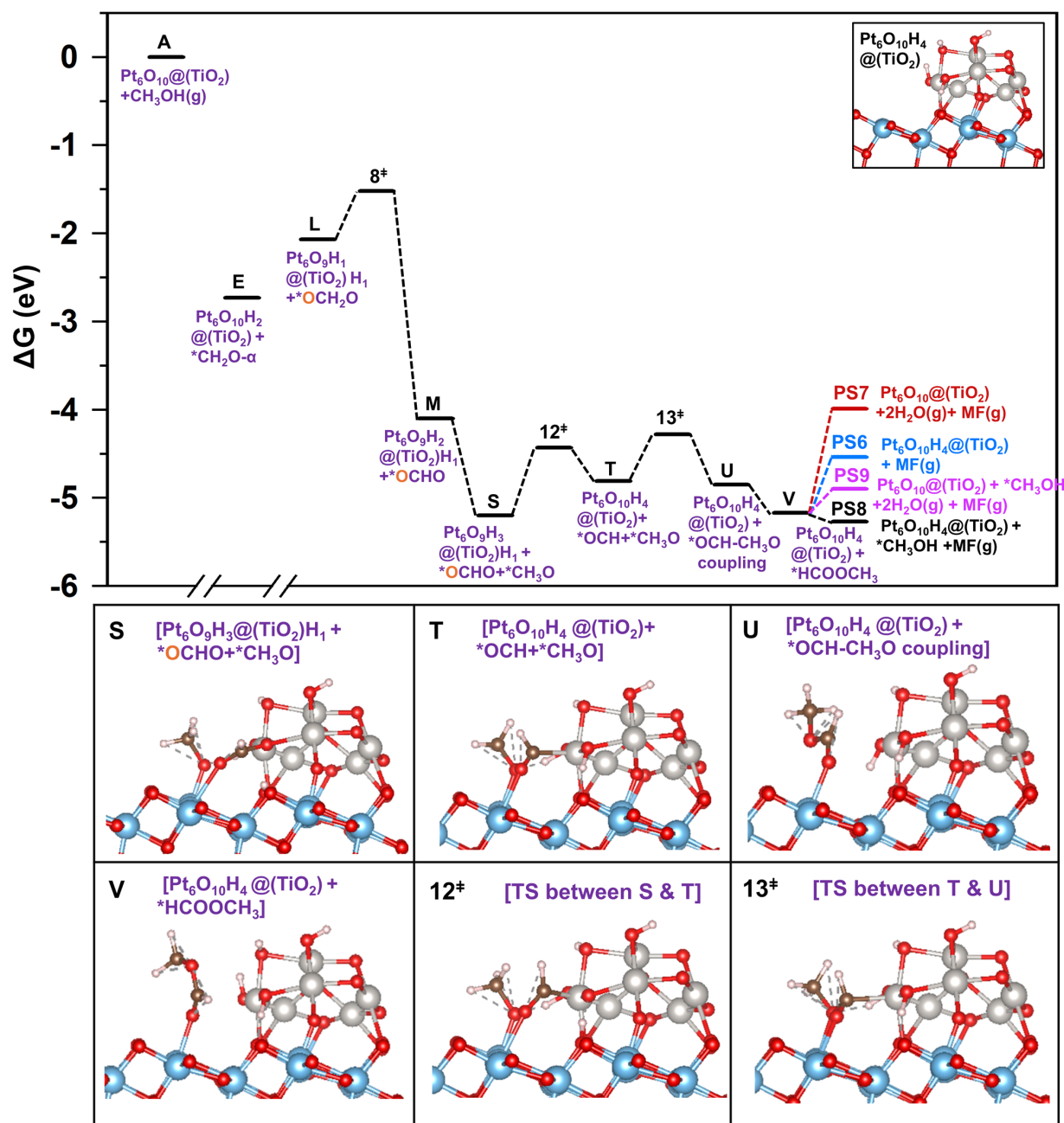


Figure 8. Reaction Gibbs free energy profile for CH_3OH oxidation to produce methyl formate at 105°C . The black pathway is the most favorable one. The symbol $\dagger$ denotes the transition states. The intermediates and the transition states are also displayed. The reaction steps between A-E and E-L are shown before.

3.8. Reaction progress on the partially reduced state of the catalyst, $\text{Pt}_6\text{O}_{10}\text{H}_4$

So far, we have investigated the formation of CO , CO_2 , and methyl formate (MF) originating from CH_3OH adsorption. While the effective energy barriers for all three processes are remarkably similar, MF formation is found to be more exothermic followed by CO_2 and then CO (**Figure S19**). This is consistent

with our experiential observations that MF is created at intermediate temperature.²⁴ MF desorption leaves us with a methanol molecule adsorbed on the partially reduced Pt oxide cluster (PS8 in Figure 8, also called PRC afterwards). This adsorbed species can undergo further O-H and C-H bond cleavage, ultimately leading to CO₂ and water formation and regenerating the bare catalyst but in a different oxidation state. We will now explore how the reaction can proceed.

The pathway starts from PRC with the O-H bond cleavage of methanol (RC2, **Figure 9**). For that, one hydrogen is migrated from the Pt oxide cluster to the TiO₂ support, creating an O atom on the cluster available to uptake the hydrogen transferred from methanol (RC2). This step is mildly endothermic, with a Gibbs free energy increase of only 0.32 eV. The associated kinetic barrier is expected to be comparable to earlier observations, as hydrogen migration processes typically involve low activation energies. Subsequently, the next step, i.e. formation of *CH₂O is thermodynamically uphill by another 0.32 eV (RC3). During this process, a bridging hydroxyl group on the cluster accepts the upcoming hydrogen atom, resulting in the formation of a water molecule. The transition state associated with this transformation (RC_23[‡]) has an activation barrier of 0.75 eV, which results in an effective barrier from PRC of 1.07 eV, accessible at the reaction conditions. Notably, this water formation step is not observed with the oxidized Pt₆O₁₀ system. Following this, hydrogen migration leads to the formation of a more stable *CH₂O species (RC4), an exothermic process.

The *CH₂O fragment subsequently undergoes rearrangement, moving from the Pt site to the adjacent bridging oxygen to form a dioxymethylene (*OCH₂O) intermediate (RC5). This step is both thermodynamically favorable and kinetically accessible, with a calculated barrier of 0.51 eV (RC_45[‡]). These results indicate that the formation of DOM is energetically more favorable both thermodynamically and kinetically, when the cluster is partially reduced. In addition we simulated the IR spectrum of DOM, which shows characteristic peaks at 1149 and 1070 cm⁻¹ (**Figure S20**). These values align well with experimental data, supporting that the reaction mechanism proceeds through the formation of DOM. Subsequently a hydrogen from the generated water transfers to the neighboring OH, producing water (RC6). The next C-H bond cleavage involves hydrogen transfer to the OH moiety on the Pt oxide cluster, yielding a *OCHO intermediate (RC7) along with two water molecules, one coordinated on the cluster via a Pt-O bond and the other stabilized through hydrogen bonding (RC6). This step involves a barrier of 1.05 eV from RC6 (RC_67[‡]). The overall effective barrier from PRC is 1.17 eV. The generation of water throughout the process is entirely consistent with experimental observations, where the water appears to play a major role in the overall reaction.²⁴

Further hydrogen migration from the carbon center to the oxygen atom leads to the formation of a *COOH species (RC8), which is stabilized by 0.6 eV relative to the previous intermediate. Finally, the remaining hydrogen is transferred from *COOH to a bridging oxygen of the cluster, releasing 0.84 eV in energy (RC9). In the presence of oxygen, the adsorbed hydrogens on the catalyst can form water, while the reduced cluster is reoxidized by incorporating oxygen, generating a bare catalyst but with the Pt₆O₁₁H₄ oxidation state (RC10). This quasi-regeneration step of the catalyst is accompanied by the release of CO₂ and water, thereby approximately closing the catalytic cycle and enabling continued methanol oxidation. We will discuss further how the catalytic cycle can be completely closed.

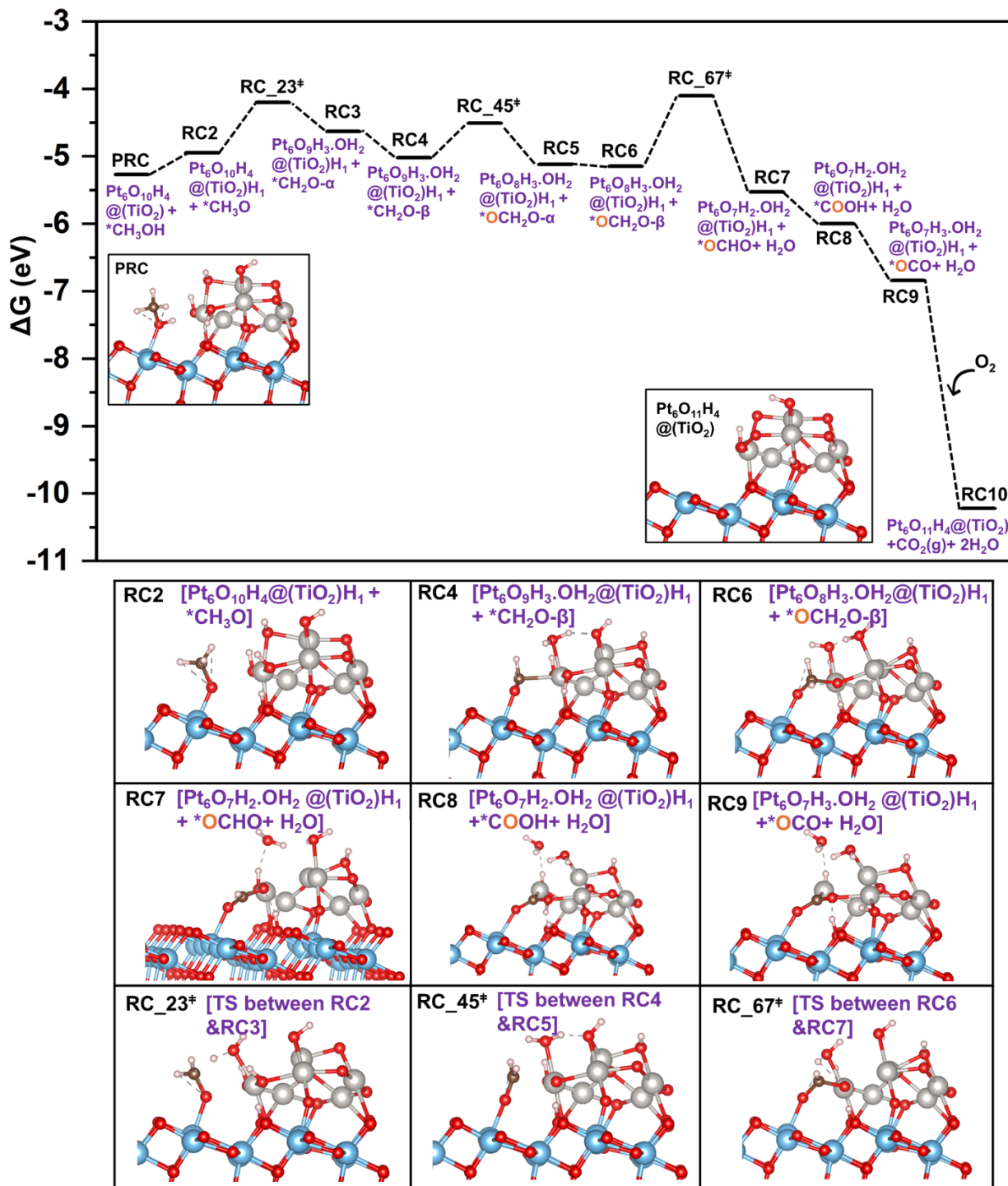


Figure 9. Potential Energy surface for methanol oxidation to CO_2 formation on the reduced cluster $\text{Pt}_6\text{O}_{10}\text{H}_4 @(\text{TiO}_2)$ at 105°C. The symbol † denotes the transition states. The O atom in orange color is a representation when this atom is shared between the intermediate and the Pt oxide cluster.

Overall, we find that CO₂ formation from the Pt₆O₁₀ cluster proceeds with an effective barrier of 1.21 eV (through 8[‡] in Figure 7 corresponding to formate formation) and no water is produced during this process. However, when another methanol molecule is adsorbed, methyl formate (MF) forms with the same effective barrier (through 8[‡] in Figure 8) and the cluster becomes partially reduced to Pt₆O₁₀H₄. Another pathway can produce CO with an effective barrier of 1.19 eV (through 5c[‡] in Figure 5 corresponding to CHO formation), also forming the partially reduced cluster. This Pt₆O₁₀H₄ structure appears as an alternate active site and the adsorption of a methanol molecule on this partially reduced catalyst leads to water formation, which is both thermodynamically and kinetically favorable. Under these conditions, DOM formation also becomes thermodynamically favorable, unlike in the case of the non-reduced Pt₆O₁₀ catalyst. This shift occurs because the water formed in the system stabilizes *OCH₂O through hydrogen bonding. Moreover, the barrier for DOM formation from *CH₂O decreases to 0.51 eV (RC_45[‡] in Figure 9), much lower than the 0.8 eV (8[‡] in Figure 7) observed previously. The water formed acts as a bridge enabling hydrogen displacement mechanisms (through RC5 to RC7 via RC6) and thereby lowering the kinetic barrier. The effective barrier for CO₂ formation on the partially reduced cluster (1.17 eV, RC_67[‡]) remains very similar to all the other calculated barriers. The similarity between these barriers shows that several pathways can be simultaneously active. A CO-free pathway proceeds through DOM and formate, in agreement with the spectroscopic signatures of these intermediates seen in the experiment. Such a pathway is of high importance because it prevents CO poisoning and it can produce CO₂ or methylformate. In addition, CO can be formed by over dehydrogenation of the formaldehyde intermediate, and is also seen from spectroscopy.

Although the Pt₆O₁₀ cluster is smaller than the ~1.5 nm particles observed experimentally, the key methanol-oxidation chemistry occurs at low-coordination Pt-O-Ti perimeter sites whose PtO₄-type environment should be preserved across larger supported Pt oxide clusters. Because these interfacial motifs control the adsorption and reaction energetics, and similar reactivity has been observed experimentally for smaller ~0.9 nm Pt oxide clusters on the same support²⁴, the mechanistic conclusions drawn from the Pt₆O₁₀ model are expected to be robust with respect to cluster size.

3.9. Catalyst redox changes during the reaction and electronic analysis

During the complete reaction progression, the catalyst undergoes dynamic structural and electronic changes. Initially, the Pt₆O₁₀ cluster is partially reduced through hydrogen transfer from adsorbed methanol to its bridging oxygen atoms. Specifically, methanol adsorption on Pt₆O₁₀@TiO₂ produces CO via a CHO intermediate, reducing the cluster to Pt₆O₁₀H₄ (Figure 5). Along the oxidation pathway leading to DOM formation, CO₂ is produced and the cluster is reduced to Pt₆O₁₁H₄ (Figure 7). In the coupling pathway, reaction of another methanol molecule yields methyl formate and again results in the reduced Pt₆O₁₀H₄ cluster (Figure 8). These reduced cluster states are found to be thermodynamically favorable.

To further address the closure of the catalytic cycle, we examined methanol reaction on Pt₆O₁₀H₄, which leads to CO₂ formation accompanied by water release and conversion of the cluster to Pt₆O₁₁H₄ (Figure 9). Direct oxidation of Pt₆O₁₁H₄ back to Pt₆O₁₀ is nontrivial, as it involves the removal of an odd number of oxygen atoms. To clarify how the catalytic cycle can nevertheless be closed, we have added a new summary figure (**Figure 10**) that integrates all explicitly studied reaction steps. This figure shows that the oxidized Pt₆O₁₀ cluster can be regenerated from the reduced clusters through reactions involving CH₃OH and O₂, with CO₂ formation.

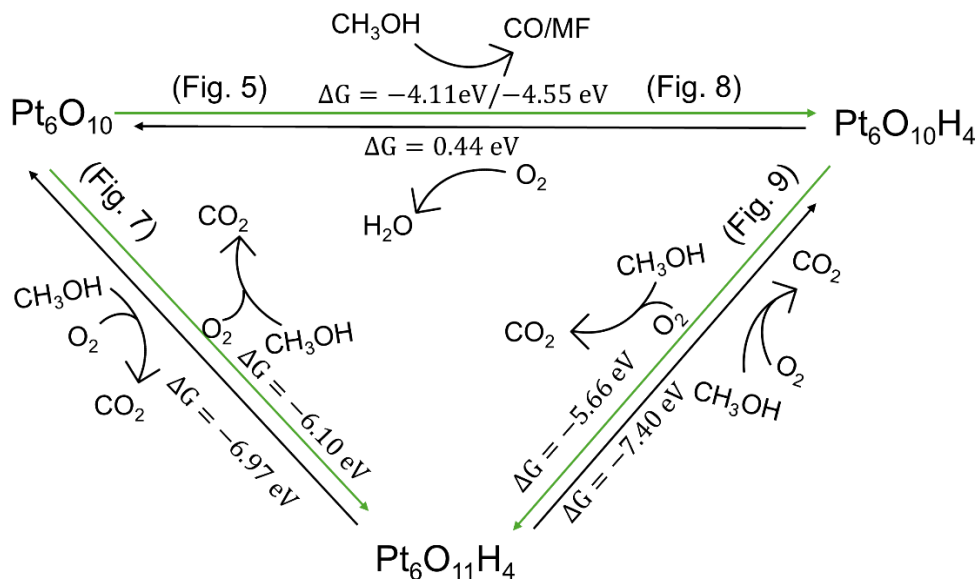


Figure 10. The proposed catalytic cycle by combining all mechanisms. For simplicity the support (TiO_2) is not shown in the picture.

Compared to other metal- TiO_2 systems, Pt/TiO_2 offers a favorable balance between dehydrogenation activity and oxygen donation at the metal-support interface, whereas less reactive noble metals (e.g., Au, Ag) bind oxygenated intermediates too weakly and more oxophilic metals (e.g., Cu, Ni) tend to over-stabilize formate species, thereby limiting efficient C-O coupling.

To unravel the mechanisms underpinning the high methanol oxidation reaction activity, we performed the Bader charge analysis in the proposed catalyst system $\text{Pt}_6\text{O}_{10}@(\text{TiO}_2)$. The analysis reveals a net charge transfer of approximately 0.24 electrons from the TiO_2 support to the Pt_6O_{10} cluster. This electron transfer suggests that the presence of the Pt_6O_{10} cluster on the TiO_2 surface may facilitate more favorable adsorption of CH_3OH . To investigate this, we computed the adsorption energies of methanol on both Pt and Ti sites, along with COHP analysis to probe the nature of the bonding. The adsorption energy of methanol is found to be lower on the Pt site (-0.70 eV) compared to the Ti site (-1.43 eV), indicating stronger interaction with the latter. The calculated methanol adsorption energy is -1.11 eV on pristine TiO_2 in absence of Pt oxide cluster, suggesting the cluster enhances the adsorption strength of methanol in the catalyst. In both cases, whether the active site is Pt or Ti, the methanol molecule binds through its oxygen atom to the metal center in $\text{Pt}_6\text{O}_{10}@(\text{TiO}_2)$. The crystal orbital Hamilton population (COHP) analysis further elucidates the bonding interactions by illustrating the distribution of bonding and antibonding states. Here, we plot -COHP, such that bonding states appear on the right (positive) side and antibonding states on the left (negative). The COHP results show greater filling of antibonding states in the Pt-O interaction relative to the Ti-O interaction, implying weaker bonding on the Pt site (**Figure S21**). This is in line with the lower d-electron filling of Ti vs Pt and corroborated by the observed bond lengths: 2.25 Å for Pt-O and 2.19 Å for Ti-O in the methanol-adsorbed configurations. Overall, these results indicate that the Ti site on the support plays a key role in activating CH_3OH by providing stronger adsorption.

To understand how the Pt oxide cluster enhances catalytic reactivity, we examined the density of states (DOS) for both the TiO_2 support and the Pt_6O_{10} -decorated catalyst, $\text{Pt}_6\text{O}_{10}@(\text{TiO}_2)$ (**Figure S22**). As illustrated in **Figure S22a**, the calculated band gap of pristine TiO_2 is 2.45 eV underestimated compared to

the experimental value of 3.12 eV due to the limitations of the GGA PBE functional. When the Pt_6O_{10} cluster is introduced, the band gap reduces significantly to 2.31 eV (**Figure S22b**). This narrowing is attributed to the formation of interfacial Pt-O-Ti bonds, which modify the electronic structure and generate new surface states. This modification in the electronic structure at the interface promotes stronger methanol adsorption and facilitates the activation of intermediates, driven by the synergistic interaction between the TiO_2 support and the Pt oxide cluster. While Pt primarily enriches the valence band, Ti contributes more to the conduction band (**Figure S23a, b**). As a result, both valence and conduction bands in the $\text{Pt}_6\text{O}_{10}@\text{(TiO}_2\text{)}$ system exhibit a greater density of states compared to pure TiO_2 , indicating enhanced electronic activity. Both parts of the interface contribute distinctively: electron donating intermediates interact on the TiO_2 side, while electron-accepting moieties preferentially interact with the high energy occupied orbitals on the Pt oxide cluster. Moreover, we analyzed the partial density of states (PDOS) of oxygen to distinguish between the oxygens in the Pt oxide cluster and those in TiO_2 (**Figure S23c**). The results show that the oxygen atoms bonded to Pt have higher occupied p orbitals, indicating that these oxygens in the Pt oxide cluster are more basic than the oxygens in TiO_2 . This aligns with the calculated p band center values on these two different oxygens, which are -2.45 eV and -2.25 eV for oxygen in the Pt oxide cluster and TiO_2 respectively. Consequently, during methanol oxidation, the hydrogens preferentially transfer to the cluster oxygens as the cluster gets more reduced.

4. Conclusions

In this paper, we explored by a combination of DFT computation and *in situ* IR spectroscopy several competitive pathways and intermediates for methanol oxidation on a Pt catalysts on anatase- TiO_2 . For the catalyst model in the simulations, we took care to determine its nature in oxidizing reaction conditions by detailed sampling of composition and configuration by GCBH simulation, finding that the Pt oxide cluster adopts a Pt_6O_{10} configuration in such conditions. We studied the methanol oxidation pathway systemically starting with this globally optimized geometry of the supported cluster catalyst $\text{Pt}_6\text{O}_{10}@\text{(TiO}_2\text{)}$. Ti site on the support plays a key role in activating CH_3OH by providing stronger adsorption, which is validated from COHP analysis. Calculations show that the Pt catalyst acts in synergy with the support. Methanol preferentially adsorbs on the TiO_2 , but the adsorption energy is significantly enhanced in the interface region, bringing adsorbed methanol in proximity to the catalyst. Highly Lewis basic O atoms on the Pt_6O_{10} cluster abstract H atoms from the methanol and initiate the reaction; CH_3OH dissociates at the interface between Pt_6O_{10} and TiO_2 with a low energy barrier. From the Gibbs Free energy profiles, we show that three reactions have remarkably similar effective activation barriers and therefore can occur in parallel: the formation of CO, of CO_2 via $^*\text{OCH}_2\text{O}$ (DOM) or of the coupling product methyl formate also occurring via the DOM intermediate.

High vacuum transmission infrared experiments corroborate our simulations. Spectroscopic analysis confirms that the reaction proceeds through the intermediate DOM ($^*\text{OCH}_2\text{O}$) and adsorbed CO is also observed. The DOM intermediate opens a pathway where the C-O bond is formed early in the reaction, hence giving a CO free route where CO poisoning is avoided. However, that path competes with the CO formation from $^*\text{OCH}_2$, and modification of the catalyst by alloying or doping could optimize the role of the DOM pathway. The experimental and simulated IR values match well to confirm the products, also validating the models used in the calculations. Our results highlight the critical role of surface oxygen availability and Lewis basicity in promoting efficient methanol oxidation over the $\text{Pt}_6\text{O}_{10}@\text{(TiO}_2\text{)}$ catalyst.

During the course of the reaction, the Pt oxide cluster exhibits dynamic redox behavior with continuous structural and electronic changes. Initially, hydrogen from adsorbed methanol transfers to the bridging

oxygen atoms of the Pt_6O_{10} cluster, reducing it to $\text{Pt}_6\text{O}_{10}\text{H}_4$ with formation of CO or MF. On this partially reduced cluster, further methanol decomposition produces CO_2 and H_2O . Reoxidation follows, bringing back the cluster to an oxidized stable form and a complete catalytic cycle can be proposed. The energy profiles are altered on the partially reduced Pt catalysts, making DOM formation thermodynamically easier. On this partially reduced catalyst, water can be formed during the methanol oxidation reaction, which is not the case on the oxidized cluster, and the formed water further promotes the catalytic reactivity. Water molecules can act as co-catalysts, actively participating in the reaction pathway through hydrogen bond interaction and enhancing the overall oxidation activity. These findings point to the potential benefits of introducing trace amounts of H_2O into the reaction environment particularly for Pt- or transition metal-based catalysts supported on oxides as a means of boosting catalytic performance and facilitating complete combustion of organic feedstocks. This work offers mechanistic insights into the redox behavior and interfacial reactivity of metal/oxide systems, which can guide the rational design of advanced catalysts for direct methanol fuel cell (DMFC) technologies.

Supporting Information

Gibbs Free energy calculation; additional IR spectra and XANES; Global Optimization details; Reaction energy diagram during CH_3OH oxidation; Methyl Formate formation from Methanol; and electronic structure analysis

Notes

The authors declare no competing financial interest.

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References

- (1) Hamnett, A. Mechanism and electrocatalysis in the direct methanol fuel cell. *Catalysis Today* **1997**, *38* (4), 445-457.
- (2) Soares, A. P. V.; Farinha, P. M.; and Kiennemann, A. Methanol Selective Oxidation to Formaldehyde over Iron-Molybdate Catalysts. *Catalysis Reviews* **2005**, *47* (1), 125-174.
- (3) Xu, M.; Lunsford, J. H.; Goodman, D. W.; Bhattacharyya, A. Synthesis of dimethyl ether (DME) from methanol over solid-acid catalysts. *Applied Catalysis A: General* **1997**, *149* (2), 289-301.
- (4) Olsbye, U.; Svelle, S.; Bjørgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga, S.; Lillerud, K. P. Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity. *Angewandte Chemie International Edition* **2012**, *51* (24), 5810-5831.
- (5) Lang, X.; Wen, B.; Zhou, C.; Ren, Z.; Liu, L.-M. First-Principles Study of Methanol Oxidation into Methyl Formate on Rutile $\text{TiO}_2(110)$. *The Journal of Physical Chemistry C* **2014**, *118* (34), 19859-19868.
- (6) Kaichev, V. V.; Popova, G. Y.; Chesalov, Y. A.; Saraev, A. A.; Zemlyanov, D. Y.; Beloshapkin, S. A.; Knop-Gericke, A.; Schlögl, R.; Andrushkevich, T. V.; Bukhtiyarov, V. I. Selective oxidation of methanol to form dimethoxymethane and methyl formate over a monolayer $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst. *Journal of Catalysis* **2014**, *311*, 59-70.

- (7) Wittstock, A.; Zielasek, V.; Biener, J.; Friend, C. M.; Bäumer, M. Nanoporous Gold Catalysts for Selective Gas-Phase Oxidative Coupling of Methanol at Low Temperature. *Science* **2010**, 327 (5963), 319-322.
- (8) Tatibouët, J. M. Methanol oxidation as a catalytic surface probe. *Applied Catalysis A: General* **1997**, 148 (2), 213-252.
- (9) Du, P.; Wu, P.; Cai, C. Mechanistic Insight into the Facet-Dependent Adsorption of Methanol on a Pt₃Ni Nanocatalyst. *The Journal of Physical Chemistry C* **2015**, 119 (32), 18352-18363.
- (10) Dong, L.; Gari, R. R. S.; Li, Z.; Craig, M. M.; Hou, S. Graphene-supported platinum and platinum–ruthenium nanoparticles with high electrocatalytic activity for methanol and ethanol oxidation. *Carbon* **2010**, 48 (3), 781-787.
- (11) Nachimuthu, S.; Lai, P.-J.; Jiang, J.-C. Efficient hydrogen storage in boron doped graphene decorated by transition metals – A first-principles study. *Carbon* **2014**, 73, 132-140.
- (12) Ferrin, P.; Mavrikakis, M. Structure Sensitivity of Methanol Electrooxidation on Transition Metals. *Journal of the American Chemical Society* **2009**, 131 (40), 14381-14389.
- (13) Skoplyak, O.; Menning, C. A.; Barteau, M. A.; Chen, J. G. Experimental and theoretical study of reactivity trends for methanol on CoPt(111) and NiPt(111) bimetallic surfaces. *The Journal of Chemical Physics* **2007**, 127 (11), 114707.
- (14) González, S.; Sousa, C.; Illas, F. Theoretical study of the chemisorption of CO on bimetallic RhCu surfaces and nanoparticles. *Surface Science* **2003**, 531 (1), 39-52.
- (15) Mehmood, F.; Greeley, J.; Zapol, P.; Curtiss, L. A. Comparative Density Functional Study of Methanol Decomposition on Cu₄ and Co₄ Clusters. *The Journal of Physical Chemistry B* **2010**, 114 (45), 14458-14466.
- (16) Choksi, T.; Greeley, J. Partial Oxidation of Methanol on MoO₃ (010): A DFT and Microkinetic Study. *ACS Catalysis* **2016**, 6 (11), 7260-7277.
- (17) Mehta, S.; Agarwal, S.; Kenge, N.; Mekala, S. P.; Patil, V.; Raja, T.; Joshi, K. Mixed metal oxide: A new class of catalyst for methanol activation. *Applied Surface Science* **2020**, 534, 147449.
- (18) Murcia-López, S.; Bacariza, M. C.; Villa, K.; Lopes, J. M.; Henriques, C.; Morante, J. R.; Andreu, T. Controlled Photocatalytic Oxidation of Methane to Methanol through Surface Modification of Beta Zeolites. *ACS Catalysis* **2017**, 7 (4), 2878-2885.
- (19) Rellán-Piñeiro, M.; López, N. The Active Molybdenum Oxide Phase in the Methanol Oxidation to Formaldehyde (Formox Process): A DFT Study. *ChemSusChem* **2015**, 8 (13), 2231-2239.
- (20) Saavedra, J.; Doan, H. A.; Pursell, C. J.; Grabow, L. C.; Chandler, B. D. The critical role of water at the gold-titania interface in catalytic CO oxidation. *Science* **2014**, 345 (6204), 1599-1602.
- (21) Zhang, C.; He, H.; Tanaka, K.-i. Catalytic performance and mechanism of a Pt/TiO₂ catalyst for the oxidation of formaldehyde at room temperature. *Applied Catalysis B: Environmental* **2006**, 65 (1), 37-43.
- (22) Reece, C.; Redekop, E. A.; Karakalos, S.; Friend, C. M.; Madix, R. J. Crossing the great divide between single-crystal reactivity and actual catalyst selectivity with pressure transients. *Nature Catalysis* **2018**, 1 (11), 852-859.
- (23) Yoon, S.; Oh, K.; Liu, F.; Seo, J. H.; Somorjai, G. A.; Lee, J. H.; An, K. Specific Metal–Support Interactions between Nanoparticle Layers for Catalysts with Enhanced Methanol Oxidation Activity. *ACS Catalysis* **2018**, 8 (6), 5391-5398.
- (24) Sapienza, N. S.; Knight, K. N.; Albrahim, M.; Yousuf, M. R.; Karim, A. M.; Morris, J. R. Autocatalysis through the Generation of Water during Methanol Oxidation over a Titania-Supported Platinum Catalyst. *ACS Catalysis* **2023**, 13 (15), 9997-10006.
- (25) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* **1999**, 59 (3), 1758-1775.
- (26) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* **1996**, 54 (16), 11169-11186.
- (27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, 77 (18), 3865-3868.

- (28) Yu, Y.-Y.; Gong, X.-Q. CO Oxidation at Rutile TiO₂(110): Role of Oxygen Vacancies and Titanium Interstitials. *ACS Catalysis* **2015**, *5* (4), 2042-2050.
- (29) Steinmann, S. N.; Corminboeuf, C. Comprehensive Benchmarking of a Density-Dependent Dispersion Correction. *Journal of Chemical Theory and Computation* **2011**, *7* (11), 3567-3577.
- (30) Howard, C. J.; Sabine, T. M.; Dickson, F. Structural and thermal parameters for rutile and anatase. *Acta Crystallographica Section B* **1991**, *47* (4), 462-468.
- (31) Makov, G.; Payne, M. C. Periodic boundary conditions in ab initio calculations. *Physical Review B* **1995**, *51* (7), 4014-4022.
- (32) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **2000**, *113* (22), 9901-9904.
- (33) Xiao, P.; Sheppard, D.; Rogal, J.; Henkelman, G. Solid-state dimer method for calculating solid-solid phase transitions. *The Journal of Chemical Physics* **2014**, *140* (17), 174104.
- (34) Greeley, J.; Mavrikakis, M. A first-principles study of surface and subsurface H on and in Ni(111): diffusional properties and coverage-dependent behavior. *Surface Science* **2003**, *540* (2), 215-229.
- (35) Williams, M. CRC handbook of chemistry and physics. *Occupational and environmental medicine* **1996**, *53* (7), 504.
- (36) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Computational Materials Science* **2006**, *36* (3), 354-360.
- (37) Phromma, S.; Wutikhun, T.; Kasamechongchun, P.; Eksangsri, T.; Sapcharoenkun, C. Effect of Calcination Temperature on Photocatalytic Activity of Synthesized TiO₂ Nanoparticles via Wet Ball Milling Sol-Gel Method. In *Applied Sciences*, 2020; Vol. 10.
- (38) Wetchakun, N.; Incessungvorn, B.; Wetchakun, K.; Phanichphant, S. Influence of calcination temperature on anatase to rutile phase transformation in TiO₂ nanoparticles synthesized by the modified sol-gel method. *Materials Letters* **2012**, *82*, 195-198.
- (39) Oudenhuijzen, M. K.; Kooyman, P. J.; Tappel, B.; van Bokhoven, J. A.; Koningsberger, D. C. Understanding the Influence of the Pretreatment Procedure on Platinum Particle Size and Particle-Size Distribution for SiO₂ Impregnated with [Pt²⁺(NH₃)₄](NO₃)₂: A Combination of HRTEM, Mass Spectrometry, and Quick EXAFS. *Journal of Catalysis* **2002**, *205* (1), 135-146.
- (40) Maynes, A. J.; Driscoll, D. M.; DeSario, P. A.; Pietron, J. J.; Pennington, A. M.; Rolison, D. R.; Morris, J. R. Electronic Metal-Support Interactions in the Activation of CO Oxidation over a Cu/TiO₂ Aerogel Catalyst. *The Journal of Physical Chemistry C* **2020**, *124* (39), 21491-21501.
- (41) Stolow, A.; Bragg, A. E.; Neumark, D. M. Femtosecond Time-Resolved Photoelectron Spectroscopy. *Chemical Reviews* **2004**, *104* (4), 1719-1758.
- (42) Xu, J.; Guo, S.; Hou, F.; Li, J.; Zhao, L. Methanol oxidation on the PtPd(111) alloy surface: A density functional theory study. *International Journal of Quantum Chemistry* **2018**, *118* (3), e25491.
- (43) Zhang, Z.; Liu, J.; Wang, J.; Wang, Q.; Wang, Y.; Wang, K.; Wang, Z.; Gu, M.; Tang, Z.; Lim, J.; et al. Single-atom catalyst for high-performance methanol oxidation. *Nature Communications* **2021**, *12* (1), 5235.
- (44) Wang, L.; He, C.; Zhang, W.; Li, Z.; Yang, J. Methanol-Selective Oxidation Pathways on Au Surfaces: A First-Principles Study. *The Journal of Physical Chemistry C* **2014**, *118* (31), 17511-17520.
- (45) Wu, X.; Chen, Y.; Yamaguchi, T. Hydrogen bonding in methanol studied by infrared spectroscopy. *Journal of Molecular Spectroscopy* **2007**, *246* (2), 187-191.
- (46) Chen, T.; Feng, Z.; Wu, G.; Shi, J.; Ma, G.; Ying, P.; Li, C. Mechanistic Studies of Photocatalytic Reaction of Methanol for Hydrogen Production on Pt/TiO₂ by in situ Fourier Transform IR and Time-Resolved IR Spectroscopy. *The Journal of Physical Chemistry C* **2007**, *111* (22), 8005-8014.
- (47) Chen, X.; He, G.; Li, Y.; Chen, M.; Qin, X.; Zhang, C.; He, H. Identification of a Facile Pathway for Dioxymethylene Conversion to Formate Catalyzed by Surface Hydroxyl on TiO₂-Based Catalyst. *ACS Catalysis* **2020**, *10* (17), 9706-9715.
- (48) Ivanova, E.; Mihaylov, M.; Thibault-Starzyk, F.; Daturi, M.; Hadjiivanov, K. FTIR spectroscopy study of CO and NO adsorption and co-adsorption on Pt/TiO₂. *Journal of Molecular Catalysis A: Chemical* **2007**, *274* (1), 179-184.

- (49) Hadjiivanov, K. I. IR study of CO and H₂O coadsorption on Pt⁺/TiO₂ and Pt/TiO₂ samples. *Journal of the Chemical Society, Faraday Transactions* **1998**, *94* (13), 1901-1904.
- (50) Huang, H.; Leung, D. Y. C.; Ye, D. Effect of reduction treatment on structural properties of TiO₂ supported Pt nanoparticles and their catalytic activity for formaldehyde oxidation. *Journal of Materials Chemistry* **2011**, *21* (26), 9647-9652.
- (51) Zhang, C.; He, H. A comparative study of TiO₂ supported noble metal catalysts for the oxidation of formaldehyde at room temperature. *Catalysis Today* **2007**, *126* (3), 345-350.
- (52) Cheula, R.; Maestri, M.; Mpourmpakis, G. Modeling Morphology and Catalytic Activity of Nanoparticle Ensembles Under Reaction Conditions. *ACS Catalysis* **2020**, *10* (11), 6149-6158.
- (53) Sun, G.; Sautet, P. Active Site Fluxional Restructuring as a New Paradigm in Triggering Reaction Activity for Nanocluster Catalysis. *Accounts of Chemical Research* **2021**, *54* (20), 3841-3849.
- (54) Sun, G.; Alexandrova, A. N.; Sautet, P. Structural Rearrangements of Subnanometer Cu Oxide Clusters Govern Catalytic Oxidation. *ACS Catalysis* **2020**, *10* (9), 5309-5317.