Catalytic consequences of the identity and coverages of reactive intermediates during methanol partial oxidation on Pt clusters

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Abstract

Rate measurements, carried out after elimination of transport corruptions, show that CH₃OH partial oxidation on Pt clusters proceeds via three distinctly different kinetic regimes defined by the operating oxidant-to-reductant (O₂-to-CH₃OH) ratio. These kinetic regimes, each with unique rate dependencies for HCHO, HCOOCH₃, and CO₂ formation, arise from a dynamic shift in the identity and coverages of reactive intermediates on Pt cluster surfaces from saturated with chemisorbed oxygen, to uncovered, and then to partially covered with methanol derived species as the oxygen chemical potential at cluster surfaces decreases with decreasing O₂-to-CH₃OH ratio. HCHO formation rates first remain insensitive to O₂ on Pt cluster surfaces saturated with chemisorbed oxygen (O/C3), then increase proportionally with O₂ as cluster surfaces depleted of oxygen and as unoccupied Pt sites become the most abundant surface intermediates, and eventually increase more than linearly with O₂ on Pt surfaces predominantly covered with CH₃OH derived intermediates. The transition in rate dependence on O₂ is accompanied by a concomitant transition on CH₃OH dependence: HCHO formation rates are linearly proportional to, then independent of, and eventually inhibited by CH₃OH as the O₂-to-CH₃OH ratio decreases. Similar transition in reaction orders is also found for HCOOCH₃ and CO₂ formation. The first-order rate coefficient for CH₃OH oxidation is a single-valued function of the operating O₂-to-CH₃OH ratio, because the ratio determines the oxygen chemical potential at Pt cluster surfaces via the kinetic coupling of O₂ and CH₃OH activation steps and, in turn, the identity and coverage of reactive intermediates, the nature and availability of active sites, and the identity of kinetically-relevant steps.

1. Introduction

Selective catalytic oxidation of alcohol to aldehyde and ketone is an important route for synthesizing carbonyl compounds useful as chemical building blocks. Oxidation of methanol, the simplest alcohol, may occur over metal [1–8], metal oxide [9–13], or mixed oxide [14–16] catalysts and form diverse products depending on the operating temperature and oxygen-to-methanol ratios. CH₃OH–O₂ reactions form COx, HCHO, HCOOCH₃, CH₃OCH₃, and CH₃OCH₂OCH₃ on metal oxide (VOx [9–11], RuO₂ [12]) or mixed oxide (SnO₂–MoO₃ [14]) structures at O₂-to-CH₃OH ratios above the stoichiometry required for HCHO formation (O₂/CH₃OH > 0.5) at moderate temperatures (373–450 K). At higher temperatures (423–650 K), the reaction forms similar products (COx, HCHO, HCOOCH₃, and CH₃OCH₃) on supported Pt [6], Pd [6], and Au [7] catalysts.

Fe₂(MoO₄)₃ [15], and Fe₂O₃–MoO₃ [16] over a wide range of O₂-to-CH₃OH ratios (0.64–4.8). CH₃OH–O₂ reactions on Group VIII and Group IB metals evolve HCHO, HCOOCH₃, and CO₂ at lower temperatures (313–400 K) (Pd [1], Pt [2,3], and Au [4]), and HCHO and CO₂ above 550 K (Ag [5] and Pt [2]). As the O₂-to-CH₃OH ratio decreases to less than 0.5, H₂ (and COx) begin to form on supported Pt (428–493 K) [6], Pd (428–493 K) [6], and Au (483–583 K) [7] catalysts.

CH₃OH–O₂ reactions on transition metal oxides (RuO₂ [12], Fe₂O₃–MoO₃ [16]) involve a Mars-van Krevelen-type redox cycle that shuffles lattice oxygen atoms (O_{lattice}) during CH₃OH turnovers [17]. Metal and lattice oxygen site pairs first cleave the O–H bond in CH₃OH, which forms adsorbed methoxy (CH₃O⁻) and O_{lattice}H⁺ intermediates, and the sequential C–H bond dissociation of CH₃O⁻ by another lattice oxygen forms O_{lattice}H⁻ and HCHO⁻ intermediates [18]. Sequential desorption of HCHO⁻ and recombinative desorption of O_{lattice}H⁺ intermediates lead to HCHO and H₂O, respectively, leaving behind a lattice oxygen vacancy on oxide surfaces [12,16,18], on which O₂ dissociates to complete a catalytic turn-
over. The H abstraction and O* addition on HCHO* lead to formate species (HCO*) that may undergo secondary reactions with CH3OH derived species to produce HCOOH + CH4 [1,19,20] and, in parallel to these steps, C–H bond cleavage on formate species (HCOO*) and their subsequent desorption evolve CO2 [19,20]. On metal surfaces, CH3OH–O2 reactions also begin with O–H scission followed by C–H activation, but these steps occur on metal atom sites, as confirmed from density functional theory calculations on uncovered Pt(1 1 1) [21] and Ag(1 1 1) [22] surfaces. Temperature-programmed desorption carried out after CH3OH decomposition on oxygen covered Pt(1 1 1) surfaces (0.25 ML, 115–140 K) provides the evidence that O–H bond cleavage remains as the initial step but with O* involvement [23]. Decomposition of methoxide, an intermediate from CH3OH activation, on bare metal surfaces [Pt(1 1 1) [21] and Ni(1 1 0) [24]], forms CO and H2, but in the presence of surface oxygen [Ni(1 1 0) [24], Cu(1 1 0) [25]], oxygen insertion and H abstraction become the predominant route to evolve formate species, which decompose sequentially to CO2 and H2.

The catalytic steps, their kinetic relevance, and the identity and coverages of surface intermediates are known to determine kinetic dependencies and carbon selectivities toward the primary (HCHO) and secondary (CO2, HCOOH, CH3OCH2OCH3) products. The specific catalytic events and their rates are known to also vary with the identity and chemical state of metal and oxygen (e.g., lattice oxygen, chemisorbed oxygen), the latter depends largely on the operating temperature [2,26] and pressures of reactants and products [5,12]. The intricate connection among the gas-phase composition, identity and types of surface sites, and relative rates of CH3OH and O2 activation leads to complex kinetic behavior with wide ranging and often contradictory kinetic dependencies. As a result, the identity of the kinetically-relevant step ranges from C–H bond activation of CH3OH derived intermediates (CH3O*) [5,12,16], desorption of the HCHO* intermediates [27], to activation of O2 [4,5].

Lattice oxygen [12], chemisorbed diatomic [28–30], or monatomic oxygen [23] atoms have been proposed to involve as active species in CH3OH–O2 reactions. Molybdenum oxide structures saturated with oxygen were found to be effective toward CH3OH activation but their reactivity decreased with depletion of lattice oxygen from their reactions with CH3OH [31]. The terminal lattice oxygen atom (Oterm) on VOx [9], MoOx [32], and mixed oxides (FeOx-MoOx) [16], together with a vicinal metal ion, forms a site pair that assists the initial O–H bond dissociation in CH3OH to form CH3O*, followed by sequential C–H cleavage of the CH3O* by another vicinal lattice oxygen [18]. Chemisorbed oxygen (O*) on Au [4,33], Ag [34], Pt [28], and Pd [35] may also promote CH3OH dissociation. Infrared reflection absorption spectroscopy (IRAS) and temperature desorption studies on CH3OH reactions with pre-adsorbed molecular oxygen on Pt(1 1 1) (0.34 ML O2 at 35–100 K [29] and 0.5 ML O2 at 100–550 K [28,36]) and pre-adsorbed atomic oxygen (0.25 ML O*) on Pd(1 1 1) [35] or Pt(1 1 1) [28,36] surfaces at 100–550 K suggest mechanistic involvements of both types of oxygen species toward CH3OH activation. Methanol adsorbs weakly on bare metal surfaces (Au(1 1 1) [33] or Au(1 1 0) [37]) but reacts readily with pre-adsorbed atomic oxygen on such surfaces (Au(1 1 1) [33], Au(1 1 0) [37], Ag(1 1 0) [34], and Cu(1 1 0) [38]) to form methoxy and hydroxyl species, in a mechanistic step similar to those proposed on lattice oxygen-metal pairs on metal oxide structures [9,12]. O* may also assist with the sequential H abstraction of CH3O* to evolve HCHO [25] or alternatively, insert into the CH3O* and, upon C–H cleavage, to form HCOO* and H* [38]. The catalytic function of oxygen has been recognized, but the mechanistic consequences of their coverages and binding strength have yet to be established.

Here, we report diverse rate dependencies and their transition during CH3OH–O2 reactions on Pt clusters, probe the nature of catalytic sites, and provide a mechanistic explanation to these kinetic phenomena. We provide the evidence that these kinetic phenomena are of true chemical origin, based on rate data obtained strictly in the kinetically controlled regime, after extensive intra- and inter-pellet dilutions to remove temperature and concentration gradients within the catalyst pellets and reactor bed. Kinetics of CH3OH oxidation are described by three distinctly different regimes, each with a unique rate equation for CH3OH conversion to HCHO, the primary product, and exhibits different carbon selectivity dependencies toward HCOOH and CO2. These regimes are caused by a dynamic transition of the coverages and identity of reactive intermediates on Pt cluster surfaces from saturated with O*, uncovered, to covered with CH3OH derived species as the oxygen chemical potential at cluster surfaces decreases. We interpret each of the regimes with a closed sequence of elementary steps and probe the change in their kinetic relevance. We vary the mean Pt cluster diameter to probe the effects of surface Pt coordination and binding strengths on rates and selectivities. The first-order rate coefficient is a single-valued function of the O2/CH3OH ratio, because O2/CH3OH ratio prescribes the identity and coverages of reactive intermediates that dictate, in turn, the specific catalytic events and their rates. These dynamic transitions of rate dependencies in response to changing surface coverages and chemical potentials are also found during alkane oxidation (CH4 [39,40], C3H6 [41]); they reflect how thermodynamic properties at catalytic sites dictate the relative abundance of surface intermediates and the identity of kinetically-relevant step during oxidation catalysis.

2. Catalyst preparation and experimental methods

2.1. Synthesis and characterizations of supported Pt clusters and preparation of catalyst samples with varying inter- and intra-particle dilution ratios

Silica (Grace, Davislis Chromatographic Silica, 330 m2 g–1 surface area, 1.25 cm3 g–1 pore volume, 0–75 μm particle size) was treated under ambient air by increasing the temperature at 0.033 K s–1 to 673 K followed by holding for 3 h at 673 K before cooling to 393 K. The sample was kept at 393 K until the impregnation step to prevent readesorption of water. Pt clusters were dispersed on the treated silica at a loading of 1.0 wt% by incipient wetness impregnation with an aqueous solution of tetraammineplatinum(II) nitrate [Pt(NH3)4(NO3)2, Sigma Aldrich, 99.995% trace metals basis], prepared from dissolving the precursor in doubly deionized water. The impregnated sample was treated at 353 K for 24 h under ambient air and then in flowing dry air (Linde, 99.999%, 0.3 cm3 g–1 s–1) by increasing the temperature at 0.05 K s–1 to 673 K, holding isothermally at 673 K for 5 h. A portion of the catalysts was subsequently treated at 773 K for 5 h under flowing dry air (Linde, 99.999%, 0.3 cm3 g–1 s–1, 0.05 K s–1 ramp) to attain larger Pt clusters. These samples were cooled to ambient temperature and then treated in 5% H2/He (Linde certified standard, 5.22%, 0.3 cm3 g–1 · s–1) by heating to 673 K at 0.033 K s–1, holding isothermally at 673 K for 1 h, and then cooling to ambient temperature. The samples were introduced to 1% O2/He (0.3 cm3 g–1 · s–1) for 6 h before exposure to ambient conditions.

The average Pt cluster diameter was measured from volumetric uptakes of H2, irreversibly chemisorbed on Pt clusters, at 298 K. The catalyst samples were first treated in flowing H2 (Linde, 99.999%, 0.2 cm3 g–1 · s–1) by heating from ambient temperature to 673 K at 0.083 K s–1 and holding for 1 h before exposure to dynamic vacuum at 673 K for 1 h and then cooling under dynamic vacuum to 298 K for H2 chemisorption measurements. H2 uptakes were measured at 298 K between 0 and 13 kPa H2; two isotherms were measured consecutively, and between these measurements,
the sample was evacuated under dynamic vacuum for 0.5 h. The fractions of exposed Pt atoms were determined from the difference between the extrapolated values from the two isotherms to zero H₂ pressure and by assuming a H-to-surface Pt adsorption stoichiometry (H/PT₁; subscript s denotes surface Pt atom) of unity. The average cluster diameters were estimated from these dispersion values by assuming hemispherical clusters with density similar to bulk Pt metal (21.45 g cm⁻³) [42].

Catalyst samples (1.0 wt% Pt/SiO₂) were diluted with SiO₂ (Grace, Davisisl Chromatographic Silica, 330 m² g⁻¹ surface area, 1.25 cm² g⁻¹ pore volume, 0–75 μm particle size) to form well-mixed physical mixtures at different SiO₂-to-catalyst mass ratios between 100 and 400. The physical mixtures were pressed into pellets before sieving to retain 125–180 μm agglomerates. These agglomerates were physically mixed with SiO₂ (Grace, Davisisl Chromatographic Silica, 330 m² g⁻¹ surface area, 1.25 cm² g⁻¹ pore volume, 125–180 μm particle size) to form the packed catalyst bed with an overall SiO₂-to-catalyst mass ratio between 2000 and 5700.

2.2. Catalytic rate and selectivity measurements

The catalyst bed (containing 0.025–0.15 mg of 1.0 wt% Pt/SiO₂) was heated in flowing H₂ (Linde, 99.999%, 0.2–1.3 × 10⁻³ cm³ g⁻¹ s⁻¹) to 673 K at 0.083 K s⁻¹ and holding for 1 h, and then cooled to reaction temperature in flowing He (Linde, 99.999%, 0.2–1.3 × 10⁻³ cm³ g⁻¹ s⁻¹) before rate measurements. CH₃OH turnover rates were measured on a packed-bed of catalyst particles (inter- and intra-particle SiO₂-to-catalyst mass ratio of 5700 and 100–400, respectively) at 310–910 K, held in a tubular micro-catalytic plug flow reactor (8.1 mm reactor ID) equipped with an axial concentric K-type thermocouple. Reactant mixtures were prepared from either 5% O₂/He (Linde certified standard, 5.03%) or pure O₂ (Linde, 99.999%), CH₃OH (Sigma Aldrich, anhydrous, 99.8%), and He (Linde, 99.999%). Gas flow rates of 5% O₂/He, pure O₂, and He were independently metered using electronic mass flow controllers to achieve a space velocity between 4.2 × 10⁴ cm³ (gcat h⁻¹)⁻¹ and 2.5 × 10⁶ cm³ (gcat h⁻¹). Methanol was introduced using a gas tight syringe (Hamilton, 5 cm³) mounted on a syringe infusion pump (KD Scientific, LEGATO 100) at constant infusion rates into a heated zone maintained at 338 K, in which it was evaporated and mixed with the gas feed stream containing O₂ and He.

Turnover rates for HCHO–O₂ and HCOOCH₃–O₂ reactions were also measured on the catalyst samples at 310–910 K in the tubular micro-catalytic plug flow reactor. Gaseous formaldehyde (0–0.13 kPa) was prepared from decomposition of paraformaldehyde (Sigma Aldrich, 95%) into a flowing purge stream of He (Linde, 99.999%, 0.0–0.67 cm³ s⁻¹) in a glass vaporizer maintained at 313 K. HCOOCH₃ vapor (0–0.92 kPa) in He was prepared from decomposition of paraformaldehyde (Sigma Aldrich, anhydrous, 99%) contained in a glass vaporizer into a stream of flowing He (Linde, 99.999%, 0–0.083 cm³ s⁻¹) at 273 K. All transfer gas lines were heated to 373 K to prevent condensation of reactants and products and polymerization of formaldehyde.

The chemical compositions of the reactant and product streams were quantified using a micro-GC (Varian CP-4900) equipped with HP-PLOT U and Mole Sieve 5A columns connected to thermal conductivity detectors. The identity of chemical species and their amounts detected by the micro-GC were confirmed using an online gas chromatograph (Agilent 7890A) with mass spectrometer (Agilent 5975C) equipped with capillary columns, Agilent HP-5MS (190091S-433, 30 m, 0.25 mm ID, 0.25 μm film), connected to a thermal conductivity detector and a flame ionization detector in series, and HP-5 (19091 J-413, 30 m, 0.32 mm ID, 0.25 μm film) connected to a mass selective detector. The concentration of CO in the product stream was quantified using a gas chromatograph (SRI 8610C) equipped with packed columns (Mol Sieve 13X and Hayesp D) connected to (i) a thermal conductivity detector and (ii) a methanator followed by a flame ionization detector, respectively. The concentration of H₂ in the product stream was quantified using a gas chromatograph (SRI 8610C) equipped with packed columns (Mol Sieve 13X and Hayesp D) connected to a helium ionization detector (HID).

3. Results and discussion

3.1. Assessing the intrinsic catalytic rates for CH₃OH–O₂ reactions on Pt clusters: rigorous removal of rate contributions from SiO₂ support, gas-phase reaction, and concentration and temperature gradients

Fig. 1a shows CH₃OH conversion during CH₃OH–O₂ reactions on 1.0 wt% Pt/SiO₂ catalyst (3.0 nm mean Pt cluster diameter, 0.05 mg 1.0 wt% Pt/SiO₂ and 0.285 g SiO₂), on SiO₂ (support, 0.285 g), and in the gas phase (without catalyst and support) as a function of reaction temperature, compared at the same reactant flow rate and compositions (1.0 kPa CH₃OH, 1.5 kPa O₂, 1.75 cm³ s⁻¹, 310–910 K). Fig. 1b and 1c show selectivities of carbon-containing products to CO, CO₂, and HCHO at 3.9% and 89.8%, respectively, at 720 K, not shown here). CH₃OH conversions were detectable on bare SiO₂, the material used for dispersing Pt clusters, at lower temperatures (>450 K, Fig. 1a) and produced CO₂, HCHO, HCOOCH₃, and H₂O (3.8% CH₃OH conversion; selectivities of carbon-containing products to CO, CO₂, HCHO, and HCOOCH₃ are 1.9%, 17.0%, 79.1%, and 2.0%, respectively, at 493 K, Fig. 1c). Acetalization of CH₃OH with HCHO, a product, on SiO₂ produced HCOOCH₃ at these temperatures (450–650 K), as also reported previously on oxides {SiO₂ [43], Al₂O₃ [12], SnO₂ [14], TiO₂ [43], and ZrO₂ [43]}. The predominant carbonaceous product was HCHO below 650 K (76.7% selectivity at 537 K) but as the temperature increased, sequential oxidation of HCHO and HCOOCH₃ became much faster relative to the initial catalytic CH₃OH turnover and formed CO and CO₂ as the dominant carbonaceous products (Fig. 1c). At the lower temperature range (350–390 K, Fig. 1a), CH₂O conversion rates on 1.0 wt% Pt/SiO₂ catalyst (3.0 nm mean Pt cluster diameter) were at least two orders of magnitude higher than the combined rates on SiO₂ and in the gas phase [rCH₂O,pt + rCH₂O, SiO₂ + rCH₂O,gas phase] = 101.2 at 373 K, Fig. 1a) and the reaction formed HCHO, CO₂, H₂O, and HCOOCH₃. As the temperature increased, the dominant carbonaceous product varied from HCOOCH₃ to HCHO and then to CO₂ (Fig. 1b). CO₁ was not detected in the effluent stream at all temperatures (<5 ppm detection limit, 310–600 K, O₂/CH₃OH = 1.5) on 1.0 wt% Pt/SiO₂ (Fig. 1b), because of much faster rates for CO than CH₃OH oxidation. The temperatures required for 50% CH₂O conversion were 472 K, 627 K, and 850 K on Pt/SiO₂, SiO₂, and in the gas phase, respectively. At low temperatures (e.g., 373 K), HCHO and HCOOCH₃ did not react with O₂ on SiO₂ and in the gas phase at detectable extents. Their conversions were found to be less than 0.05% in HCHO–O₂ (0.13 kPa HCHO and 0.5–16 kPa O₂, 1.75 cm³ s⁻¹) and HCOOCH₃–O₂ (0.80 kPa HCOOCH₃ and 0.1–40 kPa O₂, 1.75 cm³ s⁻¹) reactions. These results, taken together, confirm that primary and secondary reactions reported herein-and-after reflect catalytic turnovers of CH₃OH on Pt clusters with negligible contributions.
from SiO₂ supports and the gas phase (estimated to be <1% at 373 K).

The partial and total oxidation of methanol (Eqs. (1a) and (1b)) and the sequential reactions of HCHO with CH₃OH and O₂ (Eq. (1c)) and with O₂ (Eq. (1d)) proceed with the respective standard heat of reaction (evaluated at 298 K):

\[
\begin{align*}
\text{CH}_3\text{OH} + 0.5\text{O}_2 & \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -155.8 \text{ kJ mol}^{-1} \text{CH}_3\text{OH}^{-1} \\
\text{CH}_3\text{OH} + 1.5\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{298}^\circ = -726.5 \text{ kJ mol}^{-1} \text{CH}_3\text{OH}^{-1} \\
\text{CH}_3\text{OH} + \text{HCHO} + 0.5\text{O}_2 & \rightarrow \text{HCOOCH}_3 + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -304.5 \text{ kJ mol}^{-1} \text{CH}_3\text{OH}^{-1} \\
\text{HCHO} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -570.7 \text{ kJ mol}^{-1} \text{HCHO}^{-1}
\end{align*}
\]

These exothermic reactions (−155.8 to −726.5 kJ mol⁻¹) may increase the local temperature at catalytic sites and cause significant concentration and temperature gradients within individual catalyst pellets and across the reactor bed. These gradients are ubiquitously present in oxidation reactions, because of their exothermic nature and high rates, and often corrupt rate data and their mechanistic interpretation. Here, transport corruptions were diagnosed and then rigorously removed by extensive dilutions at the intra- and inter-pellet scales with inert solids. Dilutions decrease the rate of heat release per unit volume (heat load) and, as the diluent-to-catalyst ratio increases and the heat load concomitantly decreases to the extent that does not bring forth detectable kinetic consequences, the measured rates and selectivities reflect intrinsic values evaluated at the pressures and temperature of the contacting gas phase.

Table 1 provides the maximum amount of heat released per unit catalyst bed volume from this study together with values from CH₄–O₂ [40], C₂H₆–O₂ [41], and CH₃COCH₃–O₂ [44] reactions in reactors with comparable dimensions (8.1 mm reactor ID, 100–250 pellet diameters). The heat release rate per unit catalyst bed volume for CH₃OH–O₂ reactions (<0.04 W cm⁻³) 0.51 kPa CH₃OH, 0–6 kPa O₂, 383 K) reported herein is comparable to those of other oxidation reaction systems (<0.66 W cm⁻³, Table 1), measured in similar reactor configurations and previously tested and confirmed to be free of transport influences. Fig. 2 shows the HCHO, CO₂, and HCOOCH₃ formation rates (per exposed Pt atom) measured at different O₂ pressures (0–6 kPa O₂) while keeping the CH₃OH pressure constant (0.51 kPa CH₃OH) at 383 K on catalyst pellets diluted to different extents (intra-particle SiO₂-to-Pt/SiO₂ weight ratio of 100–400). The turnover rates (per exposed Pt atom) for HCHO, CO₂, and HCOOCH₃ formation and the selectivity values remained identical within the experimental accuracy (estimated er-

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction temperature (K)</th>
<th>Total number of active sites (10⁻⁹ mol)</th>
<th>Space velocity (10⁻⁷ cm³ (mol of reductant)⁻¹)</th>
<th>Intra-particle SiO₂-to-catalyst mass ratio</th>
<th>Inter-particle SiO₂-to-catalyst mass ratio</th>
<th>Heat of reaction (kJ mol⁻¹)</th>
<th>Reactor diameter (mm)</th>
<th>Reactor heat load (W cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OCH₃–O₂</td>
<td>473</td>
<td>66.70</td>
<td>0.12</td>
<td>50:1</td>
<td>50:1</td>
<td>−1460.4</td>
<td>8.0</td>
<td>0.66</td>
</tr>
<tr>
<td>CH₄–O₂</td>
<td>873</td>
<td>0.20</td>
<td>5.00</td>
<td>200:1</td>
<td>200:1</td>
<td>−804.3</td>
<td>8.1</td>
<td>0.35</td>
</tr>
<tr>
<td>C₂H₆–O₂</td>
<td>773</td>
<td>n.a.</td>
<td>6.00</td>
<td>300:1</td>
<td>700:1</td>
<td>−1428.5</td>
<td>8.1</td>
<td>0.01</td>
</tr>
<tr>
<td>CH₃OH–O₂</td>
<td>383</td>
<td>0.85</td>
<td>12.60</td>
<td>200:1</td>
<td>5700:1</td>
<td>−726.5</td>
<td>8.1</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Ref. [44].

Ref. [40].

Ref. [41]; n.a.: unavailable.
rors of <2%) among the samples despite the different intra-pellet dilution ratios (Fig. 2), because the overall CH₃OH conversion rates and each of the individual rates for the primary and secondary reactions were strictly proportional to the number of active site contained within the catalyst bed. These results provide the unequivocal evidence that rate and selectivity data were unaffected by temperature and concentration gradients. These findings, taken together with negligible rate contributions from SiO₂ support and homogeneous reactions of reactants and products (Fig. 1), led us to conclude that rate and selectivity data presented herein-and-after are of true chemical origin and reflect intrinsic catalytic events at Pt sites.

3.2. Primary and secondary products of methanol partial oxidation on Pt clusters

Fig. 3 shows carbon selectivities for CH₃OH–O₂ reactions as a function of CH₃OH conversion, which was varied by changing the residence time, for three O₂-to-CH₃OH feed ratios of 0.25, 1.5, and 16 on Pt clusters (1.0 wt% Pt/SiO₂, 3.0 nm mean Pt cluster diameter) at 373 K. O₂-to-CH₃OH feed ratios affect the carbon selectivity trends through their influences on the relative rates and reaction orders for the primary and secondary reactions leading to HCHO, HCOOCH₃, and CO₂ products. CO and H₂ were not formed (detection limits: 5 ppmv for CO and 1 ppmv for H₂) during CH₃OH oxidation on Pt clusters at 373 under all conditions tested here, covering the range of 0.01–45 O₂/CH₃OH ratios (0.08–5 kPa CH₃OH and 0.1–70 kPa O₂). At low O₂-to-CH₃OH ratios (e.g., 0.25), carbon selectivities were insensitive to CH₃OH conversion (Fig. 3a). Their values began to vary with CH₃OH conversion at higher O₂-to-CH₃OH ratios (O₂/CH₃OH = 1.5 and 16 in Fig. 3b and c, respectively): the carbon selectivities to HCHO decreased and those for HCOOCH₃ and CO₂ concomitantly increased as CH₃OH conversion and residence time increased. Extrapolation of carbon selectivities to zero conversion removes the rate contribution from secondary reactions and gives the selectivity values from primary CH₃OH reactions. These data indicate that at low O₂-to-CH₃OH ratios (e.g., 0.25), all products are formed directly from CH₃OH (or CH₃OH derived surface intermediates), but as the O₂-to-CH₃OH ratio increases to above 0.5, the sequential oxidation of HCHO becomes important relative to those of primary reactions, apparently because chemisorbed oxygen atoms prevalent on Pt cluster surfaces at these higher O₂-to-CH₃OH ratios are more effective for HCHO oxidation, as described in Sections 3.4 and 3.5.

The distinct variation in selectivity trends and rate dependences (to be discussed in Section 3.3) with O₂-to-CH₃OH ratios led us to categorize the rate data according to the operating O₂/CH₃OH ratios of 0.01–0.5, 0.5–10, and 10–45 and denote these categories herein and after as Kinetic Regimes 1, 2, and 3, respectively. Next, the direct and indirect routes for HCHO, HCOOCH₃, and CO₂ formation from CH₃OH–O₂ mixtures and the interconversion between these products in the various pathways labeled in Scheme 1 are analyzed for each regime. HCHO–O₂ or HCOOCH₃–O₂ reactions were carried out in addition to CH₃OH–O₂ reactions to probe the relative rates of the primary and secondary reactions. The pseudo-first-order rate constants (kᵢ) for the individual pathways in Scheme 1 are defined by the general expression of:

$$kᵢ = \frac{rᵢ}{P}$$

$$P = CH₃OH, HCHO or HCOOCH₃; i = Kinetic Regime 1, 2, or 3$$
from secondary reactions are insignificant in Regime 1, consistent with carbon selectivities that do not vary with CH3OH conversions and residence times in this regime (Fig. 3a). Thus, CO2, HCHO, and HCOOCH3 are formed directly from CH3OH derived intermediates at low O2to-CH3OH ratios (<0.05), as also reported previously [5].

As O2to-CH3OH ratios increased to 0.5–10, the rate constant for HCOOCH3 oxidation (kHCOOCH3 (2/6)) remained at a small value (3.8 mol CO2 (g atom Pt surface 5 kPa)–1, 373 K). The rate constants for the primary CH3OH–O2 reaction to HCHO (kCH3OH(2/1)), and the sequential HCHO–O2 reaction to CO2 (kCH2O(2/4)), however, both increased to magnitudes similar to each other (19–38 mol HCHO (g atom Pt surface 5 kPa)–1 and 33.7 mol CO2 (g atom Pt surface 5 kPa)–1, respectively, 373 K). These rate constant values corresponded to a rate ratio for CO2 formation from HCHO over CO2 formation from CH3OH, rHCHO(2/4) /rCO2(2) 3–1 (where rCO2(2) denotes the rate of CO2 formation from CH3OH–O2 reactions in Kinetic Regime 2), of 0.06 to 0.14 in Regime 2 (1–2 kPa CH3OH, 0.5–5 kPa O2, 0.02–0.14 kPa HCHO (produced from CH3OH–O2 reactions), 373 K). At even higher O2to-CH3OH ratios (10–45; Regime 3), rate constants for all CH3OH oxidation reactions (kCH3OH(1/1), kCH3OH(3/2), kCH3OH(1/3)), and HCHO oxidation (kCH2O(3/4)) increased to even larger values, except those for HCOOCH3 oxidation (kHCOOCH3(1/6)) and for the conversion of HCHO to HCOOCH3 (rHCHO(3/1)), which remained insignificant. These increases reflect the creation of active sites that are more effective for CH3OH and HCHO oxidation at the high O2to-CH3OH ratios. Comparing the rate constant values of Regime 3 with those of Regime 2, the rate constant for HCHO oxidation to CO2 (kCH2O(3/4)) increased to a much larger extent than the rate constants for primary reactions (kCH3OH(1/1), kCH3OH(3/2), kCH3OH(1/3)) (Table 2). This increase resulted in a concomitant decrease in HCHO selectivity and led the rate ratios for CO2 formation from HCHO to the overall CO2 formation from methanol oxidation rHCHO(2/4) /rCO2(3) 3–1, where rCO2(3) denotes the rate of CO2 formation from CH3OH–O2 reactions in Regime 3) to exceed 0.3 in Regime 3 (0.08–2 kPa CH3OH, 10–70 kPa O2, 0.01–0.3 kPa HCHO (produced from CH3OH–O2 reactions), 373 K). Taken together, these data indicate that sequential HCOOCH3 oxidation to CO2 does not occur at any significant extent under all O2to-CH3OH ratios examined in this report. The sequential HCHO oxidation to CO2, however, becomes increasingly important as the O2to-CH3OH ratio increases from Regime 1 to Regime 3, during which the ratio rHCHO(1/4) /rCO2(6) 3–1 increases from less than 0.02 to 0.45 (Table 2). These different trends of carbon selectivities with CH3OH conversion and their different values when extrapolating to zero conversion (22.4% CO2, 65.4% HCHO, and 12.2% HCOOCH3 in Regime 1, 18.6% CO2, 74.4% HCHO, and 7.0% HCOOCH3 in Regime 2, and 18.1% CO2, 74.0% HCHO, and 7.9% HCOOCH3 in Regime 3; the error in carbon selectivities is <0.5%), as shown in Fig. 3, indicate that the relative contributions of primary and secondary reactions and the rate dependencies for CO2, HCHO, and HCOOCH3 formation vary.

---

Table 2

<table>
<thead>
<tr>
<th>Kinetic Regime i</th>
<th>O2/CH3OH Ratio</th>
<th>kCH3OH(1/1)*</th>
<th>kCH3OH(2/1)*</th>
<th>kCH3OH(3/2)*</th>
<th>kCH3OH(1/3)*</th>
<th>kCH2O(3/4)*</th>
<th>kHCOOCH3(1/6)*</th>
<th>rHCHO(2/4)/rCO2(2)*</th>
<th>rHCHO(2/4)/rHCOOCH3(1/6)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01–0.5</td>
<td>0.3–2.7</td>
<td>0.1–0.9</td>
<td>0.1–0.2</td>
<td>3.7</td>
<td>b.d.</td>
<td>3.8</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.5–10</td>
<td>19.0–38.0</td>
<td>4.9–10.0</td>
<td>2.1–2.4</td>
<td>33.7</td>
<td>b.d.</td>
<td>3.8</td>
<td>0.06–0.14</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>3</td>
<td>10–45</td>
<td>160.9</td>
<td>48.0–34.0</td>
<td>13.4–45.3</td>
<td>162.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.30–0.45</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Subscripts P, i, and (n) in pseudo-first-order rate constants (k_v(n)) denote reductant identity (P = CH3OH, HCHO, HCOOCH3), Kinetic Regime i (i = 1, 2, 3), and pathway (n) (n = 1–6 in Scheme 1), r_v(n) denotes the rate of reaction pathway (n) for reductant P in Regime i and rCO2(n) denotes the rate of CO2 formation during CH3OH–O2 reactions in Regime i. [P] refers to the partial pressure of reductant P. a,b,c: Pseudo-first-order rate constants (k_v(n)), mol CO2 (g atom Pt surface 5 kPa)–1; kCH3OH(1/1) was measured from CH3OH–O2 reactions (0.08–5.0 kPa CH3OH and 0.1–70 kPa O2); d: Pseudo-first-order rate constants (kHCOOCH3(2/6)), mol CO2 (g atom Pt surface 5 kPa)–1; e,f: Pseudo-first-order rate constants (kCH2O(3/4)), mol HCHO (g atom Pt surface 5 kPa)–1; f: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; g: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; h: mol CO2 (g atom Pt surface 5 kPa)–1; i: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; j: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; k: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; l: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; m: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; n: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; o: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; p: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; q: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; r: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; s: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; t: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; u: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; v: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; w: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; x: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; y: mol HCOOCH3 (g atom Pt surface 5 kPa)–1; z: mol HCOOCH3 (g atom Pt surface 5 kPa)–1.
with reactant and product pressures. Next, we probe the effects of reactant pressure on the individual rates of HCHO, HCOOCH₃, and CO₂ formation by varying the O₂ and CH₃OH pressures independently while maintaining a constant temperature and space velocity (373 K, 1.26 × 10⁸ cm³ (gcat h)⁻¹ for Regimes 2 and 3 and 4.2 × 10⁷ cm³ (gcat h)⁻¹ for Regime 1).

3.3. Diverse kinetic dependencies during methanol partial oxidation and their connection to oxygen-to-methanol ratio and the identity and coverages of reactive intermediates on Pt cluster surfaces

Fig. 4 shows the diverse rate dependencies for the formation of primary (HCHO) and secondary (HCOOCH₃ and CO₂) products during CH₃OH–O₂ reactions on Pt clusters (1.0 wt% Pt/SiO₂, 3.0 nm mean Pt cluster diameter, 373 K), plotted in terms of the first-order rate coefficients, defined as the turnover rates for species j (j = HCHO, HCOOCH₃, or CO₂) formation divided by CH₃OH pressure (rⱼ[i] [CH₃OH]⁻¹, i = Regime 1, 2, or 3), as a function of O₂-to-CH₃OH ratio. First-order rate coefficients for HCHO, HCOOCH₃, and CO₂ formation are a single-valued function of O₂-to-CH₃OH ratio and their rate dependencies depend strictly on the range of operating O₂-to-CH₃OH ratios, which defines the operating boundaries for Kinetic Regimes 1 to 3 in the order of increasing O₂-to-CH₃OH ratio (Regime 1: 0.01–0.5 O₂/CH₃OH, Regime 2: 0.5–10 O₂/CH₃OH, and Regime 3: 10–45 O₂/CH₃OH, irrespective of individual CH₃OH and O₂ pressure values.

The rate of species j (j = HCHO, HCOOCH₃, or CO₂) formation (per exposed Pt atom) in Kinetic Regime i (i = 1, 2, or 3) is denoted as rⱼ[i] and expressed in a general form below to vary with the CH₃OH, OH, and O₂ pressures ([CH₃OH] and [O₂]):

\[ rⱼ[i] = k_{eff,i}[CH₃OH]^{x_i}[O₂]^{y_i} \] (3)

Where k_{eff,i} is the effective rate constant for species j, and \( x_i \) and \( y_i \) are the apparent reaction orders with respect to CH₃OH and O₂, respectively, in Regime i. The formation of a HCHO, CO₂, or HCOOCH₃ molecule each requires one catalytic CH₃OH sojourn in the oxidative dehydrogenation step (ODH); thus, the rates of oxidative dehydrogenation of CH₃OH, r_{ODH,i} (for Regime i), are reported as the combined rates of HCHO, CO₂, and HCOOCH₃ formation (r_{ODH,i} = r_{HCHO,i} + r_{CO₂,i} + r_{HCOOCH₃,i} for Regime i) [12]. As shown

![Fig. 4. 4a and 4b. First-order rate coefficients (rⱼ[i] [CH₃OH]⁻¹) for HCHO (\( \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \)), CO₂ (\( \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \)), and HCOOCH₃ (\( \blacktriangledown \blacktriangledown \blacktriangledown \blacktriangledown \blacktriangledown \blacktriangledown \blacktriangledown \blacktriangledown \blacktriangledown \)) formation as single-valued functions of O₂-to-CH₃OH ratio during CH₃OH–O₂ reactions at 373 K with 1.00 kPa (\( \Delta \Delta \Delta \)), 1.25 kPa (\( \Delta \Delta \)), 1.75 kPa (\( \Delta \)), 2.00 kPa (\( \Delta \bigcirc \)), 3.00 kPa (\( \Delta \bigcirc \bigcirc \)), and 4.00 kPa (\( \Delta \bigcirc \bigcirc \bigcirc \bigcirc \)) of CH₃OH on 1.0 wt% Pt/SiO₂ (3.0 nm mean Pt cluster diameter, 200 SiO₂–to-catalyst intra-particle and 5700 SiO₂–to-catalyst inter-particle dilution ratios; 4.2 × 10⁷ cm³ (gcat h)⁻¹ (4a) and 1.26 × 10⁸ cm³ (gcat h)⁻¹ (4b). Regime 1: O₂/CH₃OH = 0.01–0.5; Regime 2: O₂/CH₃OH = 0.5–10; Regime 3: O₂/CH₃OH = 10–45).

Table 3

<table>
<thead>
<tr>
<th>Kinetic Regime i</th>
<th>Regime 1* (0.01 &lt; O₂/CH₃OH &lt; 0.5)</th>
<th>Regime 2† (0.5 &lt; O₂/CH₃OH &lt; 10)</th>
<th>Regime 3‡ (10 &lt; O₂/CH₃OH &lt; 45)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAS*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{HCHO,i}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{ODH,i}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{HCOOCH₃,i}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{CO₂,i}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{HCHO, i} derived from proposed elementary steps</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ \frac{k_{1,i} k_{2,i} k_{3,i} k_{4,i} [CH₃OH]^{0.5} [O₂]^{0.5}}{(1 + k_{5,i} k_{6,i} k_{7,i} [O₂]^{0.5})^{0.5}} ]</td>
<td>[ \frac{k_{1,i} k_{2,i} k_{3,i} k_{4,i} [CH₃OH]^{0.5} [O₂]^{0.5}}{(1 + k_{5,i} k_{6,i} k_{7,i} [O₂]^{0.5})^{0.5}} ]</td>
<td>[ \frac{k_{1,i} k_{2,i} k_{3,i} k_{4,i} [CH₃OH]^{0.5} [O₂]^{0.5}}{(1 + k_{5,i} k_{6,i} k_{7,i} [O₂]^{0.5})^{0.5}} ]</td>
<td></td>
</tr>
</tbody>
</table>

*MAS denotes the most abundant surface intermediates. The subscripts j, i in the rates (rⱼ[i]), mol (g atom Pt_{surface} s⁻¹), of effective rate constants (k_{eff,i}), mol (g atom Pt_{surface} s⁻¹), and apparent reaction orders (x_i and y_i) denote carbon-containing products j (j = HCHO, CO₂, HCOOCH₃) and Kinetic Regime i (i = 1, 2, 3). Subscript ODH denotes oxidative dehydrogenation of CH₃OH.
in Table 3, the rate dependencies for the individual rates of HCHO, CO₂, and HCOOCH₃ formation (α_j, and β_j) differ from one regime to another.

For O₂-to-CH₃OH ratios above 10, the rates for HCHO, HCOOCH₃, and CO₂ formation are independent of O₂ pressure ($\beta_{HCHO} = \beta_{HCOOCH₃} = \beta_{CO₂} = 0 \pm 0.1$). These rates with respect to CH₃OH pressure are first-order for HCHO formation ($\alpha_{HCHO} = 1 \pm 0.02$), less than first-order for CO₂ formation ($\alpha_{CO₂} = 0.8 \pm 0.01$), and larger than first-order for HCOOCH₃ formation ($\alpha_{HCOOCH₃} = 1.4 \pm 0.1$). As the O₂-to-CH₃OH ratio decreases to below 10 but above 0.5, the transition from Regime 3 to Regime 2 occurs, during which the reaction orders with respect to O₂ for HCHO and CO₂ formation increase from zero to one ($\beta_{HCHO} = 1.1 \pm 0.1, \beta_{CO₂} = 1.1 \pm 0.1$) and for HCOOCH₃ from zero to near zero values ($\alpha_{HCOOCH₃} = 0 \pm 0.1, \alpha_{CO₂} = -0.2 \pm 0.1$) and for HCOOCH₃ formation from larger than one to near 0.5 ($\alpha_{HCOOCH₃} = 0.3 \pm 0.1$). A further decrease in O₂-to-CH₃OH ratio to less than 0.5 leads to another transition in reaction orders, during which the rates for HCHO and CO₂ formation ($\beta_{HCHO} = 1.7 \pm 0.2$) and a negative dependence with CH₃OH ($\alpha_{HCHO} = -0.7 \pm 0.2$) while the rates for HCOOCH₃ formation depend solely on O₂ pressure ($\alpha_{HCOOCH₃} = 2 \pm 0.2$) and are no longer vary with CH₃OH pressure ($\alpha_{HCOOCH₃} = 0 \pm 0.1$). These effects of O₂-to-CH₃OH ratios on the individual species formation rates are captured in Fig. 4a (for Regime 1) and 4b (for Regimes 2 and 3) and their effects on the carbon selectivities are shown in Fig. 5a (for Regime 1) and 5b (for Regimes 2 and 3).

In the next sections (Sections 3.4-3.6), we provide the evidence that the increase in reaction orders with respect to O₂ ($\beta_{O₂} < \beta_{H₂O} < \beta_{CO₂}$) and the concomitant decrease in reaction orders with respect to CH₃OH ($\alpha_{O₂} > \alpha_{H₂O} > \alpha_{CO₂}$) from Regime 3 to Regime 1, as summarized in Table 3, are caused by a decrease in oxygen chemical potential at Pt cluster surfaces. The decrease in oxygen chemical potential results in a dynamic transition in the coverages of reactive intermediates from saturated with chemisorbed oxygen atoms (O°) (Regime 3), uncovered of (Regime 2), to covered with methanol derived species (Regime 1). A sequence of elementary steps for methanol and oxygen activation, HCHO formation, and sequential HCHO oxidation is proposed in Scheme 2. Elementary steps for HCHO, CO₂, HCOOCH₃, and H₂O formation in Regimes 3, 2, and 1 are provided in Schemes A.1, A.2, and A.3 respectively. These elementary reaction steps in Schemes 2 and A.1-A.3 may occur concurrently in all regimes, but their relative contributions to the observed rates differ markedly, because of the difference in site abundances of chemisorbed oxygen atoms (O°), unoccupied Pt sites (°), and methanol derived species (e.g., CH₂OH°) and the extent of their participation in catalysis from one regime to another. In Scheme 2, the dominant reaction steps for each regime are presented. During the transition from one regime to another, the elementary rate constant and equilibrium constant values are expected to vary with changes in surface coverages, lateral repulsive interactions, and heats of adsorption. We focus next on analyzing the individual regimes, starting from the highest O₂-to-CH₃OH ratios (10–45), which correspond to Kinetic Regime 3, at which Pt cluster surfaces are saturated with chemisorbed oxygen atoms that assist with the initial CH₃OH activation and HCHO oxidation steps.

![Image](image_url)
3.4. Methanol partial oxidation on Pt cluster surfaces saturated with chemisorbed oxygen atoms (Regime 3)

HCHO, HCOOCH₃, and CO₂ formation rates from CH₃OH–O₂ mixtures were measured on 1.0 wt% Pt/SiO₂ (3.0 nm mean Pt cluster diameter) at 373 K by independently varying the CH₃OH and O₂ pressures from 0.08 to 1.75 kPa and 10 to 70 kPa, respectively, while maintaining the O₂–to-CH₃OH ratio at varying values between 10 and 45. The species formation rates (rₐ, subscript j denotes HCHO, CO₂, or HCOOCH₃ and subscript 3 denotes Regime 3), are shown as a function of CH₃OH pressure (0.08–1.5 kPa) in Figs. 6a, A.1a, and A.1b, respectively, for three different O₂ pressures of 20, 28, and 35 kPa and their rate dependencies with CH₃OH and O₂ (rₐ,j = kₑ₋ₐ,j[CH₃OH]ⁿ[O₂]ᵐ) are summarized in Table 3. Turnover rates for HCHO, CO₂, and HCOOCH₃ formation increase with CH₃OH pressure with apparent reaction orders of 1.0 ± 0.02, 0.8 ± 0.01, and 1.4 ± 0.1, respectively. These rates do not vary with O₂ pressure (jₐ,j = 0 ± 0.1, j = HCHO, HCOOCH₃, or CO₂). Previous studies also reported similar rate dependencies for HCHO formation during CH₃OH–O₂ reactions at high O₂–to-CH₃OH ratios on Ag (2.5–20 O₂/CH₃OH, 563–593 K) [5], RuO₂ (2.5–7 O₂/CH₃OH, 393 K) [12], and Fe₅(MoO₄)₃ (5–40 O₂/CH₃OH, 433 K) [16]. Despite the similar rate dependencies for Pt and other metal (Ag [5]) or metal oxide (RuO₂ [12] and Fe₅(MoO₄)₃ [16]) structures, the previously proposed mechanism [12,16], which requires competitive adsorption of CH₃OH and O₂ on unoccupied metal sites or oxygen vacancies (†), is not consistent with the zero-order dependence of HCHO formation rates on O₂ pressure in this regime. The zero-order dependence of all rates (for the formation of primary and secondary products) on O₂ pressure indicates that O₂ activation step is kinetically insignificant at these high O₂–to-CH₃OH ratios. Thus, Pt cluster surfaces must be saturated with reactive oxygen atoms at surfaces (or subsurfaces). The active site structures formed with these oxygen atoms do not vary with oxygen chemical potential and the accessibility to unoccupied metal or oxygen vacancy sites does not limit CH₃OH turnovers in this regime. CH₃OH activation did not occur at exposed Pt sites used for binding the reactive oxygen atoms, because if it did, an increase in O₂ pressure would deplete the concentration of unoccupied Pt sites and lead to lower CH₃OH activation rates. In this specific case, rates for CH₃OH conversion and for HCHO, HCOOCH₃, and CO₂ formation would acquire a negative dependence on O₂ pressure.

These kinetic evidence (Figs. 6a, A.1a, and A.1b) led us to propose a sequence of elementary steps involving irreversible dissociation of O₂ molecules on Pt sites and activation of CH₃OH on O° covered Pt cluster surfaces. The reversibility of the O₂ dissociation step is given by the relative magnitudes for the rates of O° recombination (also the reverse step of O₂ dissociation on Pt sites) and those of O° removal by reaction with CH₃OH. The rates of O° recombination on O° saturated Pt cluster surfaces have been previously measured from ¹⁶O¹⁸O isotope formation in ¹⁶O₂–¹⁸O₂ mixtures [44,45]. ¹⁶O¹⁸O isotope formation rates from ¹⁶O₂–¹⁸O₂ reactions were undetectable and estimated to be lower than 2.5 × 10⁻³ mol O₂ (g atom surface Pt s)⁻¹ (20 kPa of 1:1 ¹⁶O₂–¹⁸O₂ mixture) on O° covered Pt clusters at a higher temperature of 473 K [44]. Extrapolation of the ¹⁶O¹⁸O isotope formation rates on O° covered Pt surfaces from a higher temperature range (2 kPa of 1:1 ¹⁸O₂–¹⁸O₂ mixtures; activation barrier: 108 kJ mol⁻¹; 550–715 K [45]) to 373 K gave an ¹⁶O¹⁸O formation rate of 1.2 × 10⁻⁸ mol O₂ (g atom surface Pt s)⁻¹ at 65 kPa O₂. These O° recombination rates (rₒₒₒₒₐₐ) are significantly lower than the CH₃OH forward chemical turnovers with an estimated rate ratio for oxygen recombination to CH₃OH oxidative dehydrogenation, (rₒₒₒₒₐₐ)(rₒₒₒₒₒₒ)⁻¹, of <10⁻¹⁰ at 373 K (0.08 kPa CH₃OH, 65 kPa O₂). Thus, the O₂ dissociation step must be irreversible during CH₃OH oxidation in this regime and is expected to remain even more so on Pt cluster surfaces depleted of O° (Regimes 2 and 1 in Sections 3.5 and 3.6, respectively) as the probability of O° atoms to recombine and desorb as O₂ decreases markedly with decreasing O° coverages. Chemisorbed oxygen atoms must involve in CH₃OH activation, because of much larger rates on O° saturated surfaces (Regime 3) than on cluster surfaces sparse of reactive oxygen species (Regimes 2 and 1, Fig. 4). On O° saturated surfaces, CH₃OH must activate over chemisorbed oxygen atoms as the active sites, possibly via the cleavage of its O–H bond.

In this regime, the coverages of CH₃OH derived intermediates (e.g., CH₂O°) must be insignificant, because site occupation by these intermediates would lead the rates for HCHO (rₒₒₐₐ, Fig. 6a) and the combined rates for secondary product (rₒₒₒₐₒₒ+ᵢᵢ, Fig. 6b) formation to increase less than linearly with CH₃OH pressure. We note that the identity of carbon-contain-

Fig. 6. (a) HCHO formation rates (rₒₒₐₐ) (--; predicted values from linear regression of rate data with Eq. (6)), (b) sum of CO₂ and HCOOCH₃ formation rates (rₒₒₒₒₐₒₒ+ᵢᵢ), and (c) rate ratio of HCOOCH₃ to CO₂ (rₒₒₒₒₐₒₒ/rₒₒₒₒₒₒ) as a function of CH₃OH pressure during CH₃OH–O₂ reactions with 20.0 kPa (■), 28.0 kPa (□) and 35.0 kPa (▲) of O₂ on 1.0 wt% Pt/SiO₂ (3.0 nm mean Pt cluster diameter) at 373 K (1.26 × 10⁻⁶ cm³ (gcat h)⁻¹). 200 SiO₂-to-catalyst intra-particle and 5700 SiO₂-to-catalyst inter-particle dilution ratios.
ing intermediates derived from CH$_3$OH activation at high O$^\bullet$ cover-
age is difficult to identify and remain essentially invisible from spec-
troscopic studies, because of their low coverages during stea-
dy-state reactions. In addition, attempts to probe these species on
well-defined Pt single-crystal surfaces are limited by their inher-
rent constraint to attain saturation O$^\bullet$ coverages (e.g., the max-
imum O$^\bullet$ coverages were found to be less than 0.25 ML on Pt [11 1]
at 300 K [28,36]). The lack of significant and detectable coverages of
CH$_2$O derived intermediates was confirmed from chemical
titration of carbon-containing debris on Pt cluster surfaces using
O$_2$ as titrants, carried out after steady-state CH$_2$O$_2$–O$_2$ reactions
in this regime for 1 h (O$_2$/CH$_2$O$_2$ = 16, 373 K, 4.2 $\times$ 10$^5$ cm$^2$ (gcat$^{-1}$ h$^{-1}$)). The expected chemical titration products (CO$_2)$ were
not detected from these studies within the detection limits. Taken
together the rate dependencies (Fig. 6a and b, A.1a and A.1b) and
titration results, Pt cluster surfaces must be free of CH$_2$O derived
intermediates in this regime.

These results led us to propose that the kinetically-relevant step
must involve initial CH$_2$O activation assisted by reactive oxygen
atoms, which saturate the Pt cluster surfaces, followed by sequen-
tial hydrogen abstraction to form the CH$_2$O$_2$ species, as shown in
Scheme 2. Desorption of CH$_2$O$_2$ leads to HCHO [5,25] and leaves
behind a chemisorbed oxygen (O$^\bullet$) on Pt cluster. Alternatively,
the hydrogen abstraction of CH$_2$O$_2$ species forms the formate
species (HCO$_2$), which may bind to Pt surfaces at bridge or monoden-
tate configurations [46]. The formate species may combine with
another CH$_2$O$_2$ to evolve the HCOOCH$_3$ (leaving behind an O$^\bullet$) as
a secondary product [19,20], or alternatively, undergo hydrogen
abstraction and desorb as CO$_2$ [20,25]. The net rates of HCHO for-
formation are given by subtracting the rates of HCHO oxidation from
the rates of CH$_2$O$_2$ desorption (to form HCHO and O$^\bullet$):

$$r_{HCHO} = \frac{k_{3,3}[CH_2O_2]}{[T]} - \frac{k_{3,5.7}[HCHO][O^\bullet]}{[T]}$$  \hspace{1cm} (4)$$

where $k_{3,5}$ and $k_{3,5.7}$ are the forward and reverse rate constants for
HCHO desorption steps, the former leads to HCHO formation and
HCHO oxidation and for CH$_3$OH conversion to HCHO are identical,
and $k_{3,5}$ is the rate of HCHO formation, but the rate ratio for HCHO readsorp-
tion and sequential oxidation (2nd term of Eq. (6)) to HCHO forma-
tion (1st term of Eq. (6)) remains a constant value (estimated to be
0.18 $\pm$ 0.01 at 373 K, 1.0 wt% Pt/SSiO$_2$, O$_2$/CH$_3$OH = 10–45,
1.26 $\times$ 10$^8$ cm$^2$ (gcat$^{-1}$ h$^{-1}$)) because both the rate dependencies for
HCHO oxidation and for CH$_3$OH conversion to HCHO are identical,
and independent of O$_2$ pressure and increases proportionally with
the reductant (HCHO or CH$_3$OH) pressure. These rate dependencies
lead the HCHO pressure and resulting HCHO oxidation rates to be-
come proportional to CH$_3$OH pressure. The kinetic parameters for
HCHO formation in Eq. (6) were determined from linear regression
with the rate data in Fig. 6a. Their values are included in Table A.1 in
Appendix, the predicted rates are included in Fig. 6a, and the parity
plot for measured and estimated rates is included in Fig. A.2 in Appendix.

H abstraction on the CH$_2$O$_2$ intermediates (Step 3.6, Scheme 2) forms
the formate species (HCO$_2$), a common precursor for CO$_2$ and
HCOOCH$_3$. A majority of the formate species undergo hydrogen
abstraction to evolve CO$_2$ while a small portion reacts with CH$_3$OH
to evolve HCOOCH$_3$. Thus, the combined rates for CO$_2$ and HCO-
OCH$_3$ formation are proportional to the concentration of CH$_2$O$_2$ on
Pt cluster surfaces, whose coverages are given by CH$_3$OH and HCHO
pressures (Eq. (5)):

$$r_{CO_2,3} + r_{HCOOCH_3,3} = \frac{k_{3,6}[CH_2O_2][O^\bullet]}{[T]}$$
$$= \frac{k_{3,6}[CH_3OH]}{k_{3,5} + k_{3,6}} + \frac{k_{3,6}[CH_3OH][HCHO]}{k_{3,5} + k_{3,6}}$$ \hspace{1cm} (7)$$

where rate constants $k_{3,5}$, $k_{3,5.7}$, $k_{3,5}$, and $k_{3,6}$ and [T] are defined
above and in Scheme 2. The combined rates for CO$_2$ and HCOOCH$_3$ form-
tion ($r_{CO_2,3} + r_{HCOOCH_3,3}$) vary linearly with CH$_3$OH pressure,
as shown in Fig. 6b. The rate ratio of HCOOCH$_3$ to CO$_2$ formation
($r_{HCOOCH_3,3}/r_{CO_2,3}$) is, however, proportional to CH$_3$OH pressure
via a proportionality constant $k_{HCOOCH_3}-CH_3OH(k_{HCOOCH_3}-CH_3OH)$
of 0.392 $\pm$ 0.003 (Fig. 6c), which equals the ratio of rate constant for
HCOOCH$_3$ formation from the reactant of formate with CH$_3$OH
($k_{HCOOCH_3}-CH_3OH$) and that for CO$_2$ formation from H abstraction
on HCOOCH$_3$ ($k_{HCOOCH_3}-CH_3OH$), respectively, as derived in Section A.1 of Appendix.

The linear dependence of HCOOCH$_3$-to-CO$_2$ selectivity ratio
($r_{HCOOCH_3,3}/r_{CO_2,3}$) with CH$_3$OH pressure is consistent with the fact
that HCO$_2$ forms HCOOCH$_3$ only by their reaction with another CH$_3$.
OH but forms CO$_2$ directly. Next, we show that the most abundant
surface intermediates and the steps for CH$_3$OH activation undergo a
concomitant dynamic transition in response to decreasing O$_2$-to-
CH$_3$OH ratio to values smaller than 10.

3.5. Methanol partial oxidation on uncovered Pt cluster surfaces
(Regime 2)  

As O$_2$-to-CH$_3$OH ratio decreases to less than 10 but larger than
0.5, rate dependencies for HCHO, HCOOCH$_3$, and CO$_2$ formation un-
dergo a concomitant transition and acquire reaction orders un-
like those in Region 3. In Regime 2, the rate dependencies for oxidative
dehydrogenation of CH$_3$OH ($r_{ODH}$) are shown in Fig. 7a, the rates of
HCHO ($r_{HCHO}$), CO$_2$ ($r_{CO_2}$), and HCOOCH$_3$ ($r_{HCOOCH_3}$) formation
in Fig. 7b, A.3a, and A.3b, respectively, and the sum of CO$_2$ and
HCOOCH$_3$ formation rates in Fig. 7c as a function of O$_2$ pressure
(0.5–5 Kpa) for 1.0, 1.5, and 2.0 Kpa CH$_3$OH for CH$_3$OH–O$_2$
reactions on Pt clusters (3.0 nm mean Pt cluster diameter) at
373 K. Turnover rates for oxidative dehydrogenation of
CH$_3$OH and for HCHO and CO$_2$ formation are no longer
independent of but increase proportionally with O$_2$ pressure in
this regime ($r_{ODH2} = 2.0 \pm 0.1$, $r_{HCHO2} = 2.0 \pm 0.1$, and $r_{CO_22} = 0.2 \pm 0.1$, Table 3).

These rates also become insensitive to CH$_3$OH pressure ($\gamma_{ODH2} = 0 \pm 0.1$, $\gamma_{HCHO2} = 2.0 \pm 0.1$, and $\gamma_{CO_22} = 0.2 \pm 0.1$, Table 3).

These effects of CH$_3$OH and O$_2$ pressures are consistent with O$_2$ activation on uncovered Pt cluster surfaces as the kinetically-relevant step. Pt
cluster surfaces must be largely free of molecular debris from
CH$_3$OH and O$_2$ activation, because the opposite case would lead
bond activation routes are proposed for CH₃OH and C₂H₅OH activation, giving lower activation barriers for H abstraction on CH₃O than on C₂H₅O in UV photoemission spectra (UPS) during CH₃OH adsorption on Pt(111) (150–200 K) [47] and dispersion corrected density functional theory calculations on Pt(111) surfaces [48]. The adsorbed CH₃OH undergoes a series of hydrogen abstraction steps, likely assisted by O₂ to first cleave its O–H bond to form a methoxide intermediate (CH₃O⁺; Step 2.3, Scheme 2) and then the C–H bond of CH₃O⁺ to form CH₂O⁺ (Step 2.4, Scheme 2) before its eventual desorption as HCHO [49]. The catalytic involvement of oxygen in O–H bond activation has been probed and confirmed from temperature desorption spectroscopy and high-resolution electron energy loss spectroscopy (EELS) on Pt(111) surfaces partially covered with O₂ at 170 K [50,51]. The O₂-assisted O–H bond dissociation in CH₃OH was found to be more exothermic than the similar step without O₂ involvement on Pt(111) surfaces, as measured from single-crystal adsorption calorimetry (SCAC) studies [52]. The higher exothermicity is consistent with the lower activation barrier for CH₃OH activation on O₂ than on Pt, as predicted from the Brønsted–Evans–Polanyi relation and confirmed from temperature-programmed reactions of pre-adsorbed CH₃OD with O₂ (Ea = 23 kJ mol⁻¹) on 0.25 ML O₂-covered Pt(111) [115–140 K] [23] and CH₃OH decomposition on uncovered Pt(111) (Ea = 48 kJ mol⁻¹) [53]. Density functional theory calculations (DFT) of CH₃OH activation on Cu(110) surfaces show barrierless O–H bond dissociation with O₂ involvement (0.25 ML O₂), but this step acquires a barrier of 41 kJ mol⁻¹ without O₂ involvement [25,54]. DFT calculations on Cu(110) surfaces also give lower activation barriers for H abstraction on CH₄O⁺ when assisted by O₂ than by OH⁺ (Ea = 54 kJ mol⁻¹ with O₂ vs. 118 kJ mol⁻¹ with OH⁺) [25]. Similar oxygen assisted O–H and C–H bond activation routes are assisted by O₂ for CH₃OH and C₂H₅OH activation on RuO₂ structures in a Mars–van Krevelen-type redox cycle [12]. The CH₃OH activation step is kinetically coupled with the O₂ dissociation step that must maintain its irreversible nature, as found for Regime 3 (Section 3.4). The irreversible nature of O₂ dissociation is confirmed from an estimated rate ratio of oxygen recombination to CH₃OH oxidative dehydrogenation Ea,CH₃OH(r) of less than 2 × 10⁻¹¹ at 373 K, based on extrapolation of O₂ recombination rates from 550–715 K [45] to 373 K and rCH₃OH of 200 mol CH₃OH (g atom Pt/s)⁻¹ at 5 kPa O₂ and 1 kPa CH₃OH. This is expected because of lower O₂ coverages in this regime than Regime 3 and thus much lower probabilities for an O₂ to encounter a neighboring O₂ for recombative desorption.

These catalytic steps and the assumption of unoccupied Pt sites (*) as the most abundant surface intermediates ([*]= [T], where [*] denotes the surface concentration of unoccupied Pt sites and [T] the total exposed Pt sites) lead the CH₃OH oxidative dehydrogenation rates (rCH₃OH) to increase proportionally with O₂ pressure (derived in Section A.3 in Appendix):

\[ r_{CH_{3}OH} = \frac{2k_{2,1}[O_{2}]^{2}}{[T]^{2}} = 2k_{2,1}[O_{2}] \] (8)

where \( k_{2,1} \) reflects the rate constant for O₂ dissociation on Pt cluster surfaces (Step 2.1, Scheme 2), which includes a statistical factor correcting for the double counting of indistinguishable neighboring sites required for O₂ activation. CH₃OH activation is kinetically-relevant; thus, O–H and C–H bond cleavages in CH₃OH and their involvement remain kinetically invisible. Similar rate dependencies (Eq. (8)) and mechanistic conclusions on kinetically-relevant O₂ activation have also been reported for other oxidation reactions (CH₄–O₂ [39,40], CO–O₂ [40], and C₂H₆–O₂ [41] at >773 K) at high reductant and low O₂ pressures, at which the reductant effectively scavenges O₂ from cluster surfaces, leaving Pt sites uncovered and available for the kinetically-relevant O₂ dissociation. The measured rate constant for O₂ dissociation, \( k_{2,1} \), is 20 mol O₂ (g atom Pt/s)⁻¹ (373 K, from linear regression of rate data in Fig. 7a with Eq. (8); Table A.2 in Appendix Section A.4), a value lower than the extrapolated values of 750–800 mol O₂ (g atom Pt/s)⁻¹ from high temperatures (>773 K) in CH₄–O₂ and CO–O₂ mixtures to 373 K using the reported activation barriers (CH₃–O₂ mixtures: 5040 mol O₂ (g atom Pt/s)⁻¹ at 873 K, 3–20 kJ mol⁻¹ on 1.8–8.5 nm Pt cluster [39]; CO–O₂ mixtures: 4700 mol O₂ (g atom Pt/s)⁻¹ at 773 K, 8–10 kJ mol⁻¹ on 3.3 nm Pt cluster [55]). The effective activation barrier for CH₃OH conversion, which also equals the O₂ dissociation barrier, was found to be 26 kJ mol⁻¹.
dependencies for HCHO, HCOOCH₃, and CO₂ formation from CH₃-
Fig. A.5 (Appendix Section A.4). Plotted together with the measured rates in a parity plot in
regression of rate data with Eq.(8) gave the predicted ODH rates
based on the low activation energy expected for this step. Linear
able for O₂ activation, leading to rates larger than those predicted
when the activation energy on these sites is estimated to be more negative
| –145 kJ mol⁻¹ | the value for CH₂O₃ adsorption on closed packed Pt(111) surfaces [21].

Preoccupation of corner and edge sites by CO₂ or CH₂O₃ prevents these sites to involve catalytically and thus they remain kinetically invisible, but as the temperature increases and CO₂ or CH₂O₃ intermediates desorb, these sites become available for O₂ activation, leading to rates higher than those predicted based on the low activation energy expected for this step. Linear

regression of rate data with Eq. (8) gave the predicted ODH rates in
Regime 2, included in Fig. 7a as a function of O₂ pressure and plotted together with the measured rates in a parity plot in
Fig. A.5 (Appendix Section A.4).

Although the overall rates of CH₂O₃ oxidative dehydrogenation (Fig. 7a), rates of HCHO formation (Fig 7b), and combined rates of CO₂ and HCOOCH₃ formation (Fig. 7c) are determined solely by O₂ dissociation, carbon selectivities toward CO₂ and HCOOCH₃ vary with both CH₂O₃ and O₂ pressures. HCOOCH₃ formation requires dehydrogenation of CH₂O₃ to CHO² followed by reaction of CHO² with a vicinal CH₂O₃, but CO₂ formation requires only the CH₂O₃ dehydrogenation step without CH₂O₃ involvement along its reaction
path. The different molecular arising from the CH₂O₃ involvement for HCOOCH₃ formation and not for CO₂ formation lead the rate ratio of HCOOCH₃ to CO₂ formation to vary proportionally with \( CH₂O₃ / CH₂O₃ \)⁻¹ (data not shown here; \( CH₂O₃ \) denotes the concentration of adsorbed CH₂O₃ on platinum surface sites), as derived in Appendix, Section A.3.

### 3.6. Methanol partial oxidation on Pt cluster surfaces saturated with CH₂O derived species (Regime 1)

As O₂-to-CH₂O₃ ratio decreases further to less than 0.5, rate dependencies for HCHO, HCOOCH₃, and CO₂ formation from CH₃-
OH-O₂ reactions on Pt clusters (3.0 nm mean Pt cluster diameter,
373 K) undergo another transition. The effective reaction orders with respect to O₂ are nearly or equal to two for all species (\( \beta_{HCHO} = 2 \pm 0.2 \), \( \beta_{HCOOCH₃} = 2 \pm 0.2 \)) and with respect to CH₂O₃ are nearly negative one for HCHO and CO₂ formation (\( \alpha_{HCHO} = 2 \pm 0.2 \) and zero order for HCOOCH₃ formation (\( \alpha_{HCOOCH₃} = 0 \pm 0.1 \)), as summarized in Table 3. The rates of HCHO formation and combined rates of CO₂ and HCOOCH₃ formation are plotted in terms of \( K_{HCHO} \) and \( K_{HCOOCH₃} \) (subscript denotes either HCHO or lump of secondary products CO₂ and HCOOCH₃, CO₂ + HCOOCH₃), and subscript 1 denotes Regime 1 vs. the O₂-to-CH₂O₃ ratio (0.1–2.5 kPa O₂ and 2.5–4.5 kPa CH₂O₃) in
Fig. 8a and b, respectively.

These rate dependencies are consistent with CH₂O activation on Pt surfaces predominantly covered by CH₂O derived intermediates, likely CH₂O²⁻, as the kinetically-relevant step. On cluster surfaces scarce of unoccupied Pt sites, adsorbed diatomic oxygen (O₂) may assist with CH₂O²⁻ decomposition. Mechanistic involvement of O₂ was proposed in CH₂O activation on Pt(111) surfaces without further kinetic analysis at 35–100 K [29] and 100–550 K [28,36]. The involvement of diatomic oxygen leads the fraction of CH₂O²⁻ to-O₂ on Pt clusters, \([CH₂O²⁻] / [O₂] \)⁻¹, to vary proportionally to CH₂O-O₂ ratio. These assumptions lead to an expression for \( r_{ODH} / [CH₂O₃] \)⁻¹ as a function of O₂-to-CH₂O ratio according to

development in Appendix A.5):

\[
r_{ODH} = \frac{k_{1.3} [CH₂O₃] [O₂]}{[CH₂O₃] [CH₂O₃] [O₂]} = \frac{k_{1.3} K_{1.2}}{1 + k_{1.3} K_{1.2} [CH₂O₃]}\]

(9)

where \( K_{1.1} \) and \( K_{1.2} \) reflect the equilibrium constants for O₂ (Step 1.1, Scheme 2) and CH₂O₃ (Step 1.2, Scheme 2) adsorption on a Pt site, respectively; \( K_{1.3} \) and \( K_{1.4} \) are the rate constants for CH₂O²⁻ dissociation assisted by a vicinal Pt site (Step 1.3, Scheme 2) and for CH₂O²⁻ reaction with vicinal O₂ species (Step 1.4, Scheme 2), respectively. The involvement of oxygen (O₂ or O²⁻) in the initial CH₂O activation is ruled out in this regime, because oxygen involvement would lead the rate of CH₂O oxidative dehydrogenation, \( r_{ODH} \), to acquire a first-order dependence with respect to O₂. The apparent reaction order with O₂ larger than one but below two (\( \beta_{ODH} / \beta_{HCHO} = 1.7 \pm 0.2 \)) indicates that both the denominator terms, \( k_{1.3} K_{1.2} [CH₂O₃] [K_{1.2} K_{1.1} [O₂]] \)⁻¹ and 1, in Eq. (9) are of comparable magnitudes. The ratio of these terms

\[\text{Fig. 8. (a) First-order rate coefficients (}K_{HCHO} \text{)}⁻¹ \text{ for HCHO formation and (b) first-order rate coefficients for the total rates of HCOOCH₃ and CO₂ formation (}K_{ODH} \text{)}⁻¹ \text{ during CH₃OH-O₂ reactions with } 2.5 \text{ kPa (}●\text{), 3.5 kPa (}○\text{), and 4.5 kPa (}■\text{) CH₃OH on } 1.0 \text{ wt% Pt/SiO₂ (3.0 nm mean Pt cluster diameter) as a function of O₂-to-CH₃OH ratio. (c) Rate ratio of HCOOCH₃ to CO₂, } \text{HCOOCH₃} / \text{CO₂} \text{, as a function of CH₃OH pressure during CH₃OH-O₂ reactions with } 1.00 \text{ kPa (}●\text{), } 1.25 \text{ kPa (}○\text{), and } 1.75 \text{ kPa (}■\text{) of O₂ on } 1.0 \text{ wt% Pt/SiO₂ (373 K, } 4.2 \times 10^{17} \text{ cm}⁻² \text{} (\text{g}_{\text{cat}} \text{ h})⁻¹ \text{, } 200 \text{SiO₂-to-catalyst intra-particle and } 5700 \text{SiO₂-to-catalyst inter-particle dilution ratios).}]}
Carbon selectivities are independent of O2 pressure over the entire range of O2-to-CH3OH ratios in this regime, despite the variation in CH3O− and O− (Fig. 9) surface fractions, because both O2 and O− are involved only for the formation of CH2O2 intermediates and not involved in any of the sequential reactions of CH2O2 that form HCHO, HCOOCH3, and CO2. These results indicate that all products are formed from surface intermediates directly derived from CH3OH, consistent with the lack of residence time effects on selectivities in this regime (Fig. 3a, Section 3.2). The rate ratio for HCOOCH3 to CO2, however, increases linearly with increasing CH3OH pressure, as shown in Fig. 8c, because HCOOCH3 formation requires the recombination of two CH2O2 derived species, a step that becomes more favorable as CH3OH pressure and coverages of CH2O2 derived intermediates increase.

3.7. Catalytic effects of mean cluster diameter and average Pt surface coordination during methanol partial oxidation on Pt cluster surfaces saturated with O−, uncovered of reactive intermediates, and partially covered with CH3OH derived intermediates

Next, we interrogate the catalytic effects of Pt surface coordination and thus the coverages and binding strengths of the various reactive intermediates (O−, CH3O−) by varying the mean Pt cluster diameters from 3.0 nm to 4.8 nm. Pt atoms on small Pt cluster surfaces bind reactive intermediates much more strongly than those on large clusters because of their higher extent of coordinative unsaturation. These effects of surface coordination affect the coverages and binding strengths of the reactive intermediates and, in turn, alter both the rate and thermodynamic constants and the resulting rates and carbon selectivities. Figs. 10 and A.6 compare the HCHO formation and ODH rates (at 373 K), per exposed Pt atom, between two 1.0 wt% Pt/SiO2 samples with different mean Pt cluster diameters of 3.0 nm and 4.8 nm and Table 4 summarizes the associated effective rate constants for HCHO formation for all regimes. The rates on both samples showed similar rate dependencies, but their values were higher for the larger than the smaller clusters.

These reactivity trends are interpreted next by correlating the changes in binding strengths and coverages to the rate and thermodynamic parameters that govern the catalytic rates in each regime. On O− saturated surfaces (Regime 3), an increase in Pt...
surface coordination with increasing cluster diameter leads to a concomitant decrease in the average binding strength of O\textsuperscript{2−} atoms. Density functional theory calculations predict a decrease in oxygen binding strength with increasing Pt coordination: from 133 to 96 kJ mol\textsuperscript{-1} as the Pt coordination number increases from 6.5 to 9.0 on the various surface sites on Pt clusters (201 Pt atoms in cubo-octahedral structures) at low O\textsuperscript{2−} coverages (0.01 ML) [40] and from 140 to 105 kJ mol\textsuperscript{-1} as the Pt coordination number increases from 7 to 9 on fcc-like surfaces on Pt(321) surfaces [57]. At the higher O\textsuperscript{2−} coverages, the trend between the oxygen binding strengths and Pt coordination numbers is expected to remain the same, even though oxygen binding strengths are weaken by the lateral repulsive interferences between the O\textsuperscript{2−} atoms [58]. The weakly bound O\textsuperscript{2−} prevalent on the larger clusters are more basic and thus more effective in electron donation to the leaving H during the O–H bond activation in CH\textsubscript{3}OH, as reflected from an increase in the effective rate constant for HCHO formation (k\textsubscript{eff,HCHO,3}) by a factor of 2.05 ± 0.10 for the larger than the smaller Pt clusters (Table 4). Similar effects of oxygen binding strength on their reactivity toward hydrogen abstraction were reported for alkanes (CH\textsubscript{4} [39,40], C\textsubscript{2}H\textsubscript{6} [41], and CO oxidation [55,56]).

Table 4

<table>
<thead>
<tr>
<th>Mean Pt cluster diameter</th>
<th>Kinetic regimes and effective rate constants [mol (g atom Pt\textsubscript{surface} s kPa\textsuperscript{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}/CH\textsubscript{3}OH ratio</td>
<td>Regime 3\textsuperscript{a} (k\textsubscript{eff,HCHO,3})</td>
</tr>
<tr>
<td>3.0 nm</td>
<td>105 ± 5</td>
</tr>
<tr>
<td>4.8 nm</td>
<td>215 ± 5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: k\textsubscript{eff,HCHO,3}, from linear regression of rate data in Figs. 10a and 10b with Eqs. (6) and (A.8) for Regimes 3 and 2, respectively, and from non-linear regression of rate data in Fig. 10c with Eq. (3) for Regime 1. \textsuperscript{b}: k\textsubscript{eff,HCHO,2} \textsuperscript{1/2} \textsuperscript{K}0.9 on the various surface sites on Pt clusters (201 Pt atoms in cubo-octahedral structures) to reductant derived species (Regime 3) to reductant derived species (Regime 1) in response to changing oxidant-to-reductant ratio alters the kinetically-relevant step from limited by reductant activation on O\textsuperscript{2−} site pairs (Regime 3) to oxidant activation on + site pairs (Regime 2) and then to reductant activation on \textsuperscript{1} site pairs (Regime 1). These kinetic phenomena governed by changing chemical potentials at Pt cluster surfaces, as shown here using CH\textsubscript{3}OH–O\textsubscript{2} reactions, appear to be general for oxidation reactions and have also been recognized and rigorously demonstrated recently for CH\textsubscript{4} [39,40], C\textsubscript{2}H\textsubscript{6} [41], and CO oxidation [55,56].

4. Conclusion

Kinetic studies of CH\textsubscript{3}OH–O\textsubscript{2} reactions over dispersed Pt clusters on SiO\textsubscript{2} show distinct rate dependencies that vary strictly with the O\textsubscript{2}–to-CH\textsubscript{3}OH ratios, because these ratios determine the oxygen and carbon chemical potential, identity and coverages of the reactive intermediates at Pt cluster surfaces and, in turn, the nature of active site structures and rates. The kinetically-relevant step undergoes transition from limited by CH\textsubscript{3}OH activation on O\textsuperscript{2−} site pairs (Regime 3) to oxidant activation on + site pairs (Regime 2) and then to reductant activation on \textsuperscript{1} site pairs (Regime 1). These kinetic phenomena governed by changing chemical potentials at Pt cluster surfaces, as shown here using CH\textsubscript{3}OH–O\textsubscript{2} reactions, appear to be general for oxidation reactions and have also been recognized and rigorously demonstrated recently for CH\textsubscript{4} [39,40], C\textsubscript{2}H\textsubscript{6} [41], and CO oxidation [55,56].
constants for CH$_3$OH and O$_2$ activation steps, is a descriptor for the oxygen chemical potential at Pt cluster surfaces.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.01.018.

References