Mechanistic Aspects and Reaction Pathways for Oxidative Coupling of Methane on Mn/Na2WO4/SiO2 Catalysts

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Received: January 6, 2009; Revised Manuscript Received: March 15, 2009

Kinetic and isotopic methods were used to determine the identity, rate constants, and reversibility of elementary steps for primary and secondary reactions involved in the oxidative coupling of methane (OCM) on Mn/Na2WO4/SiO2. We provide evidence in this study for parallel C–H bond activation pathways, in which H-abstraction is mediated by either oxygen species on surfaces or by OH radicals formed via H2O/O2 equilibration on catalyst surfaces. OCM rates and C2+ yields are higher when H2O is present and OH-mediated pathways prevail, because of the high reactivity of OH radicals and of their lesser sensitivity to the energy of the C–H bond containing the hydrogen abstracted. These coupled homogeneous-catalytic sequences account for all observed kinetic effects of O2, CH4, and H2O on rates and selectivities for both CH4 conversion and for subsequent reactions of C2H6, C2H4 and C3 products; they are also consistent with measured kinetic and thermodynamic isotope effects for C–H bond activation mediated by surface and OH radicals. Kinetic isotope effects and isotopic scrambling studies (CD4/CH4; D2O/H2O; 18O2/16O2) indicate that C–H bond activation is irreversible and kinetically-relevant. O2 dissociation is quasi-equilibrated, but becomes irreversible as H2O/O2 ratios increase with increasing conversion and residence time. Competitive reactions of 13CH4/O2 with 12C2H6, 12C2H4, and 12C3H6 with and without added H2O show that H-abstraction from hydrocarbons is much less sensitive to C–H bond strength when OH radicals are used to abstract hydrogen instead of oxide surfaces. Maximum C2+ yields require conditions that favor OH-mediated pathways while maintaining equilibrium oxygen surface coverages and OH radical concentrations. OH-mediated pathways are more sensitive to O2 pressure than surface-mediated pathways; thus, low O2 pressures and staging strategies that maintain stoichiometric O2 requirements and low local O2 pressures can improve C2+ selectivities but only when OH radicals are maintained at equilibrium concentrations via catalytic H2O–O2 reactions. These findings and interpretations indicate that intermediate O2 pressures give maximum C2+ yields, but that their optimal value depends sensitively on prevalent H2O concentrations as they vary with conversion along the reactor. These predictions about the consequences of various operating strategies have become feasible because of the detailed and quantitative nature of the mechanism-based kinetic networks reported here for the first time.

1. Introduction

The oxidative coupling of methane (OCM) involves the conversion of CH4–O2 mixtures to higher hydrocarbons1,2 and benefits from the avoidance of sequential steps required in indirect routes involving CH4 reforming and Fischer–Tropsch synthesis,3 while producing light alkenes, which cannot be formed via these indirect routes. Previous studies have addressed the synthesis of catalysts with improved C2 yields and selectivities where Mn/Na2WO4/SiO2 catalysts4–7 have achieved among the highest reported C2+ yields 26%.8

OCM reactions involve the catalytic formation of methyl groups9,10 which desorb as free radicals (CH3·) that ultimately react via predominantly homogeneous pathways. Recombination of CH3 radicals in the gas phase forms C2H6 and subsequent dehydrogenation steps convert C2H6 to C2H4;11 CO (CO and CO3) forms via catalytic and homogeneous primary and secondary pathways. Homogeneous pathways can also form C3+ hydrocarbons, which contain weaker C–H bonds that favor their subsequent conversion to CO2. Selectivities and yields depend on the identity and dynamics of specific elementary steps involved in these primary and secondary reactions. The details of such kinetic networks remain incomplete; yet, they are essential to describe these reactions in terms of their rate constants and pressure dependences and to define and exploit the specific contributions and kinetic coupling of surface-catalyzed and gas phase reactions.

C2 selectivities typically decrease as CH4 conversion increases because primary C2 products oxidize to CO2 products favored by thermodynamics. Such sequential pathways (Scheme 1) account for the inherently limited yield of OCM processes12–16 CH4 reacts first to form C2H6 and undesired COx byproducts via surface-catalyzed and homogeneous pathways, the rates of which depend on the relevant rate constants (k1, k2; Scheme 1), the reactant pressures (CH4, O2), and the concentration of...
reaction products (C2H6, C2H4, CO2, H2O) prevalent at conversions required for practical OCM applications. C2 products are favored by high CH3 radical concentrations because their recombinaton is a bimolecular event, while competing oxidation pathways are proportional to CH3 concentration because they involve reactions with O2-derived species. CH3 oxidation depends on O2 concentrations, while CH3 recombinaton rates are independent of O2 pressure. Attainable C2+ yields depend sensitively on the relative rates of secondary reactions of C2 and C3+ products (r3-r7; Scheme 1) and of primary CH3 activation steps (r1). These secondary reactions involve the activation of C−H bonds to form the various radical intermediates (C2H5, C2H4, etc.) via homolytic pathways similar in nature to those involved in CH4 activation.9,11 As a result, the relative rates of these reactions and the concomitant attainable maximum C2 yields are essentially dictated by the relative C−H bond energies among the hydrocarbons involved in OCM.15

We report here rigorous kinetic and isotopic assessments of primary and secondary OCM pathways and their elementary steps. We also provide evidence for previously unrecognized effects of H2O on the relative rates of these steps and confirm the kinetic irrelevance of the other OCM products (C2H6, C2H4, CO2) in C−H bond activation of CH4 reactants. Specifically, we show that H2O-derived gas phase OH radicals activate C−H bonds in CH4 and C2H6 with less sensitivity to their respective C−H bond energies. We also find that the preponderance of OH-mediated homogeneous pathways (via intervening surface activation of H2O) ameliorates C2H5 combustion routes favored by the preferential binding of alkenes (C2H4, C3H6) on oxide surfaces. As a result, these OH-mediated pathways lead to higher C2 selectivities and yields than are attainable with anhydrous reactants. These data, taken together with simulations using rigorous kinetic models, provide evidence for the relevance and consequences of quasi-equilibrated surface-catalyzed formation of reactive OH radicals from O2–H2O reactants. The resulting OH-mediated pathways become the predominant route for OCM in air at 403 K for 5 h.6 The samples were then stirred in an aqueous solution of Na2WO4·2H2O (Sigma-Aldrich, 99%, 2 cm3/g-SiO2) to give 2 wt % Mn and 5 wt % Na2WO4. Finally, the samples were treated in ambient air at 403 K for 5 h and in flowing dry air (Praxair, UHP, 10 g-cat, 0.167 cm3 s−1) by increasing the temperature at 0.033 K s−1 and holding at 1173 K for 8 h. The samples were sieved again before use to retain aggregates with a narrower size range (0.25−0.35 mm).

2. Experimental Section

Catalysts were prepared using procedures reported previously.6 SiO2 (Davison Chemicals, Silica Gel grade 57) was sieved to retain aggregates 0.10−0.85 mm in diameter. These aggregates were contacted with aqueous Mn(NO3)2 solutions (50 wt %; Strem Chemicals, 2 cm3/g-SiO2) for 2 h and treated in ambient air at 403 K for 5 h.6 The samples were then stirred in an aqueous solution of Na2WO4·2H2O (Sigma-Aldrich, 99%, 2 cm3/g-SiO2) to give 2 wt % Mn and 5 wt % Na2WO4. Finally, the samples were treated in ambient air at 403 K for 5 h and in flowing dry air (Praxair, UHP, 10 g-cat, 0.167 cm3 s−1) by increasing the temperature at 0.033 K s−1 and holding at 1173 K for 8 h. The samples were sieved again before use to retain aggregates with a narrower size range (0.25−0.35 mm). OCM reactions were measured in flow and recirculating batch reactors using U-shaped quartz reactor cells (4 mm I.D.). Catalysts (0.02−0.05 g) were diluted with inert SiO2 particles (0.5 g; Fluka, 0.25−0.35 mm) and held onto quartz wool. The temperature was controlled using a Watlow controller (Series 982) and a resistively heated furnace and was measured with a K-type thermocouple contacting the outer surface of the reactor. CH2 (Praxair, 99.999%) and O2 (Praxair, 99.999%) were introduced with He (Praxair, 99.999%) as a diluent using mass flow controllers (Porter Inc. model 201). In batch experiments, the recirculation volume (275−650 cm3) was evacuated to <0.1 Pa before introducing reactants, which were continuously circulated using a graphite gear pump (Micropump, model 182-000, >2.5 cm3 s−1), with a flame ionization detector. Differential rates were obtained from time-derivatives of hydrocarbon concentration profiles in batch reactors, after regressing concentration–time data to a sixth-order polynomial. Selectivities and yields are reported on a carbon basis as cumulative integral values.

CD4 (Isotec, 99 at % D), D2O (Cambridge Isotope Laboratories, Inc., 99.9%), and 18O2 (Isotec, 99 at % 18O) were used to measure kinetic isotope effects and isotopic scrambling dynamics. Isotopic tracer studies were carried out using labeled 13CH4 (Isotec, 99 at % 13C) in the presence of 12C3H8 (Praxair, chemical purity 99.999%), 13C2H4 (Praxair, chemical purity
99,999%), or 5% $^{12}$C$_2$H$_6$/He (Praxair). Labeled $^{13}$CO (Isotec, 99% $^{13}$C) was used to measure CO oxidation rates during OCM. These isotopic studies used the gas chromatograph described above and also a HP5890 GC equipped with a mass selective detector (HP 5972) connected to a HP-PLOT Q capillary column.

Simulations were carried out using ChemKin codes and reported gas-phase rate constants and thermodynamics. This homogeneous kinetic model contains 447 reversible elementary chemical reactions and 115 species.

The surface area of the Mn/Na$_2$WO$_4$/SiO$_2$ sample, after treatment in dry flowing air at 1173 K for 8 h, was 1.3 m$^2$ g$^{-1}$, as determined from N$_2$ physisorption at its normal boiling point using the BET formalism. This treatment sinters samples to a recirculating reactor (0.02 g, 1073 K, volume: 275 cm$^3$, 10.7 kPa CH$_4$, 101 kPa total pressure, balance He. (●) 1.8 kPa O$_2$, H$_2$O removed; (■) 1.8 kPa O$_2$, 0.4 kPa H$_2$O added; (□) 1.8 kPa O$_2$, 0.9 kPa H$_2$O added; (○) 0.9 kPa O$_2$, 0.4 kPa H$_2$O added).

3. Results and Discussion

3.1. Effects of H$_2$O Pressure on CH$_4$ Conversion Rates and C$_2$+ Selectivity. Figure 1, panels a and b, shows differential CH$_4$ conversion rates per gram of catalyst; from time derivatives of concentration profiles as a function of contact time and C$_2$+ selectivities as a function of CH$_4$ conversion, respectively, on Mn/Na$_2$WO$_4$/SiO$_2$ catalysts in a gradientless batch reactor at 1073 K. At 10.7 kPa CH$_4$ and 1.8 kPa O$_2$ (filled circles; “steady state reaction”), Figure 1a shows that CH$_4$ conversion rates initially increased with contact time and then decreased as O$_2$ coreactants were depleted in all experiments for which reactants and products were kept in contact with the catalyst. C$_2$ selectivities remained nearly constant up to ~10% CH$_4$ conversion and subsequently decreased gradually as conversion increased with contact time (Figure 1b).

This enhancement in CH$_4$ conversion rate with increasing conversion (and contact time) was not caused by local high temperatures as a result of exothermic CH$_4$ oxidation reactions, because varying catalyst dilution with quartz particles (0:1 to 50:1 quartz to catalyst ratio) did not detectably influence measured rates. The recirculation strategy used here minimizes the amount of energy released per pass compared with commonly used single-pass flow reactors. Changes in catalyst structure or accessibility also do not account for the observed increase in rates, because these trends were observed again when reactor contents were replaced with fresh CH$_4$/O$_2$ reactants directly after one of these experiments and without intervening thermal treatments. We conclude, therefore, that these “activation” or “autocatalytic” trends are kinetic in origin; they must reflect either a negative kinetic order in CH$_4$ or O$_2$ reactants, which are depleted with contact time, or positive effects by one or more of the OCM products (C$_2$H$_6$, C$_2$H$_4$, CO, CO$_2$, and H$_2$O), which increase in concentration as conversion increases with contact time.

We observe in independent experiments an increase in CH$_4$ conversion rate with increasing CH$_4$ and O$_2$ pressures in the initial reactant stream. We do not find, however, any detectable effects of ethene or ethane on rates or selectivities (vide infra). Thus, negative kinetic orders in reactants or positive effects of C$_2$ products cannot account for the observed increase in CH$_4$ conversion rates with contact time. As we have shown earlier, H$_2$O may instead affect CH$_4$ reactions, consistent with the data in Figure 1, panels a and b, in which H$_2$O was either continuously removed as it formed in OCM reactions (labeled “H$_2$O removed”) or added to the initial reactant mixtures (labeled “H$_2$O added”).

The continuous removal of H$_2$O during OCM reactions led to CH$_4$ conversion rates that decreased monotonically with increasing contact time and CH$_4$ conversion, as expected from the gradual depletion of reactants and the positive OCM kinetic orders in CH$_4$ and O$_2$ pressures (filled diamonds; Figure 1a). C$_2$ selectivities decreased with contact time more strongly when H$_2$O was removed than when it was allowed to accumulate during reaction or when it was added initially together with reactants (Figure 1b). H$_2$O addition (0.4 kPa) to CH$_4$–O$_2$ reactants led to higher initial CH$_4$ conversion rates than for anhydrous reactants and to a subsequent decrease in rates as reactants were depleted (filled squares; Figure 1a). Higher H$_2$O pressures (0.9 kPa) led to even higher initial rates (open squares; Figure 1a). H$_2$O addition also increased initial C$_2$ selectivities (Figure 1b). These effects of water became weaker as CH$_4$ conversion increased, because H$_2$O concentrations increased to similar levels as conversion increased, even with anhydrous feeds.

An earlier study proposed that OH radicals formed from H$_2$O could increase CH$_4$ activation rates, but not C$_2$ selectivities,
during OCM reactions. Our results show that H2O markedly influences both rates and selectivities. These effects are discussed next in the context of the kinetic response of the various steps to CH4 and O2 pressures in the absence of H2O. We then address the specific effects of H2O in the steps required for the activation of CH4, C2H6, and C2H4 (Scheme 1) and report rate constants for surface-mediated and H2O-mediated reaction pathways using isotopic tracing methods. We also report kinetic isotope effects and scrambling rates that probe the nature and reversibility of the relevant elementary steps.

3.2. Rate Equations and Elementary Steps for CH4/O2 Reactions under Anhydrous Conditions. The kinetic response of CH4 conversion rates to CH4 and O2 pressures was measured on Mn/Na2WO4/SiO2 at 1073 K in a plug-flow reactor by varying space velocity and inlet concentrations. Rates and selectivities were extrapolated to zero CH4 conversion to measure kinetic data under strictly anhydrous conditions (using five data points at CH4 conversions below 5%). No reaction products were detected in the absence of a catalyst at these reaction conditions.

Measured CH4 conversion rates (rCH4) were proportional to PCH4 P1/2O2, as previously reported; these data are consistent with quasi-equilibrated dissociative O2 chemisorption on vicinal surface vacancies (*) to form reactive O2* species (step 1) and with kinetically-relevant steps in which these O2* species abstract H-atoms from CH4 to form adsorbed OH* and gas-phase methyl radicals (step 2). This catalytic sequence is then completed via quasi-equilibrated recombination of OH* to form H2O and surface vacancies (*).

\[ O_2 + 2* \xrightarrow{K_{O2}} 2O_2^* \]  \[ CH_4 + O_2^* \xrightarrow{k_{CH4}} CH_4^* + OH^* \]  \[ 2OH^* \xrightarrow{K_{OH2O}} H_2O + O_2^* + * \]  \[ 1/2 \]  \[ \sqrt{K_{O2}P_{O2}} \]  \[ r_{CH4} = k'_{CH4}P_{CH4}^{1/2}P_{O2}^{1/2} \]  \[ 0.005 \pm 0.01 \text{ kPa}^{-1} \]

Kinetic data cannot be used to determine whether H-abstraction occurs from gas phase CH4 or from CH4 weakly adsorbed at low coverages in step 2, because both predict rates proportional to CH4 pressure. These steps and the pseudosteady state assumption for all adsorbed species lead to CH4 conversion rates given by

\[ r_{CH4} = k'_{CH4}P_{CH4}^{1/2}P_{O2}^{1/2} \]  \[ k'_{CH4} \]  \[ 0.02 \text{ g}, 1073 \text{ K}, 101 \text{ kPa total pressure}, \text{ balance He} \]

Figure 3. Arrhenius plots for rate constants in the rate expression: rOCM = kOCM PCH4/2 + kOCM PrCH4 PrO2 (eq 19) (0.02 g, 1073 K, volume: 550 cm3, 10.7 kPa CH4, 1.8 kPa O2, 101 kPa total pressure, balance He).

K) gives an apparent activation energy (Eapp) of 290 ± 8 kJ mol1, consistent with previously reported values (280 kJ mol1). This activation energy reflects the combined contributions from the activation barrier for H-abstraction in step 2 (Ea,O2) and the enthalpy for dissociative O2 adsorption in step 1 (∆H O2)

\[ E_{app} = E_{a,O2} + \frac{1}{2} \Delta H_{O2} \]  \[ = 0.005 \text{ kPa}^{-1} \]

If O2(g) loses all degrees of freedom upon adsorption to form O2* (step 1), the measured K02 (0.005 kPa1 at 1073 K) corresponds to a ∆H O2 value of −176 kJ mol1. Equation 6 and measured Eapp values (290 ± 8 kJ mol1) then give an activation energy for step 2 (Ea,O2) of 378 kJ mol1. This energy is similar to that required to dissociate C–H bonds in CH4 (439 kJ mol1) without any concerted interactions with surfaces or other molecules; it is indicative of a late transition state along the reaction coordinate. In practice, O2* is expected to retain some translational freedom (leading to weaker M–O bonds and less negative ∆H O2 values), because the strength of O2* binding allow some surface migration at typical OCM reaction temperatures. O2 adsorption processes, however, must be exothermic
formation of mixed CH during OCM reactions was determined from the rate of CH4/CD4/O2 isotopic mixtures. The ratio of the isotopic to denote molecules with different character in the CH3 moiety is relatively small.

We have probed the kinetic relevance of C–H bond activation steps by measuring kinetic isotope effects (KIE) for CH4/O2 and CD4/O2 reactants (Table 1). Rates were measured by extrapolation to zero conversion to ensure anhydrous conditions. Normal KIE values (1.24–1.29, Table 1) were found at all O2 pressures (0.9–3.5 kPa), consistent with C–H bond activation as the kinetically relevant step, as discussed in more detail in the Supporting Information.

The extent to which C–H bond activation steps are reversible during OCM reactions was determined from the rate of formation of mixed CH3DxOy (0 < x < 4) isotopomers (here used to denote molecules with different x values) during reactions of CH3/CD3 isotopic mixtures. The ratio of the isotopic scrambling rate to the chemical conversion rate was negligible (<1) (Figure 4); these data show that C–H bond activation steps (step 2) are essentially irreversible during OCM reactions. CH3/D4 isotopomers gradually formed with increasing contact time and CH3 conversion as a result of homogeneous H-transfer reactions between CH3 and CH3 (or C2H6) (e.g., CH3 + CH3 → CH4 + C2H5).

The quasi-equilibrated nature of O2 dissociation steps (step 1) was confirmed from the rate of isotopic scrambling in dioxygen molecules during reactions of CH3/16O2/18O2 mixtures (Figure 4); these data show that C–H bond activation rate during the reaction of CH3/16O2/18O2 mixture measured a function of CH4 conversion at several O2 pressures (1.8–14.2 kPa; 42.6 kPa CH4).

Rates extrapolated to zero conversion were ~10 times larger for 16O18O isotopomers (via the reverse of step 1) than for CH4 chemical conversion (step 2). These data are consistent with fast and quasi-equilibrated O2 dissociation (eq 1). We note, however, that these relative rates differ by only a factor of ~10 and that the assumption of quasi-equilibrium may become inaccurate as CH4 pressure increases or O2 pressure decreases by commensurate factors, because these two molecules determine the rates at which Os* species react and form, respectively. The breakdown of the quasi-equilibrium assumption for O2 chemisorption as O2 is depleted with increasing conversion is addressed later (section 3.4).
are essentially zero, indicating that ethene forms only via dehydrogenation of primary C2H6 products, instead of directly from CH4 (or CH3 radicals). These data contradict previous proposals that C2H4 can form directly from CH4 via carbenic intermediates.33 Very low conversions (<1%) are essential to probe the identity of primary and secondary products because of the strong effects of H2O on OCM rates and C2 selectivities as CH4 conversion increases with residence time. Our rigorous extrapolation to low conversions shows unequivocally that C2H6, CO and CO2 are the only primary products formed from CH4/O2 reactants. CH3 radicals from CH4 (or CH3 radicals). These data contradict previous CO forms predominantly via CH3• reactions with gas-phase O2 formation rates more strongly than CO2 formation rates, recombine to form C2H6 (step 7), but may also react to give CO and CO2; CO also shows selectivity trends with residence time consistent with primary products, even though they form via CH3•, because these CH3• reactive intermediates are very reactive during OCM reactions and are present at their pseudosteady-state concentrations. Panels b and c in Figure 7 (and data from O2 pressure variations shown in Figure S1 in the Supporting Information) show that O2 pressures influence CO formation rates more strongly than CO2 formation rates, suggesting that CO2 forms predominantly via reactions of CH3• with O* (∼P(CH3)), either before or after CH3 desorption, while CO forms predominantly via CH3• reactions with gas-phase O2 (∼P(O2)). These findings are consistent with the sequence

\[ 2\text{CH}_3^+ + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M} \]  
(7)

\[ \text{CH}_3^+ + \text{O}_2 \rightarrow \text{CO} \]  
(8)

\[ \text{CH}_3^+ + \text{O}^* \rightarrow \text{CO}_2 \]  
(9)

in which M denotes a “third-body” that dissipates the energy released by radical recombination. These elementary steps and the assumptions of pseudosteady-state CH3 concentrations, quasi-equilibrated O2 dissociation, and low O2* coverages lead to rate equations of the form

\[ r_{\text{C}_2} = k_{\text{C}_2} P_{\text{CH}_3}^2 \]  
(10)

\[ r_{\text{CO}} = k_{\text{CO}} P_{\text{CH}_3} P_{\text{O}_2} \]  
(11)

\[ r_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CH}_3} P_{\text{O}_2}^{1/2} \]  
(12)

\[ P_{\text{CH}_3} = \frac{\sqrt{B^2 + 4k_{\text{C}_2} k' P_{\text{CH}_3} P_{\text{O}_2}^{1/2}} - B}{2k_{\text{C}_2}} \]  
(13)

(where \( B = k_{\text{CO}} P_{\text{O}_2} + k_{\text{CO}_2} P_{\text{O}_2}^{1/2} \))

Regressed rate constants34 were obtained from rates measured as a function of CH4 and O2 pressures (data from Figure 2, panels a and b). The curves drawn in Figure 7a–c illustrate the accuracy of these kinetic descriptions of OCM pathways. The effects of CH4 and O2 pressures on C2 selectivities are given by eq 14, which is derived from eqs 5 and 10–13, together with the regressed values of their respective rate constants

\[ \frac{r_{\text{C}_2}}{r_{\text{CO}} + r_{\text{CO}_2}} = \frac{1}{2} \left( 1 + \frac{4k_k' P_{\text{CH}_3} k_{\text{C}_2}}{(k_{\text{CO}} P_{\text{O}_2}^{1/2} + k_{\text{CO}_2} P_{\text{O}_2}^{1/2})^2} \right) \]  
(14)

At high selectivity ratios (∼>4), eq 14 can be simplified to

\[ \frac{r_{\text{C}_2}}{r_{\text{CO}} + r_{\text{CO}_2}} \approx \frac{k_k' P_{\text{CH}_3}}{(k_{\text{CO}} P_{\text{O}_2}^{1/2} + k_{\text{CO}_2} P_{\text{O}_2}^{1/2})^2} \]  
(15)

because the \((4k_k' P_{\text{CH}_3})/(k_{\text{CO}} P_{\text{O}_2}^{1/2} + k_{\text{CO}_2} P_{\text{O}_2}^{1/2})^2\) term is much larger than unity. This ratio increases with increasing CH4 pressure and decreasing O2 pressure (and thus with increasing CH4/O2 ratio) and also as surfaces become more reactive for CH4 activation to form CH3 radicals (larger \(k'\)). The \(k_k' / k_k - P\) ratio obtained for CH4 and CD4 reactants (1.25; Table 1) and its use in eq 15 indicates that C2 selectivities at a given methane pressure and oxygen reactant ratio (∼\((k_k' P_{\text{CH}_3} (k_{\text{CO}} P_{\text{O}_2}^{1/2} + k_{\text{CO}_2} P_{\text{O}_2}^{1/2})^2)\) would be ∼2% lower for CD4–O2 than for CH4–O2 reactions. Measured selectivities are almost identical for CH4 and CD4 at each O2 pressure (∼94%, ∼82%, and ∼78% selectivities at 0.9, 1.8, and 3.5 kPa O2, respectively). These similar selectivities may arise from positive but small isotope effects for kCO and kCO2, which reflect H-abstraction from methyl radicals and which cancel those for the numerator \((k_k' k'_k)\) in eq 15. We note that the form of eq 15 accurately describes primary selectivities in anhydrous mixtures and that these selectivities depend predominantly on CH4/O2 reactant ratios.

3.4. H2O-Mediated C–H Bond Activation Pathways. We examine next the mechanistic basis for the strong effects of H2O on CH4 conversion rates and C2 selectivities and yields (Figures 1a and 1b). The activation of C–H bonds in hydrocarbons by H2O without O2 co-reactants was probed using CH4/H2O/C2H6 (or CH4/H2O/o2at 1073 K in a recirculating batch reactor. CO and CO2 were not detected at any conditions, indicating that steam reforming reactions of CH4, C2H6, or C2H4 did not occur. These data also show that any prevalent H2O-mediated pathways require O2-derived O* species on catalytic surfaces for OH formation.

Laser-induced fluorescence was previously used to detect OH radicals when H2O/O2 mixtures were exposed to solid basic oxides that also catalyze OCM reactions.19–21 The presence of CH4 decreased OH concentrations present in H2O/O2 mixtures, suggesting that CH4 and H2O scavenge similar active oxygens at surfaces (O*).21 Thus, we conclude that OH radicals form via the coupling of step 3 with

\[ \text{H}_2\text{O} + \text{O}_4^* \rightleftharpoons \text{OH}^* + \text{OH}^* \]  
(16)

in which OH* and OH** denote radical and chemisorbed species, respectively. Previous studies20 have shown that OH radicals reach equilibrium concentrations on La2O3 solids (100 Pa H2O and O2; 1173 K) via

\[ \text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{OH}^* \]  
(17)

as a consequence of equilibrated steps 1, 3, and 16. OH radicals thus formed can subsequently abstract H atoms from CH4 via homogeneous pathways.
\[ \text{CH}_4 + \text{OH}^* \xrightarrow{k''_{\text{CH}_4 - \text{OH}^*}} \text{CH}_3^* + \text{H}_2\text{O} \quad (18) \]

This reaction is exothermic by 59 kJ mol\(^{-1}\) at 1073 K.\(^{35}\) When OH radicals are at equilibrium (via step 17), the rate of C—H activation (via step 18) becomes proportional to \(P_{\text{CH}_4}^{1/2}P_{\text{O}_2}^{1/4}P_{\text{H}_2\text{O}}^{1/2}\). The combined rates of CH\(_4\) reactions via surface \(O_{\text{e}^*}\)-mediated and OH-mediated H-abstractions are then given by

\[ r_{\text{CH}_4} = k'_{\text{CH}_4}P_{\text{CH}_4} + k''_{\text{CH}_4}P_{\text{CH}_4}^{1/2}P_{\text{O}_2}^{1/4}P_{\text{H}_2\text{O}}^{1/2} \quad (19) \]

where \(k''\) is given by \(k''_{\text{CH}_4 - \text{OH}^*}P_{\text{CH}_4}^{1/2}P_{\text{O}_2}^{1/4}K_{\text{CH}_4 - \text{OH}}\). \(K_{\text{CH}_4 - \text{OH}}\) is the rate constant for step 18, and \(P_{\text{O}_2}\) is the equilibrium constant for step 17. H\(_2\)O pressures were determined at each point by an oxygen balance on reactants and products. Figure 8a shows that incremental CH\(_4\) conversion rates introduced by H\(_2\)O-mediated pathways (the difference between rates with and without H\(_2\)O

**Figure 7.** C\(_2\)H\(_6\) (a), CO (b), and CO\(_2\) (c) formation rates extrapolated to zero conversion as a function of CH\(_4\) pressure measured in a flow reactor (0.05 g, 1073 K, 101 kPa total pressure, balance He). The curves denote the fitting results using optimized rate constants (eqs 10–13).

**Figure 8.** Incremental differential CH\(_4\) conversion rate (from measured differences between rates with and without H\(_2\)O) as a function of \(P_{\text{H}_2\text{O}}^{1/2}P_{\text{O}_2}^{1/4}\) (a) and (total) CH\(_4\) conversion differential rate as a function of O\(_2\) pressure (b) measured in a recirculating batch reactor. The arrows are in the direction of increasing contact time (0.02 g, 1073 K, volume: 275–650 cm\(^3\), 10.7 kPa CH\(_4\), 101 kPa total pressure, balance He, (●) 1.8 kPa O\(_2\); (■) 1.8 kPa O\(_2\), 0.4 kPa H\(_2\)O added; (□) 1.8 kPa O\(_2\), 0.9 kPa H\(_2\)O added; (○) 0.9 kPa O\(_2\), 0.4 kPa H\(_2\)O added).
and given by the second term in eq 19) are proportional to 

\[ P^{(0)}_{\text{CH}_4}/P^{(0)}_{\text{O}_2} \]  at low conversions (short contact times), consistent with quasi-equilibrated OH* formation steps (step 17) and with the kinetic relevance of OH-mediated H abstraction (step 18). The rate constants for OH-mediated H abstraction (\( k'_H', 0.21 \mu \text{mol} \text{ g}^{-1} \text{ s}^{-1} \text{ kPa}^{-3/4} \)) and surface-mediated H abstraction (\( k'_H, 0.04 \mu \text{mol} \text{ g}^{-1} \text{ s}^{-1} \text{ kPa}^{-3/2} \)) at 1073 K give corresponding rates of 1.7 and 0.7 \( \mu \text{mol} \text{ g}^{-1} \text{ s}^{-1} \) for the two terms in eq 15 at 0.4 kPa H\(_2\)O (10.7 kPa CH\(_4\); 1.8 kPa O\(_2\)), indicating the significant contributions from OH-mediated pathways at typical OCM conditions.

Figure 8a shows that differential CH\(_4\) conversion rates decrease abruptly at longer contact times, as O\(_2\) is essentially depleted from the reactant stream. These trends reflect a decrease in the rate of O\(_2\) chemisorption and an increase in the rate of scavenging of chemisorbed oxygen by H\(_2\)O as H\(_2\)O concentration increases with increasing conversion, which prevents step 1 and subsequent O\(_2^*\) reactions (step 16) from reaching equilibrium, because of their kinetic coupling with the CH\(_4\) and H\(_2\)O activation steps that remove O\(_2^*\) (steps 2 and 16, respectively). We note that O\(_2\) chemisorption (eq 1) and the O\(_2^*\) species formed are required for the ultimate activation of CH\(_4\) (step 2), C\(_2\) products, and H\(_2\)O (step 16), irrespective of whether C–H bond activation occurs directly by O\(_2^*\) species or by the OH radicals derived from such species. Figure 8b shows that differential CH\(_4\) conversion rates become proportional to O\(_2\) pressure at low O\(_2\) concentrations (<0.6 kPa) and modest H\(_2\)O pressures (>0.5 kPa), suggesting that O\(_2\) chemisorption steps indeed become kinetically relevant and nearly irreversibly (step 20, forward reaction of step 1)

\[ \text{O}_2 + 2* \rightarrow 20s^* \]  (20)

\[ r = k_{\text{OH}} P_{\text{O}_2} \]  (21)

where \( K_{\text{OH}} \) is approximately 3.6 \( \mu \text{mol} \text{ g}^{-1} \text{ s}^{-1} \text{ kPa}^{-1} \). The rate constant calculated from the collision frequency of O\(_2\) with surfaces at 1073 K is 3 \( \times 10^7 \) \( \mu \text{mol} \text{ g}^{-1} \text{ s}^{-1} \text{ kPa}^{-1} \), indicating that sticking coefficients are \( \sim 10^{-7} \), a small value consistent with the low concentration of O\(_2\) prevalent during steady-state OCM reactions. We note that, when H\(_2\)O is present at significant concentrations, its activation (step 16) is considered to remain much faster in both forward and reverse directions than H-abstraction from CH\(_4\) on the catalyst surface (step 2) at OCM practical conditions where H\(_2\)O prevails: therefore, even at low O\(_2\) concentrations, the presence of H\(_2\)O (e.g., at high CH\(_4\) conversions) leads to predominant activation of CH\(_4\) via OH-mediated instead of surface (O\(_2^*\))-mediated routes.

When prevalent O\(_2\) pressures ensure quasi-equilibrated OH* concentrations, CH\(_4/O_2/H_2O\) and CH\(_3/O_2/D_2O\) mixtures should react at similar rates because of the weak nature of the consequent thermodynamic H/D isotope effects on OH/OD concentrations. The data in Table 1 show that the measured KIE for CH\(_4/O_2/D_2O\) mixtures, given by

\[ \text{KIE} = \left( \frac{k''_{\text{CH}_4-\text{OH}}}{k''_{\text{CD}_4-\text{OH}}} \right) \left( \frac{k'_{\text{OD}}}{k'_{\text{OD}}} \right)^{1/4} \]  (22)

is 1.08. In eq 22, \( K_{\text{OD}} \) and \( k''_{\text{CH}_4-\text{OH}} \), \( k''_{\text{CD}_4-\text{OH}} \) are the equilibrium and rate constants for steps 23 and 24, respectively.

Using available thermodynamic data for entropy and enthalpy and their temperature dependence, \( (K_{\text{OH}}/K_{\text{OD}})^{1/4} \) was estimated to be 1.04 at 1073 K. Experimental data for the rate constant of step 24 are unavailable at relevant temperatures (~1000 K), but the \( (K_{\text{CH}_4-\text{OH}}/K_{\text{CH}_4-\text{OD}})^{1/4} \) ratio is expected to be near unity at 1073 K because both numerator and denominator terms involve the activation of a C–H bond and the formation of a O–H bond. Thus, the overall KIE value (eq 22) is expected to be very close to unity, consistent with measured values (1.08, Table 1).

OH-mediated pathways for activation of C–H bonds in CH\(_4\) in kinetically-relevant steps (step 18) would give normal KIE values for CD\(_4–O_2–H_2O\) reactants. Table 1 shows that the measured KIE value was 1.44 for these reactants, consistent with kinetically-relevant C–H bond cleavage in CH\(_4\) (step 18). The absence of CH\(_2\)D\(_4\) (0 < x < 4) isotopomers during reactions of CH\(_4/D_2O/O_2\) or CD\(_4/H_2O/O_2\) mixtures confirms the irreversible nature of CH\(_4\) activation steps (steps 2 and 18) and avoids the isotopic dilution of methane that would otherwise prevail. These measured KIE values reflect the combined contributions of surface-catalyzed and OH-mediated C–H bond activation. The rates and corresponding KIE for OH-mediated pathways (the second term in eq 19) can be obtained by subtracting the rates for anhydrous pathways (the first term in eq 19) obtained in section 3.2 from the measured rates for each methane isotopomer. The KIE value for OH-mediated pathways, given by

\[ \text{KIE} = \frac{k''_{\text{CH}_4-\text{OH}}}{k''_{\text{CD}_4-\text{OH}}} \]  (23)

\[ \text{CD}_4 + \text{OD}^* \xrightarrow{k''_{\text{CD}_4-\text{OH}}} \text{CD}_3^* + \text{HDO} \]  (24)

where \( k''_{\text{CH}_4-\text{OH}} \) and \( k''_{\text{CD}_4-\text{OH}} \) are rate constants for steps 18 and 26, respectively, is 1.58. We note that this small KIE value for H-abstraction by OH* is consistent with high reactivity of OH* leading to relatively product character and to a relatively late transition state, in which C–H bonds would be essentially cleaved. The involvement of less reactive radicals, such as H, O, and HO\(_2\) in C–H bond activation, as discussed in the next section, would lead to KIE values larger than for abstraction of H atoms exclusively by OH.

We examine next the temperature dependence of OH-mediated pathways (the second term in eq 19) by measuring \( k' \) at 993–1123 K and O\(_2\) pressures sufficient for quasi-equilibrated O\(_2\) chemisorption (>1.5 kPa) (Figure 3). This activation energy \( (E_{\text{app}}; 161 \pm 9 \text{ kJ mol}^{-1}) \) reflects the combined contributions from the activation barrier for H-abstraction from CH\(_4\) by OH* (\( E_{\text{a,OH}} \) (eq 18), and the enthalpy for quasi-equilibrated OH radical formation reactions (\( \Delta H_{\text{OH}} \), step 17)

\[ E_{\text{a,app}} = E_{\text{a,OH}} + \frac{1}{4} \Delta H_{\text{OH}} \]  (25)

\[ \text{CD}_4 + \text{OD}^* \xrightarrow{k''_{\text{CD}_4-\text{OH}}} \text{CD}_3^* + \text{HDO} \]  (26)

The reported value of \( \Delta H_{\text{OH}} \) (for step 17) at 1073 K is 650 kJ mol\(^{-1}\),\(^3\) thus, eq 27 gives a \( E_{\text{a,OH}} \) value for C–H bond activation by OH radicals of nearly zero (0 ± 9 kJ mol\(^{-1}\)). Such
small activation barriers (27 kJ mol\(^{-1}\))\(^{38}\) have been previously reported for this reaction (step 18). These activation energies are much smaller than those for surface-mediated C–H bond activation pathways (290 kJ mol\(^{-1}\)), confirming the very reactive nature of OH radicals compared with chemisorbed oxygen (O(\(*\)) species and the proposed late nature of transition states for OH-mediated C–H bond activation pathways.

3.5. Effects of H\(_2\)O on Primary and Secondary Reactions in Oxidative Coupling of Methane. 3.5.1. Isotopic Tracer Studies for OCM Reaction Pathways. Accurate measurements of kinetic constants in sequential reaction pathways (scheme 1) require the use of isotopic tracers, in which \(^{13}\)CH\(_4\)/O\(_2\) reactants are used together with unlabeled versions of the various \(^{12}\)C\(_2\) molecules, such as C\(_2\)H\(_6\), with weaker C–H bonds than those in CH\(_4\) compared with more reactive abstractors. \(^{13}\)CH\(_4\) conversion rates and \(^{13}\)C\(_2\)H\(_6\)/\(^{13}\)CO\(_2\) product ratios were not affected by adding \(^{12}\)C\(_2\)H\(_6\) or \(^{12}\)C\(_2\)H\(_4\) to \(^{13}\)CH\(_4\)/O\(_2\) reactants in either empty reactors or in those containing catalysts. These data confirm our previous conclusions that C\(_2\) products cannot give rise to the changes in rates and selectivities observed as conversion increases with increasing contact time (Figure 1a).

First-order rate constants for all reactions in Scheme 1 were measured by isotopic tracing using \(^{13}\)CH\(_4\)/O\(_2\) reactants mixed with \(^{12}\)C\(_2\)H\(_6\), \(^{12}\)C\(_2\)H\(_4\), or \(^{12}\)C\(_2\)H\(_8\) in the presence and absence of added H\(_2\)O on Mn/Na\(_2\)WO\(_4\)/SiO\(_2\) at 1073 K. Measured rates were extrapolated to zero conversions so that they reflect the H\(_2\)O pressure in the starting reactant mixture in both cases (0 or 0.4 kPa H\(_2\)O) before H\(_2\)O forms via OCM reactions. Table 2 shows rate constants under anhydrous conditions (“surface-mediated” pathways) and via OH-mediated pathways, estimated by comparing data with and without added H\(_2\)O. The rate constants for steps 1–7 in Scheme 1 (\(k'_1\)–\(k'_7\)) are all nonzero for OH-mediated pathways, indicating that H\(_2\)O provides independent pathways for the activation of C–H bonds in all hydrocarbons. Thus, the beneficial effects of H\(_2\)O and the concomitant contributions of OH-mediated pathways must reflect the different (and more desirable) preference with which these pathways activate C–H bonds in CH\(_4\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), and C\(_3\)H\(_6\) relative to the corresponding steps mediated by O(\(*\)) species at surfaces, which prevail under anhydrous conditions.

The \(k'_1/k'_2\) ratios (\(k'_2\) for steps in Scheme 1) were larger for OH-mediated (\(~8\)) than for surface-mediated (\(~5\)) routes (Table 2), consistent with the higher initial C\(_3\) selectivities measured when H\(_2\)O was present (Figure 1b). These data reflect an increase in CH\(_3^+\) formation rates as a result of additional CH\(_4\) activation pathways mediated by OH radicals and introduced by H\(_2\)O molecules and their activation on catalyst surfaces (step 18). These higher radical concentrations increase the rate of bimolecular CH\(_3^+\) recombination steps (eq 10) relative to that for unimolecular CH\(_3^+\) oxidation to CO\(_2\) (eqs 11 and 12). CH\(_3\) radical formation via OH-mediated pathways (\(r_{CH_3} = k^*P_{CH_3}P_{O_2}^{1/2}P_{H_2O}^{3/4}\)) gives a selectivity ratio of the form

\[
r_{C_2}/(r_{CO} + r_{C0_2}) = \frac{1}{2} \left(1 + \frac{4k'_C k'_P P_{CH_3} P_{O_2}^{1/2} P_{H_2O}^{3/4}}{(k_{CO} + k_{CO_2} P_{O_2} P_{H_2O}^{3/4})} \right)
\]

which simplifies to eq 29 at the high prevalent selectivity ratios (>4)
The ratio expected from rate constants measured under anhydrous conditions is $\sim 13$, while measured values are $\sim 8$, apparently because of small contributions from less reactive (and more sensitive to C–H bond strengths) radicals (e.g., H, HO2), which would give ratios higher than predicted from eq 29, because of higher $k_{CO}$ and $k_{CO_2}$ values.

Next, we compare the relative rates of activation of C–H bonds in CH4, C2H6, and C2H4 via H-abstraction on surfaces (O,*) and with OH radicals in the context of the rate constants reported in Table 2. The ubiquitous decrease in C2+ selectivities observed with increasing CH4 conversion and contact time reflects the relative reactivities of reactants and products, which arises, in turn, from their different rate constants. Figure 10 shows the ratios of C2H6 and C2H4 activation rate constants relative to those for CH4 activation via surface-catalyzed and OH-mediated routes together with the homolytic dissociation energies for each of the C–H bonds involved. These ratios are smaller for OH-mediated than for surface-mediated pathways, consistent with the higher C2 yields attained when H2O was present (Figure 1b). These rate constant ratios decreased monotonically with increasing C–H bond energies for OH-mediated pathways (Figure 10), consistent with the sole kinetic-relevance and homolytic character of the H-abstraction steps involved. Rate constant ratios agree well with those expected from ratios reported for the corresponding rate constants for H-abstraction by OH radicals via homogeneous reactions at 1073 K (CH4, 1.6 $\times$ 10^{12}; C2H6, 5.5 $\times$ 10^{12}; C2H4, 1.2 $\times$ 10^{12} cm3 mol$^{-1}$ s$^{-1}$), consistent with the involvement of these gas-phase radicals in the kinetically-relevant steps for the activation of C–H bonds in CH4 and C2H6. The activation barriers for such steps follow Brønsted–Evans–Polanyi relations:

$$|\Delta E_a| = \alpha |\Delta H_f^\ddagger|$$

where $\alpha$ is the Brønsted–Evans–Polanyi parameter, $\Delta E_a$ is the difference between the activation energies for two homologous steps, and $\Delta H_f^\ddagger$ is the difference between the respective reaction enthalpies (in this case given by differences in C–H bond strengths). Similar monotonic trends were not evident for surface-mediated pathways (Figure 10), for which C2H4 molecules appear to react much faster than expected from the strength of their C–H bonds, apparently because their $\pi$-electrons lead to stronger interactions with Lewis acid sites on oxide catalyst surfaces.

The combined rate constants for C2H6 activation ($k_1 + k_2$) were $\sim 30$ times larger than for CH4 activation ($k'_1 + k'_2$) in the case of the surface-mediated pathways prevalent under anhydrous conditions, as expected from the weaker C–H bonds in C2H6 (423 kJ mol$^{-1}$) compared with those in CH4 (439 kJ mol$^{-1}$). This ratio was much smaller (6.8) for OH-mediated pathways, even though both surface-mediated and OH-mediated routes involve kinetically-relevant C–H bond activation in CH4 and C2H6. Thus, the different specificity for C–H bond activation via these pathways must reflect differences in the reactivity of the two abstractors involved (i.e., OH$^\ddagger$ and O,*) and in their sensitivity to C–H bond energies.

Abstractors that form stronger bonds with H-atoms react with lower sensitivity to the strength of the C–H bond being activated. We have previously shown that reactions with energetic H-abstractions, such as OH radicals, react less selectively with the weaker C–H bonds in HCHO (relative to stronger C–H bonds in CH4) than more stable radicals, such as O and HO2. OH radicals are among the most thermodynamically unstable and reactive H-abstractors; they form very strong O–H bonds within the stable H2O molecules formed in such processes. The ratio of the rate constants for H-abstraction from ethane and methane by gas-phase OH radicals ($k_{CH_2}^{OH}/k_{CH_4}^{OH}$) is 3.3 $\sim$ 4.4, consistent with the involvement of these gas-phase radicals in the kinetically-relevant steps for the activation of C–H bonds in CH4 and C2 hydrocarbons. The activation barriers for such steps follow Brønsted–Evans–Polanyi relations.

$$\frac{r_{C_2}}{r_{CO} + r_{CO_2}} = \sqrt[3]{\frac{k_{C^0} k_{P} p_{H_2}^{1/2}}{(k_{CO} p_{O_2}^{1/2} + k_{CO_2}) r_{CO_2}^{3/4}}}$$

(29)

Figure 10. Ratio of rate constants for conversion of C2H6 ($k'_1 + k'_2$) and C2H4 ($k_1 + k_2$) to that for conversion of CH4 ($k'_1 + k'_2$) as a function of C–H bond dissociation energies. (●) Surface-mediated pathway; (■) OH-mediated pathway; (○) H abstraction by OH radicals in the gas-phase.
Small concentrations of higher hydrocarbons (predominantly C3H6) were detected as CH4 conversion increased, because recombination reactions of methyl radicals with C2 products and respective radicals become important as C2 concentrations increase (e.g., C2H3 + CHH2 → C3H6; C3H3 + CHH2 → C3H6 + H). Therefore, we include C3H6 reactions in Scheme 1. The rate of C3 formation and oxidation were probed by isotopic tracing using C3H6O2/(H2O) reactants. The k/f/k′ ratios for OH-mediated pathways (~2) of C3H6 are much smaller than for surface-mediated pathways (~12) (Table 2). The rate constants for C3H6 oxidation (k/f) are much larger than for C2H6 (k/f) or C2H4 (k′/f) oxidation via the respective OH-mediated and surface-catalyzed pathways, consistent with the weak nature of allylic C−H bonds in C2H6 (372 kJ mol⁻¹).12 These results suggest that chain growth contributes significantly to yield losses in OCM reactions, as proposed previously.13 The observed selectivity to higher hydrocarbons (C1+) was relatively low (~4.5%) at the modest pressures used here (4−10 kPa CH4). Higher pressures, required for relevant OCM practice, favor radical recombination and may lead to higher C2+ formation rates and to more significant C2+ yield losses via rapid oxidation of higher alkanes and alkenes.

Figure 11, panels a and b, shows measured OCM product selectivities and yields, together with predictions from a kinetic treatment based on the steps in Scheme 1 and independently measured rate constants for surface-catalyzed and OH-mediated routes (Table 2). Maximum C2 and C2+ yields were 24% and 26% (Figure 11b), respectively, similar to the highest reported yields.8 The network in Scheme 1 accurately describes measured yields as a function of CH4 conversion (Figure 11b). In contrast, rate constants for surface-mediated pathways predict maximum C2+ yield of only 14%,14 because of the high k/f/k′ (~4) and k/f/k′ (~12) ratios for the surface-mediated pathways that prevail under anhydrous conditions. Maximum attainable C2+ yields are limited in practice by the relative reactivity of C2 (and C1+) and CH4 at conditions where highly reactive OH radicals predominate account for the kinetically-relevant H-abstraction from hydrocarbon reactants and products.

3.5.2. Simulation of OH-Mediated Pathway Model and Attainable OCM Yields. Next, we report simulation results to illustrate the effects of OH radical formation on OCM rates and selectivities, using available ChemKin codes26 and reported rate and equilibrium constants for relevant gas phase reactions.14 Previous studies have treated the coupling of homogeneous and surface-catalyzed routes via the formation of organic radicals through C−H bond activation on O₄⁻ species. Here, we include a fast surface reaction that forms equilibrium concentrations of OH radicals, which are not attainable via purely homogeneous kinetic routes

\[
O_2 + 2H_2O \rightarrow 4OH^-
\]

This is implemented by using arbitrarily large pre-exponential factors for the forward and reverse steps of this reaction, while maintaining their rate ratio consistent with the thermodynamics of the overall reaction. Figure 11b shows C2+ yields predicted by these simulations. At conditions similar to those used in our experiments (10 kPa CH4, O2 1.7 kPa, 1073 K) and with O2 addition after its depletion (the arrows in Figure 11b), C2+ yields are similar to measured values (~30%; Figure 11b). This agreement with experiment is reassuring in view of the absence of undesired side reactions of C2+ products on catalyst surfaces in this model and suggests that OH radicals indeed account for most H-abstraction events at relevant H2O concentrations. These simulations were extended to reactant pressures and temperatures unattainable in our experimental setup within safe operating regimes but potentially useful in OCM industrial practice. Throughout these simulations, we have maintained quasi-equilibrated OH radical formation steps; therefore, C2 yields represent upper bounds, because they neglect less selective surface-mediated steps or OH concentrations below equilibrium levels. The inlet ratio of CH4 to O2 was set to 6, as in our experiments, and O2 was added after its pressure decreased below 0.1 kPa until C2 yields reached a maximum value. Figure 12 shows the highest attained C2 yields at each temperature and CH4 inlet pressure. Higher CH4 pressures decreased C2 yields because they favor chain growth and the formation of reactive C1+ species, which form CO, more rapidly than CH2 or C2H6. Temperatures above 1073 K increased C2 yields, because the activation barrier for OH reactions with CH4 is higher than for the respective reaction with C2H6, C3H4, and C4+. This is implemented by using arbitrarily large pre-exponential factors for the forward and reverse steps of this reaction, while maintaining their rate ratio consistent with the thermodynamics of the overall reaction. Figure 11b shows C2+ yields predicted by these simulations. At conditions similar to those used in our experiments (10 kPa CH4, O2 1.7 kPa, 1073 K) and with O2 addition after its depletion (the arrows in Figure 11b), C2+ yields are similar to measured values (~30%; Figure 11b). This agreement with experiment is reassuring in view of the absence of undesired side reactions of C2+ products on catalyst surfaces in this model and suggests that OH radicals indeed account for most H-abstraction events at relevant H2O concentrations. These simulations were extended to reactant pressures and temperatures unattainable in our experimental setup within safe operating regimes but potentially useful in OCM industrial practice. Throughout these simulations, we have maintained quasi-equilibrated OH radical formation steps; therefore, C2 yields represent upper bounds, because they neglect less selective surface-mediated steps or OH concentrations below equilibrium levels. The inlet ratio of CH4 to O2 was set to 6, as in our experiments, and O2 was added after its pressure decreased below 0.1 kPa until C2 yields reached a maximum value. Figure 12 shows the highest attained C2 yields at each temperature and CH4 inlet pressure. Higher CH4 pressures decreased C2 yields because they favor chain growth and the formation of reactive C1+ species, which form CO, more rapidly than CH2 or C2H6. Temperatures above 1073 K increased C2 yields, because the activation barrier for OH reactions with CH4 is higher than for the respective reaction with C2H6, C3H4, and C4+. These simulations show, however, an optimum intermediate temperature for maximum C2 yields (e.g., ~1250 K at 10 kPa CH4) partly because, for a given conversion, the ratio of the concentrations of C2H4 to CH3 increases with temperature so that higher hydrocarbon formation (C3, C4; e.g., CH3 + C2H3 → C3H4) (and their subsequent combustion) becomes comparatively faster than C2 formation (CH3 + CH3 → C2H6) in this kinetic model. In practice, the higher measured activation energies for surface-mediated pathways (290 kJ
mol^{-1}) compared with OH-mediated pathways (161 kJ mol^{-1}; Figure 3) would lead to increasing contributions from less selective surface-mediated routes as the reaction temperature increases, making these higher C2 yields at high temperature unattainable.

We have also examined pathways for CO oxidation during OCM using 12CH4/13CO/O2 isotopic mixtures (Figure 13) with and without added H2O; H2O can introduce water–gas shift pathways (CO + H2O ⇌ CO2 + H2) that form CO2 without direct involvement of O2. Measured 13CO oxidation rates were proportional to 13CO pressure and independent of H2O concentrations. These results indicate that CO oxidation occurs via surface-mediated pathways on O, species that also activate C–H bonds and that water–gas shift reactions do not occur at detectable rates on Mn/Na2WO4/SiO2 even at >1000 K. First-order CO oxidation rate constants (Scheme 1) are significantly larger than for CH4 activation with O* (k_4/(k'_1 + k'_2) ~ 7, Table 2), suggesting that CO2 is formed preferentially instead of CO via surface-mediated pathways. The presence of H2O increased both 12CO and 13CO formation rates (from 13CH4) because OH-mediated CH4 activation routes also form 13CO and 13CO2 (k'_3; Scheme 1). These results also show that OH radicals do not react with CO to form CO2 either directly (to form CO2 and H) or via reactions with other species derived from OH radicals.

Figure 14 shows measured CO/CO2 ratios for experiments in which water was (i) added; (ii) allowed to accumulate during OCM; or (iii) removed as it formed in OCM reactions. CO/CO2 ratios remained relatively low (~0.5), even at high CH4 conversions, when H2O was continuously removed because prevalent surface-mediated pathways convert hydrocarbons predominantly to CO2 (step 9). As H2O formed in OCM reactions were allowed to accumulate, CO/CO2 ratios increased with increasing concentration and H2O concentration. The addition of H2O to CH4–O2 reactants gave higher CO2/CO ratios, because OH-mediated pathways lead to radical species that preferentially form CO from hydrocarbons via homogeneous pathways. CH4 and C2 oxidation in empty reactors led to very high CO/CO2 ratios (~5), consistent with the preferential formation and significant stability of CO in homogeneous oxidation pathways and with the known free radical pathways that form significant amounts of CO during homogeneous combustion at low temperatures.38
Oxidative Coupling of Methane

Figure 15. Effects of O2 partial pressure (a) on C2+ selectivity (b) as a function of CH4 conversion measured in a recirculating batch reactor (0.02 g, 1073 K, volume: 550 cm³, 4.0 kPa CH4, 101 kPa total pressure, balance He. (●) O2 added; (○) staged O2 introduction.

TABLE 3: Rate of CH4 Conversion and Rate Ratio of CH4 Conversion for C2 Formation to CO Formation at Different Kinetic Regimes (r1, r2 in Scheme 1, See Eqs 15, 29, and 31)

<table>
<thead>
<tr>
<th>surface O*</th>
<th>gas phase OH</th>
<th>O2 chemisorption limiting</th>
</tr>
</thead>
<tbody>
<tr>
<td>rCH4</td>
<td>k′(CH4)1(O2)0.25</td>
<td>k′′(CH4)1(O2)0.25(H2O)0.25</td>
</tr>
<tr>
<td>r1/r2</td>
<td>[(kC1PCH4)/(kC2P02) + kC02]^(1/2)</td>
<td>[(kC1PCH4)/(kC2P02) + kC02]^(1/2)</td>
</tr>
</tbody>
</table>

The dependence of hydrocarbon conversion rates (CH4, C2H6, C3H8, and C4H10) on O2 pressure is the same for all hydrocarbons and a given H-abstractor (OH or O*). The data in Figure 15b show that C2 yields are essentially unaffected by O2 pressure. At CH4 conversions above 40%, C2+ selectivities were actually lower for staged O2 introduction than for co-fed experiments. At the low O2 pressures prevalent in these staged experiments, the concurrent presence of H2O leads to irreversible and rate-determining O2 chemisorption steps at all conversion levels; in this kinetic regime, O2 pressures do not affect primary C2 selectivities (r1/r2) at low conversions (eq 31, Table 3). As H2O forms during OCM reactions, quasi-equilibrated H2O-O* reactions form OH radicals that become the predominant H-abstractors and all C–H bond activation pathways become faster as H2O concentrations increase with increasing conversion levels.

We probe next the sensitivity of each reactant and product conversion rate (r1 – r2) to O2 pressure. In the absence of H2O, surface oxygens (O*&) are involved in kineticl-relevant C–H bond activation steps for both CH4 reactants and OCM products and rates are proportional to O*& concentrations (and thus to P02^(1/2)) for all C–H bond activation steps. As H2O forms during OCM reactions, quasi-equilibrated H2O-O* reactions form OH radicals that become the predominant H-abstractors and all C–H bond activation steps become proportional to P02^(1/2) (eq 19) when O2 chemisorption (step 1) is quasi-equilibrated and to P01 as this latter step becomes irreversible and kineticl-relevant (Figure 8b, step 20).

The equations for these ratios when OCM reactions occur via the three routes mentioned above are shown in Table 3. The effects of O2 pressure on selectivity are stronger for OH-mediated pathways (eq 29, r1/r2 ∼ (A^2 P02^4)^-1, where A = kCO/P02^(1/2) + kCO2) than for surface-mediated pathways (eq 15, r1/r2 ∼ (A^2 P02^4)^-1). For O2-limiting pathways, this selectivity ratio becomes proportional to r1/r2 ∼ (A^2 P02^4)^-1 (eq 31) and least sensitive to O2 pressure. This accounts, at least in part, for the preferential effects of O2 pressure on selectivity at low conversions (Figure 1) and for the apparent insensitivity to O2 pressures at high conversions that lead to irreversible O2 chemisorption steps and low O*& coverages. These trends reflect, in turn, the concurrent decrease in O2 chemisorption rates and the increase in the rate of scavenging of chemisorbed oxygen via OH-mediated CH4 activation pathways, which become faster as H2O concentrations increase with increasing conversion levels.

The dependence of hydrocarbon conversion rates (CH4, C2H6, C3H8, and C4H10) on O2 pressure is the same for all hydrocarbons and a given H-abstractor (OH or O*). The data in Figure 15b show that C2 yields are essentially unaffected by O2 pressure. At CH4 conversions above 40%, C2+ selectivities were actually lower for staged O2 introduction than for co-fed experiments. At the low O2 pressures prevalent in these staged experiments, the concurrent presence of H2O leads to irreversible and rate-determining O2 chemisorption steps at all conversion levels; in this kinetic regime, O2 pressures do not affect primary C2 selectivities (r1/r2) at low conversions (eq 31, Table 3), as discussed above. Low O2 pressures, however, decrease the rate of all surface-catalyzed reactions involving O*&, including those leading to OH radicals involved in homogeneous C–H bond activation steps, because they all have positive kinetic orders.
in $\text{O}_2$ (eqs 19 and 21). The consequent decrease in CH$_3$ concentrations leads to lower C$_2$ selectivities, because of the bimolecular nature of CH$_3$ recombination steps that form C$_2$ (eq 10), which depend on CH$_3$ concentrations more strongly than the unselective unimolecular pathways that form CO from CH$_3$ radicals (eqs 11 and 12).

We note that similar experiments and kinetic analyses on SrO/La$_2$O$_3$ solids, which also catalyze OCM, did not detect significant effects of H$_2$O on rates or selectivities. These catalysts gave lower maximum yields than Mn/Na$_2$WO$_4$/SiO$_2$. These findings indicate that OH formation rates depend sensitively on the identity of the catalyst and that the unique selectivity and yields reported on Mn/Na$_2$WO$_4$/SiO$_2$ reflect, at least in part, its ability to form quasi-equilibrated OH radical concentrations from H$_2$O–$\text{O}_2$ at conditions also required for surface-mediated OCM pathways.

Maximum OCM yields would require conditions in which OH radicals act as the predominant H-abstractors, but which also maintain quasi-equilibrated O$_2$ chemisorption steps. OH-mediated pathways are more sensitive to O$_2$ pressure than surface O$_2^-$-mediated pathways; thus, decreasing O$_2$ pressures would improve selectivities as long as OH concentrations can be maintained at equilibrium levels, a requirement that can be met only at sufficiently high O$_2$ pressures. These findings and interpretations suggest that intermediate O$_2$ pressures are optimal and that these optimal values depend sensitively on the prevalent H$_2$O concentration at a given point in the reactor and on its concomitant effect on the rate OH-mediated pathways. The consequences of these optimization strategies can be accurately probed as a result of the unprecedented detail in the kinetic models that we report here for the first time and of the use of experimental reactors that can be used to rigorously validate the kinetic models and their use in these staging protocols.

4. Conclusions

Attainable C$_2$ yields for OCM are limited by the intrinsic reactivity of C$_2$ (and C$_3$-) relative to CH$_4$ at conditions where highly reactive OH radicals are responsible for the kinetically-relevant H-abstraction from each hydrocarbon. Our rigorous kinetic measurements revealed the supplementary and predominant C–H activation pathways mediated by OH free radicals formed from H$_2$O/O$_2$ mixtures during OCM on Mn/Na$_2$WO$_4$/SiO$_2$. Isope effects and scrambling experiments using CD$_2$/CH$_2$ and/or D$_2$O/H$_2$O showed that C–H bond activation was irreversible and kinetically-relevant both in the presence and the absence of H$_2$O, and that O–H bond activation steps were not involved in the kinetically-relevant steps. Scrambling experiments using $^{13}$O$_2$–$^{16}$O$_2$ showed that O$_2$ dissociation was quasi-equilibrated only at high O$_2$/H$_2$O ratios. At low O$_2$/H$_2$O ratios, O$_2$ chemisorption steps became no longer quasi-equilibrated and nearly irreversible, and limit the overall conversion rates, where the OCM selectivity is insensitive to O$_2$ pressures. Isotopic tracer studies using $^{13}$CH$_2$/O$_2$/H$_2$O with $^{12}$C$_2$H$_6$, $^{13}$C$_2$H$_4$ or $^{12}$C$_2$H$_6$ mixtures showed that rate constant ratios $k_{c_{\text{CH}}}/k_{\text{CH}}$ and $k_{\text{CH}_2}/k_{\text{CH}_2}$ were smaller for OH-mediated pathways than for surface-mediated pathways, consistent with improved C$_2$ selectivities and yields in the presence of H$_2$O, which are ascribed to (1) enhanced steady-state CH$_3$ radical concentrations introduced by OH-mediated pathways and the second-order nature of CH$_3$ radicals for their coupling, compared to the first-order nature of their oxidation process, (2) the reactive nature of OH radicals which give unselective H-abstraction to intrinsic C–H bond strengths in hydrocarbons compared to O$_x^*$ as less reactive H-abstractors, and (3) avoiding strong adsorption of C$_2$H$_4$ on surfaces that favor its oxidation, by the gas-phase OH radical routes. C$_2$ and higher hydrocarbon formation, which have bimolecular nature of carbonaceous radicals and are favored at high pressures, in turn lead to rapid combustion and reduce maximum attainable yields. Mechanism-based rate equations comprising rate-determining C–H bond activation by surface-mediated and OH-mediated routes accurately describes the effects of pressure and residence time on rates and attainable C$_2$ yields. The maximum C$_2$ yields measured were unaffected by staging introduction of O$_2$ in OCM reactors because of the same dependence of O$_2$ pressure on the C–H bond activation rates for CH$_4$, C$_2$H$_6$, and C$_2$H$_4$ and the insensitivity of OCM selectivity to O$_2$ pressure at O$_2$ chemisorption limiting conditions.

Acknowledgment. This study was supported by BP as part of the Methane Conversion Cooperative Research Program at the University of California at Berkeley. The authors acknowledge Drs. Ayman D. Allian, Aditya Bhan, Josef Macht, and Xinyu Xia, and Mr. Rajamani Gounder of the University of California at Berkeley for extensive technical comments and suggestions about the contents and interpretations in this manuscript. The technical guidance of Drs. Theo Fleisch and Sander Gaemers of BP are also acknowledged with thanks.

Supporting Information Available: Additional explanation of experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(22) Gaffney, A. M. U.S. Patent, 4788372.
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(34) The rate constant optimization is calculated using Athena Visual Studio Version: 10.7. Stewart and Associates Engineering Software, Inc. More details are available in Supporting Information (Scheme S1, Table S1, and Figure S2).
(41) Dumesic, J. A.; Rudd, D. F.; Aparicio, L. M.; Rekoske, J. E.; Treviño, A. A. The Microkinetics of Heterogeneous Catalysis; American Chemical Society: Washinton, DC, 1993.

JP9001302