Kinetic and Catalytic Consequences of Reactive Oxygen Atoms during CH_4 Conversion on Group VIII Metal Clusters

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Introduction

CH_4 reforming on Group VIII metal clusters can be described by a kinetically coupled CH_4 decomposition-oxidation cycle [1-2]. The initial dissociation of C-H bonds on vicinal metal atoms limits reforming rates; the subsequent scavenging of CH_x species by O* and OH* species derived from H_2O or CO_2 is fast and quasi-equilibrated. These oxidation steps are kinetically-irrelevant and cause O_2 selectivity to be determined by water-gas-shift thermodynamics. The use of O_2 as the co-reactant leads to higher rates than with H_2O or CO_2. Herein, we provide mechanistic evidence for CH_4-O_2 reactions on Pt, Ru, Rh, and Pd clusters by combining kinetic and isotopic data with density functional theory (DFT). O_2 forms chemisorbed O* species as [O*-O*] or [O*-*] site pairs that activate C-H bonds, where * is a vicinal vacancy in a near-saturated O* monolayer. We show the kinetic consequences of these chemisorbed O* species for the CH_4 conversion rates and CO/CO_2 selectivities by varying the O* coverage through changes in O_2/CH_4 ratios. We detect three kinetic regimes (KR) with distinct kinetic equations and activation energies with changing O* coverages; these regimes reflect a shift in the kinetically-relevant step from C-H bond activation on [O*-O*] or [O*-*] to O_2 dissociation on [*-*] with decreasing oxygen chemical potentials at cluster surfaces.

Results and Discussion

The extent to which O* species form CO and CO_2 during CH_4-O_2 reactions was probed by changes in residence time on 0.2 wt% Pt/Al_2O_3 (8.5 nm Pt clusters) under conditions of strict kinetic control achieved by extensive intraparticle and catalyst bed dilution. CO/CO_2 ratios were < 0.02 at 873 K for all conditions leading to detectable O_2 in effluent streams. CH_4 partial oxidation therefore does not occur at the molecular scale and CO and H_2 form only via sequential combustion-reforming pathways, not only on Pt, but also on Rh, Ru, and Pd catalysts. CH_4 combustion turnover rates shift from a linear dependence on CH_4 to rates that are proportional to P_{CH4}^2/P_{O2} with decreasing O_2/CH_4 reactant ratios. These kinetic shifts reflect a concomitant shift in the nature and reactivity of the sites from [O*-O*] to [O*-*] site pairs involved in kinetically-relevant C-H activation steps. At very low O_2/CH_4 ratios, rates became proportional to O_2 pressure and limited by O_2 dissociation on [*-*] site pairs. At O_2/CH_4 ratios above 0.8, the rate constant for isotopic scrambling during CH_4-${}^{16}O_2$-${}^{18}O_2$ reaction was identical to that for ${}^{16}O_2$-${}^{18}O_2$ exchange in the absence of CH_4, consistent with quasi-equilibrated O_2 dissociation during CH_4-O_2 reactions. A normal C-H/C-D kinetic isotope effect (KIE) of 1.7 and the first-order CH_4 rate dependence show that C-H activation is kinetically-relevant and proceeds on O*-saturated surfaces. Lower O_2/CH_4 ratios (< 0.4) led to a 100-fold increase in turnover rates, which obey the equation $k_{C\text{-}H}^2 P_{CH4}^2/(k_2 P_{O2})$, where $k_{C\text{-}H}$ and k_2 are the rate constants for C-H bond activation on [O*-*] and O_2 dissociation, respectively. In this regime (KR 2), vacancies (*) appear within O* monolayers to form highly active [O*-*] site pairs for C-H bond activation as a result of the preferential interaction of C and H atoms with * and O*, respectively. Isotopic oxygen exchange rates were smaller in the presence than in the absence of CH_4, indicating that O_2 dissociation steps are no longer equilibrated and that the chemical potential of oxygen at the surface is lower than in the gas phase and determined by the relative rates of O_2 dissociation and of O* removal by CH_4 reactions. In this regime, KIE values (4.1) are larger than expected for C-H bond activation, because rates depend on $k_{C\text{-}H}^2$. O_2/CH_4 ratios below 0.06 led to a narrow range of conditions in which rates became first-order in O_2 and independent of CH_4 pressures (KR 1). These data, the lack of detectable KIE (1.0±0.05), and the low measured activation energies (< 3 kJmol^{-1}) indicate that O_2 dissociation becomes the sole kinetically-relevant step. In spite of these complex dynamics, pseudo-first order rate constants (r_{CH4}/P_{CH4}) become a single-value function of O_2/CH_4 ratios as shown in Figure 1, because O_2/CH_4 determines the O* coverages and chemical potentials at cluster surfaces. Theoretical calculations were carried out on closed packed (111) metal surfaces to elucidate the role of O* and * on the C-H activation paths. Weakly bound O* at near saturation coverage were found to be quite basic; together with a vicinal oxygen vacancy (*), they assist the initial C-H bond dissociation to form hydroxyl and methyl intermediates. The activation barriers for C-H bond activation on [O*-*] site decreased with decreasing Pt-O bond strength, consistent with prevalent Brønsted-Evans-Polanyi (BEP) relations between activation barriers and O* binding energy. Effects of oxygen basicity were probed experimentally by varying the cluster sizes thus varying the metal average coordination numbers on the cluster surface. Large Pt clusters (8.5 nm) have an O_2 exchange rate constant that is approximately three times higher than small Pt clusters (1.8 nm), a trend reflecting the weakening of O*-Pt bond strength and an increase in O* basicity with increasing cluster size, which could be responsible for the observed increase in rates with cluster size in KR 1-3. Similar studies were carried out on Rh, Ru, and Pd clusters; the CH_4-O_2 reaction, however, proceeds almost exclusively on O* saturated surfaces on Rh, Pd and Ru, because oxygen binds strongly on these metals and leads to a lower concentration of vacancies (*) formed (relative to Pt) at any given O_2/CH_4. These [O*-*] site pairs only become available on Pd, Ru, and Rh at a much higher temperatures or lower O_2/CH_4 ratios.

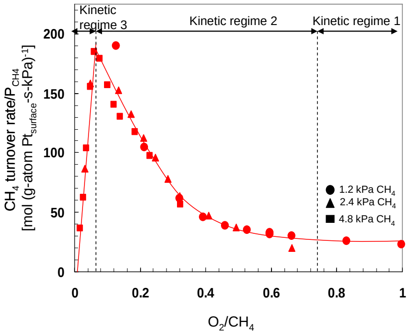

Figure 1. Kinetic phase diagram depicting a universal correlation of rate/P_{CH4} and O_2/CH_4 ratios during CH_4-O_2 reaction on Pt clusters. (8.5 nm Pt clusters, 0.2 wt% Pt/Al_2O_3, 873 K, 2×10^{-8} g-h-cm^{-3})

Significance

This work provides fundamental insight and understanding for oxygen assisted C-H bond activation which is important for describing the complex reaction dynamics observed in CH_4 and hydrocarbon conversion processes involving O_2.

References

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