Structure, Dynamics and Reactivity of Group VIII Metal and Oxide Clusters during Reactions of Methane with Oxygen

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Introduction

Reactions of methane with CO_2, H_2O, or O_2 on supported Group VIII metals are important routes to produce H_2 and synthesis gas. Our previous studies on Pt, Ir, Rh, Ru, and Ni provided a rigorous and unifying mechanistic interpretation of CH_4 reforming and decomposition reactions [1-5], involving kinetically coupled sequential CH_4 decomposition and CH_x* oxidation cycles. The activation of C-H bonds in methane is the sole kinetically-relevant step within these cycles. These steps are coupled with the removal of surface CH_x species by activated oxygen intermediates derived from the co-reactants. Co-reactant activation steps are fast and quasi-equilibrated and therefore kinetically irrelevant. Here, we investigate the consequences of altering the relative rates in the decomposition-oxidation cycle by using a more reactive oxidant (O_2). Extensive kinetic and isotopic tracer studies illustrate the modifications of the catalytic sequence and the dynamic shift of the active surface intermediates when O_2 is used as the co-reactant during CH_4 reactions on Group VIII metal clusters. The distinct reactivity observed during O_2 depletion can be explained by a dynamic shift in the identity of the most abundance surface intermediate (MASI) involved in C-H activation. The structure and reactivity of these intermediates are compared with C-H bond activation rates estimated from first-principle density functional theory (DFT) calculations.
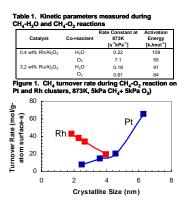
Materials and Methods

Supported metal catalysts were prepared by incipient wetness impregnation of supports (Al_2O_3, MgO, ZrO_2) with aqueous solutions of the precursor salts, as previously described [1-5]. Reaction rates were measured under conditions of strict kinetic control, without corruptions by concentration and temperature gradients in plug-flow and recirculating batch reactors. Quantum chemical calculations of CH_4 decomposition were performed using plane-wave gradient corrected density functional theory (DFT) as implemented in the Vienna *ab initio* Simulation Package (VASP). The (111) surface of face-centered cubic metals (Ni, Rh, Pd, Ir, Pt) and the (0001) surface of hexagonal closed-packed metals (Ru) were modeled with a 4-layer 3x3 unit cell containing 36 metal atoms. A 3x3x1 Monkhorst-Pack mesh was used to sample the first Brillouin zone. The optimized structures were converged to within 0.001 eV. The effects of chemisorbed oxygen atoms were probed by simulating the CH_4 activation steps on surfaces with various oxygen coverages.

Results and Discussion

Under conditions of strict kinetic control, H_2 and CO did not form until O_2 was depleted via combustion reactions that form only CO_2 and H_2O, consistent with the much higher reactivity of CO relative to CH_4 measured from $CH_4/^{13}CO/O_2$ reactant mixtures ($>10^2$ times faster on Ru, Rh, and Pt at 873K). We find that direct catalytic partial oxidation is not possible at the molecular scale, but occurs indirectly under transport-limited conditions via

sequential combustion-reforming routes. CH_4-O_2 reaction rates were proportional to CH_4 pressure for Pt, Rh, and Ru catalysts and independent of co-reactant (O_2) pressure on Pt (above ~2 kPa), Rh and Ru (above 0.2 kPa O_2) at 873 K. As for CH_4 reactions with H_2O and CO_2, C-H activation is the sole kinetically-relevant step in CH_4-O_2 reactions; normal kinetic isotope effects (1.5-1.8 at 873 K) were similar to those measured for reforming reactions (1.4-1.8 at 873K). These data indicate that under these conditions above 0.2 kPa O_2, Rh and Ru surfaces are saturated with O* during CH_4-O_2 reactions, a conclusion confirmed by oxygen desorption dynamics and *in-situ* X-ray absorption spectra, while the Pt surfaces remained unsaturated over a wider range of O_2 concentrations. In the regime where the rates are independent of O_2, the first-order rate constants for CH_4-O_2 reaction were significantly higher compared to those measured using H_2O or CO_2 as the co-reactant, indicating that oxygen-covered surfaces activate C-H bonds much more effectively than clean metal surfaces prevalent during reforming reactions (Table 1). On Ru and Rh, turnover rates increased with decreasing cluster size because of the higher fraction of coordinatively unsaturated surface atoms prevalent on small clusters (Figure 1). As O_2 co-reactants are depleted, combustion rates increased sharply and acquired a negative kinetic order in O_2, which reflects the emergence of vacancies within a saturated oxygen monolayer and the high reactivity of vacancy-oxygen site pairs in C-H bond activation. These negative order kinetics prevailed on Pt clusters over a much wider O_2 pressure range (up to ~2 kPa), but became detectable on Rh and Ru only at very low pressures (<0.2 kPa), because the weaker binding of chemisorbed oxygen on Pt (relative to Rh and Ru) led to a greater number of vacancy-oxygen site pairs. On Pt, turnover rates decreased as clusters become smaller (Figure 1), because the higher binding energy of oxygen on coordinatively unsaturated surface atoms leads to smaller number of vacancies at each O_2 partial pressure. The reactivity differences among uncovered, oxygen-saturated, and intermediate coverage surfaces were probed by estimating activation barriers and overall reaction energy changes for the dissociation of C-H bonds on each surface using DFT calculations. These simulations indicate a late transition state structure and an endothermic process; the estimated activation barriers increased with increasing reaction energy in a manner consistent with Brønsted-Evans-Polanyi relations. The effects of O* were probed by performing these simulations on Rh(111), Pt(111), and Ru(0001) surfaces modified by chemisorbed oxygen at several coverages. These computations are consistent with a significant modification of the transition state, activation barrier, and reaction energy with increasing oxygen coverage on these metals.

Table 1. Kinetic parameters measured during CH_4-H_2O and CH_4-O_2 reactions

Catalyst	Co-reactant	Rate Constant at 873K [s⁻¹kPa⁻¹]	Activation Energy [kJmol⁻¹]
0.4 wt% Rh/Al₂O₃	H₂O	0.22	109
	O₂	7.1	55
3.2 wt% Ru/Al₂O₃	H₂O	0.18	91
	O₂	0.61	84

Figure 1. CH_4 turnover rate during CH_4-O_2 reaction on Pt and Rh clusters, 873K, 5kPa CH_4+ 5kPa O_2)

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