Theoretical Insights into Catalytic C_1 Conversion Processes

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Introduction

The catalytic conversion of natural gas into energy, liquid fuels and chemicals via reforming, partial oxidation and combustion processes occur through similar elementary C-H and O_2 bond activation steps which differ only in the nature of the active sites, whether or not oxygen is present and the local surface coverage of oxygen that result under operating conditions. The prevailing chemistry is ultimately controlled by the surface coverage and reactivity of chemisorbed oxygen. Experimental results for the partial oxidation of methane over supported Pt clusters, for example, reveal the presence of four different kinetic regimes which can be described by unique rate expressions that result for methane over the bare, low oxygen-covered, high-covered, and fully-covered metal surfaces. First-principle density functional theoretical calculations and kinetic Monte Carlo simulation are used here to elucidate the elementary C-H and O_2 activation steps at different surface sites and to establish the influence of surface coverage on the activity to form CO and CO_2 over different transition metal surfaces. The results are used to understand the diverse experimental kinetic regimes in methane partial oxidation and to elucidate the reactivity of other C_1 and C_2 intermediates, such as those derived from methanol or dimethyl ether over Pt as well as other transition metals.

Methods

Nonlocal gradient corrected plane wave density functional theoretical calculations were used to calculate the activation barriers as well as the overall reaction energies for a comprehensive set of elementary steps involved in methane reforming, partial oxidation and combustion as a function of oxygen coverage. The results were used to analyze the controlling reaction mechanisms at different oxygen coverages in order to understand the experimental results. The results were also used as input into an ab initio kinetic Monte Carlo simulation that was used follow the influence of process conditions on the resulting pathways. The reforming studies were carried out over a range of different transition metals whereas the studies the partial oxidation and combustion of methane were carried out predominantly over Pt alone.

Results and Discussion

Rigorous experimental studies along with detailed theoretical calculations have proposed three distinct sites for C-H bond activation in methane on surfaces containing chemisorbed oxygen: 1) two vacant metal sites [*-*], 2) two chemisorbed oxygen atoms [O*-O*] or (3) vicinal chemisorbed oxygens and vacant metal sites [O*-*]. The relative partial pressures of methane and oxygen control the relative concentrations for each of these pairs on the surface. In the absence of oxygen, the rate is governed by the initial activation of the C-H bond of methane which involves a late three-center transition state characteristic of oxidative addition of C-H bonds to metals. The activation barriers for methane, as well as for reactions of subsequent CH_x products that form, were linearly correlated with the carbon binding energies, as expected from bond-order conservation principles. Oxygen ultimately reacts with CH_X surface intermediates to form CO. Comparisons between theory and experiment suggests that the calculated barriers for methane activation over Ru and Rh are typically smaller than those measured, apparently because of structural changes in the metal during reaction or the possible formation of unreactive sub-surface carbon on Rh and Ru.

At low oxygen surface coverages, the C-H activation barrier for methane and for other CH_x intermediates increase slightly as the result of repulsive interactions between the CH_X--H moiety and chemisorbed oxygen in the transition state. The C-H activation barrier, however, decreases significantly, however, as oxygen coverage increases. The adsorbed oxygen becomes more basic as the surface coverage increases; this effectively decreases the barrier for C-H activation as shown in Fig. 1. The decrease in the barrier with increasing oxygen coverage coincides with the increase in the rate of methane activation found experimentally at intermediate oxygen coverages which balances the presence of reactive oxygen and available metal sites.

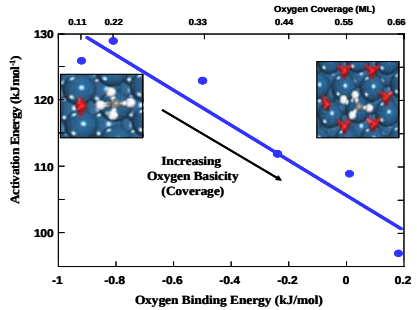

Figure 1. The effect of oxygen coverage on the calculated barrier for the activation of the C-H bond in methane over Pt(111).

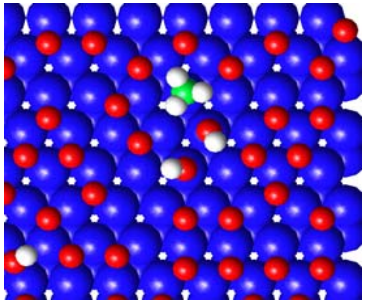

Figure 2. Snapshot from the kinetic Monte Carlo simulation of the partial oxidation of methane activation.

At higher oxygen coverages, the O*-O* pair becomes the most abundant surface species. Methane activation barriers are higher on O*-O* pairs than on *-O* site pairs, consistent with the lower C-H activation over stoichiometric transition metal oxides. The decrease in the rate at higher coverages is due to the loss of available metal sites and to the concurrent increase in the less reactive [O*-O*] sites. The oxygen surface coverage is controlled by the balance of oxygen dissociation onto the surface, and the removal via the recombination of atomic oxygen to create vacant sites and reaction with methane to form CO, CO_2 and water. The barriers for oxygen dissociation recombination increase linearly with coverage whereas the barrier for the removal of oxygen decreases linearly with coverage. The kinetic simulations reveal that the relative partial pressures of methane and oxygen ultimately dictate the surface coverage of oxygen which controls the rate of the reaction as well as the selectivity. The rate of reaction of the CO that forms on the surface with oxygen is found to be orders of magnitude higher than the rate of CO desorption as such any CO that forms is rapidly converted to CO_2 in the presence of oxygen.