Structural Requirements and Elementary Steps in Methane Reactions on Supported Metal Clusters

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We report here kinetic and isotopic evidence for elementary steps involved in the conversion of CH4 to synthesis gas and to carbonaceous structures via reactions of CH4 with CO2 and H2O as co-reactants. These elementary steps are shown to be generally applicable to these reactions on supported Rh, Pt, Ir, Ru, and Ni clusters at conditions relevant to their industrial practice.

On all metals except Pd, CH4/CO2, CH4/H2O, and CH4 decomposition turnover rates are limited solely by C-H activation of CH4 on essentially uncovered cluster surfaces. Turnover rates are proportional to CH4 pressure and independent of the identity or the concentration of co-reactants and products. Turnover rates are similar for CHx/CO2, CHx/H2O and CHx decomposition reactions and increased with metal dispersion. These trends appear to reflect the higher reactivity of coordinatively unsaturated exposed metal atoms prevalent on smaller clusters. Activation energies are similar for reactions of CH4 with CO2 and H2O and for CH4 decomposition on each catalyst. These activation energies and turnover rates are consistent with density functional theory estimates on (111) surfaces for each metal, but activation energies are significantly higher than reported for CHx decomposition on surfaces of single crystals. For these metal clusters, supports did not influence turnover rates, except indirectly through their effect on metal dispersion, as expected from the sole kinetic relevance of C-H bond activation steps and their catalysis by the surfaces of these metal clusters.

The identity and kinetic relevance of proposed elementary steps were confirmed from the relative rates of CH4 and CD4 reactants, which gave normal isotope effects (1.5-1.8) for CH2/CO2, CH2/H2O, and CH4 decomposition reactions on Rh, Pt, Ir, Ru, and Ni clusters, indicating that C-H activation is the only kinetically-relevant step. CH2/D2 and CH2/H2O reactant mixtures gave identical rates, indicating that H2O dissociation steps and H2O-derived intermediates are not kinetically-relevant. CH2/CD2/CO2 mixtures formed H2 and CO much faster than CH2/H2O and CH4/CD4.CO2 isomer interconversions were quasi-equilibrated. Dihydrogen and water formed from CH2/D2 were in isotopic equilibrium at all chemical conversions; thus, their respective desorption and interconversion steps are quasi-equilibrated.

The quasi-equilibrated nature of these steps implies that water-gas shift reactions must also be at equilibrium during CH4 reforming, a prediction confirmed experimentally on all catalysts at all reaction conditions. As a result, H2/CO product ratios on Rh, Pt, Ir, Ru, and Ni clusters are determined only by the thermodynamics of the water-gas shift reaction and unaffected by catalyst identity or reactivity. These elementary steps and their kinetic relevance provide a unifying mechanistic framework for CH4 reforming and decomposition reactions previously treated independently and for water-gas shift reactions. These findings also provide a mechanistic framework that accurately describes the nucleation and growth of carbon filaments and the formation of encapsulating carbon structures during CH4 reforming reactions at conditions favoring such carbon structures. We find that the nucleation and growth of filaments depends on the thermodynamic activity of surface carbon species, which is proportional to specific functions of reactant and product concentrations predicted by the mechanistic model proposed here. The structure and dynamics of carbon filaments are consistent with filament growth limited by diffusion, a process driven in turn by a gradient in carbon activity between cluster surfaces and growing carbon filaments.

On Rh, Pt, Ir, Ru, and Ni clusters, the rate of co-reactant activation is fast and quasi-equilibrated and clusters surfaces remain essentially uncovered by reactants, products, or reactive intermediates. Pd cluster surfaces, however, have intrinsic reactivities more than ten-fold greater than any other Group VIII metal. This high reactivity leads to an imbalance between the rates CH4 and co-reactant activation, to a much more complex kinetic behavior, and to strong effects of support on co-reactant activation rates and on overall reforming and deactivation dynamics. The high C-H bond activation turnover rates on Pd surfaces prevent equilibration of CO2 or H2O activation and of water-gas shift reactions in the time scale of CH4 reactions. 12CH4/12CO2/13CO reactant mixtures did not form detectable amounts of 13CO2, in contrast with the isotopic equilibration between CO and CO2 prevalent during CH4 reforming on all other Group VIII metals.

On Pd, the formation of CHx/Dx isotopomers from CHx/D2/CO2 reactant mixtures occurred at rates comparable to chemical conversion rates. H2 and CO products inhibit reforming rates because of the presence of appreciable coverages of CHx* adsorbed intermediates during catalysis. This reversibility of C-H bond activation steps led to inhibition of turnover rates by H2 also because of the role of chemisorbed hydrogen on the recombination of CHx* species to re-form CH4 reactants on Pd-based catalysts. CO inhibits reforming rates by increasing the surface coverage of chemisorbed carbon and CHx species, formed via CO dissociation. The thermodynamic activity of chemisorbed carbon depends on the rates of CH4 and CO dissociation on Pd; also, and in marked contrast with other Group VIII metals, this activity depends on CO2 dissociation. The mechanistic treatment developed from these kinetic data also led to an accurate assessment of the contributions of specific elementary steps to reforming turnover rates and to the first reported measurements of C-H bond activation rate constants on Pd cluster surfaces.

Finally, we will discuss selectivity issues in CH4 reactions at high temperatures on Group VIII metal clusters in the context of CHx/O2 reactions and provide evidence that partial oxidation reactions can occur only via sequential combustion-reforming pathways on all Group VIII metal surfaces. The direct and nearly autothermal formation of H2-CO mixtures via CH4-O2 reactions on Group VIII metals was not observed. The presence of chemisorbed oxygen leads C-H bond activation to dynamics that were strongly influenced by density of vacancies on cluster surfaces nearly saturated with chemisorbed oxygen. The nature of these C-H bond activation steps and the effects of oxygen coverage on their rate constants are difficult to determine experimentally. They can be probed, however, using theoretical treatments of C-H bond activation of oxygen-covered metal surfaces, as will be shown during this lecture.