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

Aritomo Yamaguchi [1], Ya-Huei (Cathy) Chin [1], Mingshi Li[1,3],
Michael Janik[2,4], Matthew Neurock[2], and Enrique Iglesia [1]*

[1]*Department of Chemical Engineering, University of California, Berkeley, CA 94720*
[2]*Department of Chemical Engineering, University of Virginia, Charlottesville, VA, 22904*
[3] *Current Address: Jiangsu Polytechnic University, Changzhou, 213016, China*
[4] *Current Address: Department of Chemical Engineering, Pennsylvania State University, PA 16802.* * iglesia@berkeley.edu

We report here kinetic and isotopic evidence for elementary steps involved in the conversion of CH_4 to synthesis gas and to carbonaceous structures via reactions of CH_4 with CO_2 and H_2O as co-reactants. These elementary steps are shown to be generally applicable to these reactions on supported Rh, Pt, Ir, Ru, Pd and Ni clusters at conditions relevant to their industrial practice.

On all metals except Pd, CH_4/CO_2, CH_4/H_2O, and CH_4 decomposition turnover rates are limited solely by C-H activation of CH_4 on essentially uncovered cluster surfaces. Turnover rates are proportional to CH_4 pressure and independent of the identity or the concentration of co-reactants and products. Turnover rates are similar for CH_4/CO_2, CH_4/H_2O and CH_4 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 CH_4 with CO_2 and H_2O and for CH_4 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 CH_4 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 CH_4 and CD_4 reactants, which gave normal isotope effects (1.5-1.8) for CH_4/CO_2, CH_4/H_2O, and CH_4 decomposition reactions on Rh, Pt, Ir, Ru, and Ni clusters, indicating that C-H activation is the only kinetically-relevant step. CH_4/D_2O and CH_4/H_2O reactant mixtures gave identical rates, indicating that H_2O dissociation steps and H_2O-derived intermediates are not kinetically-relevant. $CH_4/CD_4/CO_2$ mixtures formed H_2 and CO much faster than $CH_{4-x}D_x$ isotopomers, indicating that C-H bond activation is essentially irreversible. Dihydrogen and water formed from $CH_4/CO_2/D_2$ were in isotopic equilibrium at all chemical conversions; thus, their respective desorption and interconversion steps are quasi-equilibrated. CO_2 and CO reached isotopic equilibrium in $^{12}CH_4/^{12}CO_2/^{13}CO$ mixtures, indicating that CO_2 dissociation is also quasi-equilibrated.

The quasi-equilibrated nature of these steps implies that water-gas shift reactions must also be at equilibrium during CH_4 reforming, a prediction confirmed experimentally on all catalysts at all reaction conditions. As a result, H_2/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 CH_4 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 CH_4 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 CH_4 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 CO_2 or H_2O activation and of water-gas shift reactions in the time scale of CH_4 reactions. $^{12}CH_4/^{12}CO_2/^{13}CO$ reactant mixtures did not form detectable amounts of $^{13}CO_2$, in contrast with the isotopic equilibration between CO and CO_2 prevalent during CH_4 reforming on all other Group VIII metals.

On Pd, the formation of $CH_{4-x}D_x$ isotopomers from $CH_4/D_2/CO_2$ reactant mixtures occurred at rates comparable to chemical conversion rates. H_2 and CO products inhibit reforming rates because of the presence of appreciable coverages of CH_x* adsorbed intermediates during catalysis. This reversibility of C-H bond activation steps led to inhibition of turnover rates by H_2 also because of the role of chemisorbed hydrogen on the recombination of CH_x* species to re-form CH_4 reactants on Pd-based catalysts. CO inhibits reforming rates by increasing the surface coverage of chemisorbed carbon and CH_x species, formed via CO dissociation. The thermodynamic activity of chemisorbed carbon depends on the rates of CH_4 and CO dissociation on Pd; also, and in marked contrast with other Group VIII metals, this activity depends on CO_2 and H_2O activation rates. The supports used to disperse Pd metal clusters can become involved in activation of co-reactants and influence the rates of CH_4 reforming and of catalyst deactivation. 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 CH_4 reactions at high temperatures on Group VIII metal clusters in the context of CH_4-O_2 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 H_2-CO mixtures via CH_4-O_2 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.