STRUCTURAL REQUIREMENTS AND ACTIVATION PATHWAYS IN REACTIONS OF METHANE CATALYZED BY SUPPORTED METALS

Junmei Wei and Enrique Iglesia

Department of Chemical Engineering, University of California at Berkeley,
Berkeley, CA, 94720, USA

CH_4 reactions with CO_2 or H_2O lead to synthesis gas mixtures, which are used to produce valuable fuels and chemicals. Rigorous assessments of the relevant elementary steps and of the effects of metal dispersion and support on reaction rates and selectivities have remained elusive. Here, we report isotopic tracer and kinetic studies that provide a simple mechanistic picture and a unifying kinetic treatment of CH_4/CO_2, CH_4/H_2O, and CH_4 decomposition reactions on supported Rh, Ni, Pt, Ru, and Ir catalysts. The required kinetic processes are exclusively limited by the first activation of a C-H bond in CH_4 and the relevant rate constant is unaffected by the presence or the concentration of co-reactants (H_2O, CO_2) or by the identity of the support. The elementary steps proposed and confirmed by kinetic and isotopic evidence provide a rigorous basis for treating the dynamics of carbon formation during CH_4 reforming. On all metals, turnover rates increased with increasing metal dispersion. This reflects the higher reactivity of coordinatively unsaturated surface atoms for C-H bond activation reactions.

The kinetic effects of CH_4, H_2O, and CO_2 pressures on CH_4 reaction rates were measured at 850-1000 K and 0.1-1.5 MPa total pressure over a wide range of reactant ratios. Transport artifacts were excluded using dilution strategies. Measured reaction rates were corrected for the distance of the overall reaction from thermodynamic equilibrium in order to obtain rigorous values of the forward kinetic rates. On all catalysts, CH_4 reactions rates were proportional to CH_4 pressure, independent of co-reactant pressure, and identical for CH_4/CO_2, CH_4/H_2O, and CH_4 decomposition reactions, indicating that these reactions are mechanistic equivalent and that C-H bond activation is the sole kinetically-relevant step in all three reactions. These conclusions were confirmed by identical CH_4/CD_4 kinetic isotope effects for reforming and decomposition reactions and by undetectable H_2O/D_2O isotopic effects. The kinetic relevance of C-H bond activation is consistent with the relative rates of chemical conversion and isotopic mixing in $CH_4/CD_4/CO_2$ mixture and with the isotopic evidence for the quasi-equilibrated nature of co-reactant activation and H_2 and H_2O desorption obtained from reactions of $CH_4/CO_2/D_2$ and $^{12}CH_4/^{12}CO_2/^{13}CO$ mixtures. Taken together, these quasi-equilibrated steps involved in H_2O, H_2, and CO formation lead to equilibrated water-gas shift reactions. These elementary steps provide also a rigorous basis for a kinetic treatment of carbon formation processes during CH_4 reactions at high temperatures on metal surfaces and for the assembly of carbon filaments as specific side products of these reactions [1].

Turnover rates were obtained from forward reaction rates and metal dispersions. Turnover rates and metal dispersions are based on strongly chemisorbed H_2 or on H_2-O_2 titration measurements. Turnover rates for CH_4-H_2O reaction increase with increasing dispersion and decreasing size of Rh, Ir, Pt, Ru and Ni clusters supported on various oxides (Figure 1). Identical turnover rates and dispersion effects rates were observed CH_4-CO_2 reactions, as expected from the rigorous kinetic equivalence of CH_4-CO_2 and CH_4-H_2O reactions. On all metals, turnover rates increased monotonically with increasing metal dispersion, suggesting that the coordinatively unsaturated surface atoms prevalent in small crystallites are significantly more active than those in the low-index planes predominately exposed on larger metal crystallites. Similar effects have been measured and predicted theoretically for model metal surfaces [2,3]. These low-coordination surface atoms appear to provide more stable binding sites for CH_x and H products and for the relevant activated complexes. Similar CO oxidation rates were measured before and after CH_4 reactions on all of the noble metals, indicating that metal dispersion is not affected by unreactive deposits or sintering during catalysis. The identity of the support does not influence turnover rates, and previous literature claims for support effects, attributed to co-reactant activation on the supports, are inconsistent with these data and with the kinetic irrelevance of co-reactant activation steps. Supports, however, influence metal dispersion, and in this manner, they can affect turnover rates.

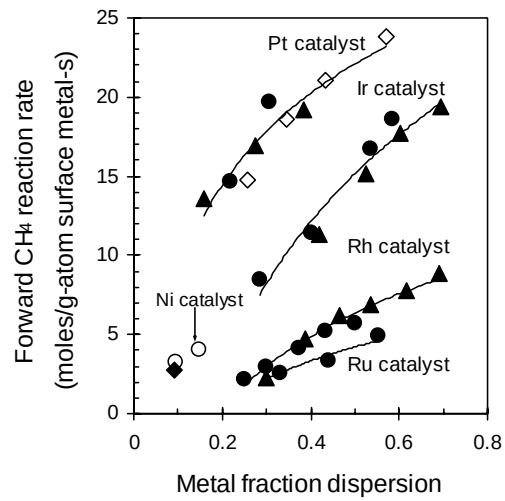

Figure 1. Forward CH_4 turnover rates for H_2O reforming of CH_4 on different metal clusters as a function of metal dispersion on various supports (873 K, 20 kPa CH_4, (▲) ZrO_2, (●) γ-Al_2O_3, (◇) ZrO_2-CeO_2 as support, (○) MgO-A (♦) MgO-B).

This study was supported by BP as part of the Methane Conversion Cooperative Research Program at the University of California at Berkeley.

References

(1) Wei, J.; and Iglesia, E. submitted to J. Catal.
(2) Beebe, T.P.; Goodman, D.W.; and Kay, B.D. *J. Chem. Phys.*, **1987**, 87, 2305.
(3) Watwe, R.M.; Bengaard, H.S.; Rostrup-Nielsen, J.R.; Dumesic, J.A.; and Norskov, J.K. J. Catal., 2000, 189, 16.