Mechanism and Site Requirements for Activation and Chemical Conversion of Methane on Supported Pt Clusters and Turnover Rate Comparisons among Noble Metals

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Isotopic tracer and kinetic studies are used to probe the identity and reversibility of elementary steps required for \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) reforming of \( \text{CH}_4 \) on supported Pt clusters and to demonstrate a rigorous kinetic and mechanistic equivalence for \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) reforming, \( \text{CH}_4 \) decomposition, and water-gas shift reactions. Reforming rates are exclusively limited by \( \text{C} \text{H}_x \) bond activation on essentially uncovered Pt crystallite surfaces and unaffected by the concentration or reactivity of co-reactants (\( \text{H}_2\text{O}, \text{CO}_2 \)). Kinetic isotopic effects are consistent with the sole kinetic relevance of \( \text{C} \text{H}_x \) bond activation \((k_{\text{H}_2}/k_0 = 1.58\text{-}1.77 \text{ at } 873 \text{ K})\); these isotope effects and measured activation energies are similar for \( \text{H}_2\text{O} \) reforming, \( \text{CO}_2 \) reforming, and \( \text{CH}_4 \) decomposition reactions. \( \text{CH}_4/\text{CO}_2 \) cross exchange rates are much smaller than the rate of methane chemical conversion in \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) reforming reactions; thus, \( \text{C} \text{H}_x \) bond activation steps are irreversible, except as required by the approach to equilibrium for the overall reforming reaction. Reactions of \( ^{13}\text{CH}_4/^{13}\text{CO}_2/^{13}\text{CO} \) mixtures led to identical \( ^{13}\text{C} \) fractions in \( \text{CO} \) and \( \text{CO}_2 \), indicating that \( \text{CO}_2 \) activation is quasi-equilibrated and kinetically irrelevant. Binomial water and dihydrogen isotopomer distributions during reactions of \( \text{CH}_4/\text{CO}_2/\text{D}_2 \) mixtures indicate that these products form in quasi-equilibrated steps. Turnover rates for \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) reforming and \( \text{CH}_4 \) decomposition increased with increasing Pt dispersion, suggesting that coordinative unsaturated surface Pt atoms, prevalent in small crystallites, are more reactive than Pt atoms in low-index surfaces for \( \text{C} \text{H}_x \) bond activation. Pt dispersion but not turnover rates were influenced by the identity of the support (\( \text{ZrO}_2, \gamma\text{-Al}_2\text{O}_3, \text{ZrO}_2/\text{CeO}_2 \)). Similar CO oxidation rates were measured before and after \( \text{CH}_4 \) reactions, indicating that Pt dispersion is not affected by unreactive deposits or sintering during catalysis. These mechanistic conclusions and metal dispersion effects appear to apply generally to \( \text{CH}_4 \) reactions on Group VIII metals, but the surface reactivity of Pt clusters in \( \text{C} \text{H}_x \) bond activation reactions is greater than for similar size clusters of other metals. Turnover rates are compared here, for the first time, for most catalytically important noble metals (Rh, Ir, Pt, Ru) as a function of their metal dispersion on several supports. These turnover rates rigorously exclude transport and thermodynamic artifacts and provide a direct comparison of the reactivity of noble metal clusters for catalytic reactions of \( \text{CH}_4 \) on materials and at conditions relevant to industrial practice.

1. Introduction

\( \text{CH}_4 \) reactions with \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) on supported Ni,\textsuperscript{1,2} Rh,\textsuperscript{3,4} Ru,\textsuperscript{5,6} Ir\textsuperscript{7} and Pt\textsuperscript{2,3,8} lead to \( \text{H}_2/\text{CO} \) mixtures useful as precursors to fuels and petrochemicals. Pt appears to be one of the most active and stable metals for these reactions,\textsuperscript{13,19–23} Pt/\text{ZrO}_2, for instance, has been used in \( \text{CH}_4/\text{CO}_2 \) reactions for 500 h without detectable deactivation.\textsuperscript{21–23} Rigorous comparisons among different metals are difficult because of ubiquitous transport and thermodynamic artifacts and of incomplete assessments of the number and cleanliness of exposed metal atoms.

Redox cycles involving parallel \( \text{CH}_4 \) activation on Pt clusters and \( \text{CO}_2 \) dissociation on reduced support sites were proposed for \( \text{CH}_4/\text{CO}_2 \) reactions on Pt/\text{ZrO}_2.\textsuperscript{11} Such cycles would turn over with rates dependent on the relative abundance and reactivity of metal and support sites, which must act in concert to activate \( \text{CH}_4 \) and remove carbon atoms via reactions with \( \text{CO}_2 \) (or \( \text{H}_2\text{O} \)). Infrared spectra of \( \text{CO}_2 \) adsorbed on Pt/\text{Al}_2\text{O}_3, Pt/\text{TiO}_2, and Pt/\text{ZrO}_2 \) at 775 K indicated that carbonates formed on supports, which led to the proposal that Pt activates \( \text{CH}_4 \) and chemisorbed carbon reactants with carbonates at metal—support interfaces.\textsuperscript{19–22} \( \text{CO}_2/\text{CH}_4 \) reforming at interfaces on Ni catalysts\textsuperscript{3} were later proposed also for Pt-based catalysts.\textsuperscript{9,10} This proposal claimed that \( \text{CH}_4 \) activation reversibly formed adsorbed \( \text{CH}_x \) and H species on Pt and then reacted with \( \text{CO}_2 \) dissociation fragments in equilibrated steps that form \( \text{CH}_3\text{O} \), which irreversibly decomposed to \( \text{CO} \) and \( \text{H}_2 \) and led to a complex rate equation:

\[
r_{\text{CH}_4} = \frac{aP_{\text{CH}_4}P_{\text{CO}_2}}{bP_{\text{CO}_2}P_{\text{H}_2} + (1 + cP_{\text{CH}_4})P_{\text{CO}_2}}
\]

where \( x \) is the number of H-atoms in \( \text{CH}_x\text{O} \).

Rostrup-Nielsen and Hansen\textsuperscript{2} reported similar activation energies for \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) reforming with \( \text{CH}_4 \) on Pt/MgO, suggesting that the two reactions share kinetically relevant steps. Yet, measured reforming rates were about five times greater with \( \text{H}_2\text{O} \) than with \( \text{CO}_2 \) co-reactants, a finding attributed to rate-determining \( \text{CO}_2 \) dissociation steps during \( \text{CH}_4/\text{CO}_2 \) reactions, despite the similar measured activation energies.

The effects of surface structure on reaction rates remain unresolved for \( \text{CH}_4 \) reactions on metal catalysts. Several studies showed that \( \text{C} \text{H}_x \) bond activation in alkanes is structure-
TABLE 1: Pt Dispersion (D), Crystallite Diameter (d), and Forward CH₄ Turnover Rates on Pt-Based Catalysts (873 K, 20 kPa CH₄, 25 kPa CO₂ or H₂O, 100 kPa Total Pressure, Balance Ar)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Pt dispersion</th>
<th>crystallite diameter (nm)</th>
<th>CH₄→CO₂ (s⁻¹)</th>
<th>CH₄→H₂O (s⁻¹)</th>
<th>CH₄ decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6 wt % Pt/ZrO₂–CeO₂</td>
<td>0.256</td>
<td>3.9</td>
<td>15.0</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>0.8 wt % Pt/ZrO₂–CeO₂</td>
<td>0.345</td>
<td>2.9</td>
<td>18.6</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>0.4 wt % Pt/ZrO₂–CeO₂</td>
<td>0.435</td>
<td>2.3</td>
<td>21.1</td>
<td>22.5</td>
<td>18.6</td>
</tr>
<tr>
<td>0.2 wt % Pt/ZrO₂–CeO₂</td>
<td>0.572</td>
<td>1.7</td>
<td>23.8</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>1.6 wt % Pt/ZrO₂</td>
<td>0.159</td>
<td>6.3</td>
<td>12.8</td>
<td>13.1</td>
<td>12.4</td>
</tr>
<tr>
<td>0.8 wt % Pt/ZrO₂</td>
<td>0.276</td>
<td>3.6</td>
<td>16.4</td>
<td>16.9</td>
<td>15.8</td>
</tr>
<tr>
<td>0.4 wt % Pt/ZrO₂</td>
<td>0.383</td>
<td>2.6</td>
<td>19.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6 wt % Pt/Al₂O₃</td>
<td>0.219</td>
<td>4.4</td>
<td>11.2</td>
<td>14.7</td>
<td></td>
</tr>
</tbody>
</table>

a Zr/Ce(mole) = 4. b Estimated from fraction Pt dispersion using equation D = 1/d. c Initial CH₄ decomposition turnover rate on Pt surface.

Activation and Chemical Conversion of Methane on Pt

sensitive by the definition of Boudart, a conclusion consistent with experimental and theoretical studies on well-defined surfaces; these latter studies indicate that coordinatively unsaturated surface atoms lead to higher CH₄ sticking and dissociation rates than atoms on close-packed surfaces. For instance, CH₄ dissociation rates using molecular beams are higher on Pt than on close-packed Pt(111) surfaces at even higher temperatures (800 K), and alkane dissociation did not occur, except possibly at minority defect sites, on Pt(111). CO₂–CH₄ and H₂O–CH₄ catalytic turnover rates increased with increasing Rh and Ru dispersion, consistent with higher rates on coordinatively unsaturated atoms. We have not found similar systematic studies of Pt dispersion effects on CH₄ reforming turnover rates.

Oxides used to support Pt clusters and metal-support interfaces are often implicated in bifunctional CH₄ reforming pathways, but they also determine metal dispersion and transport properties, and in doing so, can introduce thermodynamic and transport corruptions into kinetic measurements. CH₄ conversions during CH₄–CO₂ reactions were higher on Pt/ZrO₂ than on Pt/SiO₂ or Pt/Al₂O₃, a finding attributed to CO₂ dissociation on ZrO₂, but neither Pt dispersion nor turnover rates were measured. Oxidic support effects would be detected when bifunctional pathways require Pt-support interfaces, but they cannot influence reaction rates directly when C–H bond activation on metal surfaces is the only kinetically relevant step, as inferred from relative bond energies in CH₄ and CO₂ (or H₂O) and from studies on well-defined metal surfaces.

Detailed kinetic and isotopic studies of CH₄→H₂O, CH₄→CO₂, and CH₄ decomposition reactions on Pt are unavailable; reported reaction rates have not been, for the most part, corrected for approach to equilibrium, measured under kinetic-controlled conditions, or normalized by the number of exposed Pt atoms. We report here, for the first time, a comparison of CH₄ reaction turnover rates on catalytically relevant noble metals (Pt, Ir, Rh, Ru) for a wide range of metal dispersion (0.15–0.70) and supports. We also report kinetic and isotopic evidence for the identity and reversibility of elementary steps required for H₂O and CO₂ reforming of CH₄ on supported Pt clusters and demonstrate a rigorous kinetic and mechanistic equivalence for CO₂ and H₂O reforming, CH₄ decomposition, and water-gas shift reactions. These studies provide conclusive kinetic and isotopic evidence for the sole kinetic relevance of C–H bond activation and for the essentially uncovered state of Pt clusters during steady-state catalysis and for the general relevance of these conclusions to other noble metals. We also find that Pt surfaces are the most active metal among Group VIII metals for C–H bond activation and for CH₄ reforming with H₂O or CO₂. Turnover rates increased with increasing Pt dispersion on Al₂O₃, ZrO₂, and ZrO₂–CeO₂, but they did not depend on the identity of the support, as also found for Rh, Ir, and Ru catalysts. The activation of the co-reactant (CO₂ or H₂O) is fast relative to C–H bond activation steps and therefore not kinetically relevant. These conclusions are consistent with those recently reported for Rh and Ru clusters; they appear to apply generally to chemical conversion of CH₄ on Group VIII metals.

2. Experimental Methods

2.1. Synthesis and Characterization. Pt/Al₂O₃, Pt/ZrO₂, and Pt/ZrO₂–CeO₂ with varying Pt content (0.2–1.6 wt %) were prepared by incipient wetness impregnation of Al₂O₃, ZrO₂, and ZrO₂–CeO₂ with aqueous H₂PtCl₆·6H₂O solutions (Aldrich, Lot# 10013LO, 99%). Samples were dried in ambient air at 393 K and then treated in flowing dry air (Airgas, UHP, 1.2 cm³/g–s) at 873 K (0.167 K s⁻¹) for 5 h. Samples were reduced in H₂ (Airgas, UHP, 50 cm³/g–s) at 873 K (0.167 K s⁻¹) for 2 h. Al₂O₃ (160 m²/g) was prepared by heating Al(OH)₃ (Aldrich, >98 wt %) at 1533 K (Alfa, CAS # 15336–18–2, 99.5%) at a constant pH of 10, maintained by controlled addition of 14.8 M NaOH. The precipitate was filtered and washed by red-dispersing powders in a NH₄OH solution (pH 10, ~333 K) until Cl ions were no longer detected by AgNO₃ (Cl⁻ < 10 ppm). ZrO₂–CeO₂ powders were then dried in ambient air at 393 K overnight and treated in flowing dry air (Airgas, UHP, 1.2 cm³/g–s) at 923 K (0.167 K s⁻¹) for 5 h. Supported Rh, Ru, and Ir catalysts were also prepared by incipient wetness and detailed synthesis and characterization procedures are reported elsewhere.

Pt dispersion was measured using volumetric methods from uptakes of strongly chemisorbed hydrogen at 373 K. These dispersions (shown in Table 1) were used to estimate average crystallite diameters by assuming hemispherical geometry using:

\[ D = \frac{1}{d} \]  

where \( D \) is the fractional dispersion and \( d \) is the crystallite diameter (in nm).

2.2. Catalytic and Stoichiometric Reactions of Methane. The microreactor system was described previously (quartz or steel tube with 8 mm inner diameter and with a type K thermocouple enclosed within a sheath in contact with the catalyst bed). Reaction rates were measured on catalysts (5 mg; 250–425 μm particles) diluted with inert support within the pellets (25 mg) and then diluted the catalyst bed with acid-
washed quartz powder (500 mg) of similar size. Reactant mixtures consisted of 50% CH₄/Ar (Matheson) and 50% CO₂/Ar (Matheson) certified mixtures with He (Airgas, UHP) as a diluent. H₂O was introduced using a syringe pump (Cole-Parmer, 74900 series), and transfer lines were kept above 373 K after H₂O introduction to avoid condensation. The effects of CH₄ and CO₂ pressures on CH₄ reaction rates were measured at 823–1023 K and 100–1000 kPa total pressure over a wide range of reactant concentrations. The effect of H₂O pressure on CH₄ reaction rates was measured at 823–1023 K and 100 kPa total pressure. Reactant and product concentrations were measured with a Hewlett-Packard model 6890 gas chromatograph equipped with a Carboxen 1000 packed column (3.2 mm × 2 m) and a thermal conductivity detector.

Pt/ZrO₂ (0.8, 1.6 wt %, 20 mg) and Pt/ZrO₂–CeO₂ (0.4 wt %, 20 mg) samples diluted with 500 mg of quartz powder were used to measure rates of CH₄ and CD₄ decomposition (without co-reactants) at 873–973 K. CH₄ conversions were measured by on-line mass spectrometry (Leybold Inficon, Transpector Series). Reactant mixtures with 20% CH₂/Ar or 20% CD₂/Ar were prepared using 50% CH₄/Ar (Matheson, certified mixture) or pure CD₄ (Isopec, chemical purity > 99.0%) and Ar (Airgas, UHP). Intensities at 15 and 18 amu were used to measure CH₄ and CD₂ effluent concentrations, respectively. Ar was used as an internal standard. Initial CH₄ decomposition rates were used to estimate rate constants for CH₄ decomposition, based on the observed linear dependence of decomposition rates on CH₄ partial pressures.

2.3. Isotopic Tracer Studies and Kinetic Isotope Effects. Isotopic tracer studies of CH₄ reforming reactions were carried out on 0.4 wt % Pt/ZrO₂–CeO₂ using a transient flow apparatus with short hydrodynamic delays (<5 s). Chemical and isotopic compositions were measured using on-line mass spectrometry (Leybold Inficon, Transpector Series). CD₄, D₂O (Isopec, chemical purity > 99.0%), 5% D₂/Ar, and ³¹CO (Isopec, chemical purity > 99.0%) were used as reactants without further purification. Intensities at 15 and 17–20 amu were used to measure the concentration of methane isotopomers. CH₄ and CD₄ fragmentation patterns were measured and those for CHD₃, CH₂D₂, and CH₃D were calculated using reported methods.⁴⁹ Intensities at 18, 19, and 20 amu were used to determine water isotopomers and those at 28, 29, 44, and 45 amu to measure ¹⁴CO₂, ¹³CO, ¹²CO₂, and ¹³CO₂ concentrations, respectively. Kinetic isotope effects were measured from the relative reaction rates with CH₄/CO₂ and CD₄/CO₂ reactants for CO₂ reforming and with CH₄/H₂O, CD₄/H₂O, and CD₂/D₂O reactants for steam reforming. Detailed experimental conditions are shown with the corresponding data in the results section.

2.4. CO Oxidation Rates. CO oxidation was used as a structure-insensitive reaction to detect any changes in the number of exposed Pt atoms as a result of catalytic CH₄ reforming reactions. Pt/ZrO₂ (0.4, 0.8, and 1.6 wt %, 10 mg) catalysts diluted with 500 mg of quartz powder were used to measure CO oxidation reaction rates at 413 K, 0.19 kPa CO, and 0.19 kPa O₂. These rates were measured before and after reforming reactions by measuring reactant and product concentrations using gas chromatography and the same protocols described above for CH₄ reactions. Mixtures of 25% O₂/He (Matheson, certified mixture) and 81.5% CO/N₂ (Matheson, certified mixture) were used as reactants.

3. Results and Discussion

3.1. Kinetic Dependence of Forward CH₄ Reaction Rate on Partial Pressure of Reactants. The kinetic response of CH₄ reforming rates to CH₄, CO₂, and H₂O concentrations was measured on 1.6 wt % Pt/ZrO₂ at conditions leading to stable rates, without detectable carbon formation, sintering of metal particles, or transport artifacts. Figure 1 shows net CH₄ turnover rates as a function of residence time at 873 K on 1.6 wt % Pt/ZrO₂ with different pellet sizes and different diluent/catalyst ratios within pellets. Varying the diameter of catalyst pellets (250–425 vs 63–106 μm) or the extent of dilution within the pellets (5:1 to 10:1) did not influence CH₄ turnover rates (Figure 1), indicating that measured net rates are unaffected by transport artifacts. Undiluted pellets and beds, often used in previous studies, led to lower reaction rates as a result of mass and heat transfer restrictions. Forward CH₄ turnover rates were obtained from measured rates by rigorously correcting them for reactant depletion and approach to equilibrium in CO₂ (eq 3) or H₂O (eq 4) reforming reactions:

\[
\eta_1 = \frac{[P_{\text{CO}^2}][P_{\text{H}_2}]^2}{[P_{\text{CH}_4}][P_{\text{CO}^2}]} \times \frac{1}{K_{\text{EQ1}}} 
\]

\[
\eta_2 = \frac{[P_{\text{CO}^2}][P_{\text{H}_2}]}{[P_{\text{CH}_4}][P_{\text{H}_2}]} \times \frac{1}{K_{\text{EQ2}}} 
\]

where \([P_j]\) is the average partial pressure of species \(j\) (in atm) within the catalyst bed and \(K_{\text{EQ1}}\) and \(K_{\text{EQ2}}\) are equilibrium constants for each reaction at a given temperature. The fractional distance from equilibrium (1 – \(\eta\)) ranges from 0.70 to 0.97 for the experiments reported here. Net turnover rates \(r_\eta\) are used to determine forward turnover rate (\(r_f\)) using

\[
r_f = r_\eta (1 - \eta) 
\]

This equation accurately described all observed effects of reactor residence time on rates, as indicated by the curve in Figure 1. All rates reported from this point forward represent the rate of forward reforming reactions.

Figure 2 shows the effects of average CH₄, CO₂, and H₂O pressures, defined as the linear average of their inlet and outlet
values, on forward CH₄ turnover rates at 873 K on 1.6 wt % Pt/ZrO₂. This linear average is an accurate representation of the kinetic driving force for the small axial concentration gradients prevalent in this study, and becomes rigorous if reaction rates are first-order in CH₄, as shown by the data in Figure 2. Turnover rates for forward CO₂ and H₂O reforming reactions increased linearly with increasing CH₄ partial pressure (Figure 2a); they were not influenced by CO2 or H₂O partial pressures (Figure 2b). Turnover rates were very similar for these two reactions, indicating that co-reactants are required by stoichiometry, but their activation or subsequent reactions are not kinetically relevant. Forward turnover rates were not influenced by CO and H₂ pressures (0–10 kPa), whether varied by changing residence time or by addition of H₂ or CO to CH₄—CO₂ or CH₄—H₂O reactants. These reaction products influence the approach to equilibrium (Æ) and thus net rates, but not forward rates (from eqs 3–5).

CH₄ reforming reactions can be accurately described by a first-order dependence on CH₄ and a zero-order dependence on CO₂, H₂O, H₂, or CO:

\[ r_f = kP_{CH_4} \]

This first-order rate equation is identical for CH₄—CO₂ and CH₄—H₂O reactions at all reaction temperatures (823–1023 K) on all Pt-based catalysts examined here. Figure 3 shows the effects of CH₄ and CO₂ pressures on forward CH₄ turnover rates at 873 K over a much larger pressure range (100–1000 kPa). Forward CH₄ turnover rates increased linearly with increasing CH₄ partial pressure throughout this wider pressure range, which includes conditions relevant to industrial practice. Rates were not influenced by CO₂ pressure or by the pressure of H₂, CO, or H₂O formed during reaction.

Figure 2b shows that CH₄ turnover rates for H₂O and CO₂ reforming are similar for a given CH₄ pressure. These rates are also similar to those measured during the initial stages of CH₄ decomposition on 1.6 wt % Pt/ZrO₂ (without H₂O or CO₂ co-reactants) (Figure 4, Table 2). First-order rate constants for H₂O (k_H₂O) and CO₂ (k_CO₂) reforming and for CH₄ decomposition (k_decomp) are similar within experimental error at each temperature (Figure 5); this leads to activation energies for CO₂ (83 kJ mol⁻¹) and H₂O (75 kJ mol⁻¹) reforming and for CH₄ decomposition reactions (78 kJ mol⁻¹) that are also similar within our ability to measure them.

These similarities in turnover rates, rate constants, and activation energies for the three reactions indicate a common kinetically relevant step, which cannot involve species derived from co-reactants. The first-order CH₄ dependence and the measured kinetic insensitivity to co-reactants indicate that CH₄
kinetically relevant step is the common kinetically relevant step. C–H bond activation on essentially uncovered Pt surfaces is the sole activation on 1.6 wt % Pt/ZrO₂ (873 K, 20 kPa CH₄, 25 kPa CO₂ or H₂O, 100 kPa total pressure, balance Ar).

TABLE 2: Forward CH₄ Reaction Rates, Rate Constants, Activation Energies, and Pre-exponential Factors for CH₄ Reactions on 1.6 wt % Pt/ZrO₂ (873 K, 25 kPa CH₄, 25 kPa CO₂ or H₂O, or D₂O, 100 kPa total pressure, balance Ar)

<table>
<thead>
<tr>
<th>co-reactant</th>
<th>turnover rate (s⁻¹)</th>
<th>rate constant (kJ/mol)</th>
<th>activation energy (kJ/mol)</th>
<th>pre-exponential factor (s⁻¹ kPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>12.8</td>
<td>0.64</td>
<td>83</td>
<td>5.9 × 10⁴</td>
</tr>
<tr>
<td>H₂O</td>
<td>13.1</td>
<td>0.66</td>
<td>75</td>
<td>2.0 × 10⁴</td>
</tr>
<tr>
<td>None</td>
<td>12.4</td>
<td>0.62</td>
<td>78</td>
<td>2.9 × 10⁴</td>
</tr>
</tbody>
</table>

Initial CH₄ turnover rate on Pt surface. Calculated on the basis of transition-state theory treatments of CH₄ activation steps proceeding via an immobile activated complex. 51

TABLE 3: Kinetic Isotope Effects for CH₄ Reactions on 1.6 wt % Pt/ZrO₂ (873 K, 25 kPa CH₄ or CD₄, 25 kPa CO₂, H₂O, or D₂O, 100 kPa total pressure, balance Ar)

<table>
<thead>
<tr>
<th>reaction</th>
<th>kinetic isotope effect (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rCD₄/H₂O, rCD₄/D₂O</td>
<td>1.07</td>
</tr>
<tr>
<td>rCH₄/H₂O, rCD₄/H₂O</td>
<td>1.69</td>
</tr>
<tr>
<td>rCD₄/O₂, rCD₄/D₂O</td>
<td>1.77</td>
</tr>
<tr>
<td>rCH₄/none, rCD₄/none</td>
<td>1.58</td>
</tr>
</tbody>
</table>

k-factors are 3–10 times larger than experimental values, a level of agreement that is adequate in view of incompleteness of transition state treatments, and which can be improved by allowing modest two-dimensional mobility of activated complexes.

3.2. Kinetic Isotope Effects. The kinetic relevance of C–H bond activation steps in CH₄ decomposition was confirmed by measuring isotope effects from forward turnover rates for CH₄−CO₂ and CH₄−H₂O reactant mixtures at 873–973 K on 1.6 wt % Pt/ZrO₂. Kinetic isotope effects for H₂O reforming were similarly measured from forward turnover rates for CH₄−H₂O and CD₄−H₂O reactants. The irrelevance of co-reactant activation and of subsequent reactions of intermediates formed from water co-reactants were confirmed from the similar turnover rates measured with CD₄−H₂O and CD₄−D₂O mixtures. Kinetic isotope effects for CH₄ decomposition were measured from initial rates of CH₄ and CD₄ decomposition.

Normal kinetic isotope effects were obtained for CH₄−CO₂ and CH₄−H₂O reactions and for CH₄ decomposition (Table 3); their values were identical within experimental accuracy for all three reactions at each reaction temperature. Kinetic isotope effect values at 873 K were 1.69, 1.77, and 1.58 for CO₂ reforming, H₂O reforming, and CH₄ decomposition, respectively. These results confirm the involvement of similar kinetically relevant C–H bond activation steps in these three reactions. CD₄−H₂O and CD₄−D₂O reactant mixtures gave similar turnover rates (k₁/k₀ = 1.05–1.12), indicating that activation of co-reactants and any reactions involving adsorbed species formed from co-reactants are not involved in kinetically relevant steps.

Kinetische isotope effects for CH₄ activation on Pt(111) and Pt(110)(1 × 2) surfaces have been measured using molecular beam methods. Walker et al. 52 reported a kinetic isotope effect of 2 at 1000 K for CH₄ sticking probabilities on Pt(110)(1 × 2). We have not found previous kinetic isotope studies for catalytic H₂O and CO₂ reforming or for stoichiometric decomposition of CH₄ on Pt. The values reported here for Pt resemble those we have recently obtained in parallel studies on Ru (1.40–1.51), 53 Rh (1.54–1.60), 54 and Ni (1.62–1.71), 55 on which isotope effects were also similar for H₂O reforming, CO₂ reforming, and CH₄ decomposition; these values also resemble those reported by others for CH₄ decomposition on Ni (1.60) at 773 K. 56 Several studies 56, 57 however, detected no kinetic isotope effects for CO₂ reforming on Ni, apparently because near-
equilibrium methane conversions led to measurements of little kinetic relevance.

3.3. Elementary Steps in Chemical Conversion of Methane. The similar kinetic rate expressions for H2O and CO2 reforming and decomposition reactions, taken together with isotopic tracer studies and measured kinetic isotope effects, led us to propose a common sequence of elementary steps for CH4 reactions on Ru, Rh, and Ni catalysts. Here, we extend this mechanism, which contains all steps required for reforming, decomposition, and water-gas shift reactions, to Pt surfaces. Relevant elementary steps are shown in Scheme 1, where → denotes an irreversible step, and ⇄ represents a quasi-equilibrated step; $k_i$ is the rate constant and $K_i$ the equilibrium constant for step $i$.

CH4 reacts in a sequence of elementary steps to form chemisorbed carbon and hydrogen. If unoccupied sites (*), corresponding to free Pt ensembles, are the most abundant chemisorbed carbon and hydrogen. If unoccupied sites (.), # and %, corresponding to Pt ensembles chemisorbed CO and H2, are the most abundant chemisorbed carbon and hydrogen. If unoccupied sites (*) and $K_i$ are the equilibrium constant for step $i$.

Hickman and Schmidt used a similar sequence and rate parameters reported on model surfaces to describe nonisothermal space velocity at 873 K on 1.6 wt % Pt/ZrO2 (Reaction conditions: 25 kPa CO2, 25 kPa CH4, 100 kPa total pressure, balance Ar, $\eta_{WGS} = \sqrt{(P_{CO}/P_{H2O})/P_{H2}/P_{CO2}/K_{WGS}}$).

3.4. Isotopic Tracer Studies of C–H Bond Activation Steps. The reversibility of C–H bond activation during CO2 and H2O reforming on Pt catalysts was probed by measuring rates of formation of deuterated isotopomers during reactions of CH4/CD4/CO2 and CH4/CD4/H2O mixtures on 0.4 wt % Pt/ZrO2–CeO2 at 763–973 K. Reversible C–H bond activation would lead to similar chemical conversion and cross-exchange rates, because the latter merely reflects the reverse of C–H dissociation. Cross-exchange would occur more slowly than chemical conversion when C–H bond activation is irreversible.

Chemical conversion and isotopic scrambling rates were measured with CH4/CD4/CO2 (1:1:2) or CH4/CD4/H2O (1:1:2) mixtures using on-line mass spectrometry, after removing H2D2–,O at 218 K (to avoid interference between its fragments and those for CHDx–,CDHx–). CHDx– formation rates are shown in Figure 7 at 873 K. The CH4/CD4 cross exchange turnover rate, defined as the sum of CHDx, CH2D, and CHD2 (twice) formation rates, is 1.9 s$^{-1}$, while the forward turnover rate for methane chemical conversion is 19.0 s$^{-1}$. The approach to equilibrium, $\eta$, during reaction was 0.10, while the ratio of the reverse (cross-exchange) to the forward (chemical conversion) CH4 activation rates is also 0.10. This indicates that CHDx, CH2D, and CHD3 isotopomers form merely because the overall reaction itself approaches equilibrium and becomes reversible, which requires that the rate-determining step, when one exists, be exactly as reversible as the overall catalytic sequence. In effect, C–H bond activation on Pt at 873 K is irreversible, except for the extent to which reversibility is thermodynamically required by the approach to equilibrium for the overall chemical reaction.

CH4/CD4 cross exchange and chemical conversion rates are shown in Table 4 during reactions of CH4/CD4/H2O mixtures at several reaction temperatures. At all temperatures, methane chemical conversion rates are much higher than CH4/CD4 cross exchange rates; thus, kinetically relevant C–H bond activation steps are irreversible also during H2O reforming reaction, except as required by overall thermodynamics.

3.5. Isotopic Tracer Studies of Co-Reactant Activation Steps. The reversibility of CO2 activation steps (step 2 in Scheme 1) was determined from reactions of 12CH4/13CO2/13CO
TABLE 4: Methane Chemical Conversion and CH₄/CD₄ Cross Exchange Rates During Reaction of CH₄/CD₄/H₂O Mixture on 0.4 wt % Pt/ZrO₂−CeO₂ Catalyst (12.5 kPa CH₄, 12.5 kPa CD₄, 25 kPa H₂O, 100 kPa total pressure, balance Ar)

| reaction temperature(K) | methane chemical conversion turnover rate (s⁻¹) | cross exchange rate (s⁻¹) | r_exchange | η
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>873</td>
<td>20.2</td>
<td>1.8</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>923</td>
<td>44.1</td>
<td>4.8</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>973</td>
<td>72.7</td>
<td>6.7</td>
<td>0.09</td>
<td>0.12</td>
</tr>
</tbody>
</table>

a Forward methane chemical conversion rate. b Total methane isotopomers formation rate. c Ratio of total methane isotopomers formation rate to the methane chemical conversion rate. d η = ([PnCO][PnH])/(([PnCO][PnH]) + K);

Figure 7. Methane turnover rates and CH₄/CD₄ cross exchange rates during the reaction of CH₄/CD₄/CO₂ mixture on 0.4% Pt/ZrO₂−CeO₂ catalyst (5 mg of catalyst, 873 K, 12.5 kPa CH₄ and CD₄, 25 kPa CO₂, 100 kPa total pressure, balance Ar).

reactants. Reversible CO₂ dissociation would lead to rapid formation of ¹³CO₂ via its microscopic reverse, while an irreversible step would preserve the isotopic purity of the ¹²CO₂ reactants.

Reactions of ¹³CH₄/¹²CO₂/¹³CO (1:1:0.4) mixtures on 0.4 wt % Pt/ZrO₂−CeO₂ at 923 K led to similar ¹³C fractions in the CO (0.25) and CO₂ (0.23) present in the reactor effluent, even though reactants were isotopically pure ¹²CO₂ and ¹³CO. This ¹³C content corresponds to complete chemical and isotopic equilibration between CO and CO₂, even at the low CH₄ conversion (15%) and approach to equilibrium (η = 0.12) prevalent in these experiments. These data confirm that CO₂ activation steps are much faster than the kinetically relevant steps for H₂O activation; thus, CO₂ activation steps must be quasi-equilibrated and kinetically irrelevant. In effect, steps 2 in Scheme 1 occur many times in both directions in the time scale required for a CH₄ chemical conversion turnover, a situation that also preserved surfaces essentially uncovered by CH₄−derived reactive intermediates. By inference from kinetic analogies between CH₄−CO₂ and CH₄−H₂O reactions, we conclude that H₂O activation steps are also likely to be quasi-equilibrated during H₂O reforming.

3.6. Isotopic Probes of Hydrogen and Hydroxyl Recombination Steps. Water forms during CH₄ reforming of CH₄ via reverse water-gas shift (RWGS) reactions. More rigorously, H₂O forms because chemisorbed O-atoms from CO₂ and chemisorbed H-atoms from CH₄ occasionally react to form water, in a reaction that is nonrigorously treated as a separate stoichiometric (water-gas shift) reaction in most previous studies. The expected reactants and products of water-gas shift reactions exist at their equilibrium relative concentrations during CH₄ reforming.

TABLE 5: Distribution of Water Isotopomers during Reaction of CH₄/CO₂/D₂ Mixtures on 0.4 wt % Pt/ZrO₂−CeO₂ (873 K, 16.7 kPa CH₄, 16.7 kPa CO₂, 3.3 kPa D₂, 100 kPa Total Pressure, Balance Ar)

<table>
<thead>
<tr>
<th>isotopomer</th>
<th>measured (H/D = 1.43)</th>
<th>binomial (H/D* = 1.41)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.33</td>
<td>0.34</td>
</tr>
<tr>
<td>HD₂</td>
<td>0.48</td>
<td>0.49</td>
</tr>
<tr>
<td>D₂O</td>
<td>0.16</td>
<td>0.17</td>
</tr>
</tbody>
</table>

(Figure 6); thus, water and dihydrogen formation must involve quasi-equilibrated elementary steps.

The isotopic composition of products formed from CH₄/CO₂/ D₂ (1:1:0.2) mixtures on 0.4 wt % Pt/ZrO₂−CeO₂ at 873−973 K was measured by on-line mass spectrometry. The H/D fraction expected if H-atoms in any CH₄ molecules converted to synthesis gas and D-atoms in the added D₂ contributed to surface intermediates is 1.41. The measured H/D ratios were 1.43 and 1.44 in water and dihydrogen, respectively, indicating complete equilibration between gas-phase dihydrogen and water molecules and their corresponding chemisorbed precursors. Water isotopomers formed from CH₄/CO₂/D₂ mixtures obey a binomial distribution (Table 5), as expected from quasi-equilibrated H* and OH* recombination (step 5 in Scheme 1). The quasi-equilibrated nature of the steps leading to water and dihydrogen, taken together with the expected equilibration of nondissociative CO chemisorption, would lead to thermodynamic equilibrium for water-gas shift reactions, as found experimentally. Binomial distributions were also observed for dihydrogen isotopomers at 873−973 K, as expected from reversible and quasi-equilibrated hydrogen recombinative desorption steps (step 4 in Scheme 1) during CH₄ reforming reactions.

3.7. Effects of Pt Dispersion and of Support on CH₄ Reactions. Methane activation studies on model surfaces have concluded that activation of C−H bonds depends sensitively on surface structure; specifically, surface steps and kinks are much more active than atoms on close-packed surfaces. Surface roughness and coordinative unsaturation increase as metal clusters become smaller. To our knowledge, no systematic studies of Pt cluster size effects on CH₄ activation or reforming rates are available.

The effects of Pt dispersion on CH₄ reforming turnover rates are shown in Table 1 and Figure 8 for CH₄−CO₂, CH₄−H₂O, and CH₄ decomposition reactions. CH₄ turnover rates for each reaction increased monotonically with increasing Pt dispersion, suggesting that coordinatively unsaturated Pt surface atoms, prevalent in small crystallites, are indeed more active than atoms on the low-index surfaces predominately exposed on larger crystallites. Surface atoms with fewer Pt neighbors appear to bind CH₄ and H species more strongly and to stabilize activated
complexes involved in the formation of these intermediates, thus decreasing C–H bond activation energies.

Thermal desorption and low-energy electron diffraction studies showed that the activation energy for dissociative chemisorption of ethane on Pt(110)–(1 × 2) surface is 25 kJ/mol lower than on close-packed Pt(111) surfaces. Activation barriers for dissociation of CH₄ molecular beams on stepped Pt(533) surfaces were 30 kJ/mol lower than that on close-packed Pt(111). Activation barriers on steps were about 150 kJ/mol smaller than on terraces; activation barriers on steps were about 150 kJ/mol smaller than on terraces. Molecular beam studies showed that initial ethane trapping probabilities on open Pt(110)–(1 × 2) surfaces were greater than on close-packed Pt(111). These effects of coordinative unsaturation appear to be ubiquitous for molecule dissociation reactions. In fact, theory and experiment showed that N₂ dissociation on Ru is about 10⁶ times faster on steps than on terraces; activation barriers on steps were about 150 kJ/mol smaller than on terraces. Molecular beam studies showed that H₂ dissociation is nonactivated on stepped Pt(332), but proceeds with an activation barrier of 2–6 kJ/mol on Pt(111).

Figure 8 and Table 1 also show the effects of support on forward CH₄ turnover rates for CH₄ reforming and decomposition reactions on Pt-based catalysts. The identity of the support did not influence measured turnover rates, but it can influence Pt dispersion. Once measured rates are rigorously normalized by the number of exposed Pt surface atoms, CH₄ reaction rates depend only on the size (and structure) of Pt clusters and not on the identity of the support. In any case, any potential involvement of the support in activation of CO₂ and H₂O co-reactants is inconsequential, because reaction rates depend only on C–H bond activation rates.

One study reported much higher conversions during CO₂ reforming on Pt/ZrO₂ than on Pt/SiO₂ and suggested that ZrO₂ promotes CO₂ dissociation, but neither Pt dispersions nor turnover rates were reported. Thus, these support effects may reflect secondary effects of supports on Pt dispersion or on the extent to which mass or heat transfer influenced reaction rates. Another study suggested that CH₄ conversion is controlled by Pt-support contact perimeter, because of the bifunctional nature of CO₂–CH₄ reforming pathways on Pt. These support effects are inconsistent with the kinetic irrelevance of co-reactant activation, shown here for reaction conditions resembling those in these previous studies, or with the lack of support effects reported in this study.

Similar dispersion and supports effects and similar actual values of turnover rates were measured for CH₄–H₂O, CH₄–CO₂, CH₄ decomposition reactions on the Pt catalysts of this study (Table 1, Figure 8), as expected from the rigorous mechanistic equivalence among these reactions. Similar effects of metal dispersion, also equivalent for all three reactions, were measured in parallel studies of CH₄ reforming and decomposition reactions on Rh, Ru, and Ir catalysts.

Figure 9 shows similar effects of metal dispersion on turnover rates for CH₄–CO₂ and CH₄–H₂O reactions on other supported noble metals (Rh, Ir, Ru) in addition to the Pt catalysts of this study. For each metal, at least two supports were used to disperse metal clusters and no effects of support on turnover rates were detected. On all metals, CH₄ turnover rates increase with increasing metal dispersion. Pt surfaces are more active than those of the other noble metals for any given cluster size. This appears to be the first rigorous and direct comparison of the reactivity of supported Group VIII metal clusters for catalytic reactions of CH₄ using materials and conditions relevant to industrial practice. The exclusion of transport artifacts and reverse reactions and the measurement of rates normalized by the relevant exposed surface area of metal clusters make these rate comparisons a rigorous and sole reflection of the kinetic reactivity of such metal surfaces.

3.8. Characterization of Supported Pt Clusters by CO Oxidation. Here, we confirm the accuracy of chemisorptive Pt dispersions measured before reaction and their relevance to the state of Pt surfaces in working catalysts. These measurements are critical to ensure that observed dispersion effects and measured activation energies do not reflect blockage of exposed Pt atoms by unreactive carbon residues during initial catalytic turnovers, which could occur to varying extents as metal dispersion or reaction conditions vary. We note that we have not detected any transient effects during the first few seconds of exposure to CH₄–CO₂ or CH₄–H₂O reactants, but typical turnover times are short (<0.1 s), and any such initial transients may not be detected when they occur concurrently with short but unavoidable hydrodynamic delays (~2 s).

These measurements also address significant differences between activation energies obtained from sticking coefficients on model surfaces and from chemical conversion and stoichiometric decomposition rates of CH₄ on supported Pt catalysts, which may reflect changes in the state of catalytic surfaces during reaction. Activation energies reported here (83 and 75 kJ/mol for CO₂ and H₂O reforming, respectively) and in previous CO₂ reforming studies on Pt-based catalysts are much larger than those measured or calculated on model Pt surfaces. For example, atom-superposition
electron-delocalization molecular orbital methods gave an activation barrier of 43 kJ/mol for CH₄ activation on Pt(111) surfaces. Activation energies of 20 and 35 kJ/mol were reported for the CH₄ sticking coefficient using molecular beam methods on Pt(110) and Pt(111), respectively. Our kinetic study indicates that reactions of H₂O or CO₂ with CH₄-derived chemisorbed carbon are fast and lead to essentially uncovered surfaces during CH₄ reforming reactions. Yet, we cannot rule out that unreactive carbonaceous deposits, without detectable reactivity in reactions with co-reactants, form during the first few turnovers. For example, sites with the greatest coordinative unsaturation and reactivity could form irreversibly chemisorbed carbon, leaving less reactive surface Pt atoms to catalyze CH₄ conversion turnovers. These carbon deposits must be totally unreactive during CH₄ reforming, because their surface density would otherwise vary with the concentration or reactivity of the co-reactant, leading to apparent positive orders in the co-reactant reactant concentration and to different rates with H₂O and CO₂.

Here, we use CO oxidation, a recognized structure-insensitive reaction (see also insensitivity of turnover rates to dispersion in Figure 8a) to detect any changes in the number of exposed Pt atoms during CH₄ reforming, whether these changes occur via blockage of surface sites or sintering of small Pt clusters. We note that chemisorption measurements after reaction are not possible, because of the very small catalyst amounts required for isothermal rate measurements (5 mg). CO oxidation rates on a fresh 1.6 wt % Pt/ZrO₂ catalyst and on this catalyst after CO₂ and H₂O reforming are identical within experimental accuracy (Figure 10). This shows unequivocally that the number of exposed Pt atoms is unchanged during reaction and that unreactive carbon residues are present at very low coverages (<5%), if at all.

We cannot rule out that some initially exposed surface atoms, with remarkable reactivity in stoichiometric CH₄ activation but unable to turn over, become unavailable during initial contact with reforming reactants and do not contribute to catalytic rates. Their number would have to be extremely small, because CO oxidation rates would otherwise be detectably influenced by CH₄ reforming reactions. We conclude, however, that such sites, if present, cannot turn over; thus, they are not relevant to the analysis and prediction of catalytic rates of CH₄–H₂O and CH₄–CO₂ reactions. These results raise important questions about the nature of model surfaces and methods that are appropriate for experimental and theoretical studies of CH₄ reactions. They also highlight the essential requirement that experiment and theory rigorously address complete catalytic cycles, and not merely stoichiometric steps presumably involved in such cycles.

4. Conclusions

Isotopic tracer and kinetic measurements led to a simple mechanistic picture and a unifying kinetic treatment of CH₄–CO₂, CH₄–H₂O, and CH₄ decomposition reactions, as well as water-gas shift, on Pt-based catalysts. Reforming and decomposition rates were first-order in CH₄ concentration and independent of the concentration or identity of the co-reactants, suggesting that reaction rates are exclusively limited by C–H bond activation on metal cluster surfaces and that co-reactant activation is not kinetically relevant. These conclusions are consistent with the similar activation energies measured for CH₄ reforming and decomposition reactions. The normal CH₄/CD₄ kinetic isotope effects measured were similar for all three CH₄ reactions and thus also independent of co-reactant identity.
Water and dihydrogen formation steps are quasi-equilibrated, as shown from their binomial isotoptomers distributions during reactions of CH$_2$/CO$_2$/D$_2$ mixtures. The identical $^{13}$C contents in CO and CO$_2$ molecules during $^{12}$CH$_4$/$^{12}$CO$_2$/$^{13}$CO reactions indicate that CO$_2$ activation steps are reversible and quasi-equilibrated. The quasi-equilibrated nature of these steps is consistent with the observed chemical equilibrium among reactants and products of the water-gas shift.

Forward CH$_4$ turnover rates increased monotonically with increasing Pt dispersion for CO$_2$ reforming, H$_2$O reforming, and CH$_4$ decomposition reactions, suggesting that coordinative unsaturation increases C$\equiv$H bond activation reactivity. Supports (ZrO$_2$, $\gamma$-$\text{Al}_2$O$_3$, ZrO$_2$-$\text{CeO}_2$) influence Pt dispersion, but not turnover rates, indicating that co-reactant activation on supports, if it occurs, is not kinetically relevant. The rates of structure-insensitive CO oxidation reactions are similar before and after CH$_4$ reforming; thus, the latter reaction does not influence the insensitive CO oxidation reactions are similar before and after CO$_2$ activation steps are reversible and quasi-equilibrated.

These metal dispersion effects and the mechanistic conclusions reached from kinetic and isotopic studies are similar to those found in parallel studies of supported Rh, Ru, Ir, and Ni catalysts and appear to apply in general to CH$_4$ reactions on Group VIII metals. Pt surfaces, however, are the most reactive among the metal clusters examined.

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References and Notes