Chemical conversion of CH$_4$ into larger molecules is practiced by initially forming H$_2$–CO mixtures over metal catalysts. These reactions use CO$_2$ or H$_2$O as co-reactants in processes which also produce H$_2$, that is then used in refining and petrochemical processes and in fuel cells. The strong bonds in CH$_4$ (439 kJ mol$^{-1}$) and the endothermic nature of re-forming reactions call for high temperatures and stable catalysts.[2–4] Supported Ir clusters catalyze CO$_2$–CH$_4$ reactions without detectable carbon formation,[5–7] with turnover rates higher than those found with other Group VIII metals, except Pt.[2]

Experimental and theoretical studies on model surfaces[8,9] have suggested that C–H bond activation is sensitive to surface structure and requires coordinatively unsaturated sites.[10,11] The effects of cluster size and of concomitant changes in surface coordination on re-forming turnover rates remain unexplored for Ir catalysts. Contradictory conclusions about the kinetic relevance of C–H activation steps within catalytic sequences remain, and catalytic supports have often been claimed to be required for the activation of CO$_2$ or H$_2$O co-reactants.[6–7]

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**Methane Activation**

**Structural and Mechanistic Requirements for Methane Activation and Chemical Conversion on Supported Iridium Clusters**

*Junmei Wei and Enrique Iglesia*

Chemical conversion of CH$_4$ into larger molecules is practiced by initially forming H$_2$–CO mixtures over metal catalysts. These reactions use CO$_2$ or H$_2$O as co-reactants in processes which also produce H$_2$, that is then used in refining and petrochemical processes and in fuel cells. The strong bonds in CH$_4$ (439 kJ mol$^{-1}$) and the endothermic nature of re-forming reactions call for high temperatures and stable catalysts.[2–4] Supported Ir clusters catalyze CO$_2$–CH$_4$ reactions without detectable carbon formation,[5–7] with turnover rates higher than those found with other Group VIII metals, except Pt.[2]

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C–H bond dissociation controls CH4 conversion rates on many metal clusters, but CH4 re-forming kinetics and support and cluster-size effects have not been examined with respect to Ir catalysts. Herein we report evidence for the pathways involved in CH4–CO2, CH4–H2O, and CH4-decomposition reactions on Ir.

CH4 reaction rates are solely limited by C–H bond cleavage on Ir surfaces that remain essentially uncovered during catalysis. Turnover rates do not depend on the concentration or identity of the co-reactant; in these cases, turnover rates increase with increasing Ir dispersion, but they do not depend on the identity of the support (Al2O3, ZrO2).

CH4 reaction rates were measured on Ir catalysts (5 mg; 0.2, 0.4, 0.8, 1.6 wt % of Ir) diluted as pellets (25 mg inert support; pellet size 250–425 μm) and within the bed (500 mg ground quartz) to avoid temperature and concentration gradients; rates were unaffected by dilution, confirming the absence of these artifacts. Kinetic effects of CH4, H2O, and CO2 pressures on reaction rates were measured at 823–1023 K and 100–1000 kPa for reactant ratios (CO2, H2O)/CH4 of 0.5–4 by correcting measured rates for approach to equilibrium to obtain rates for forward re-forming reactions.[2]

Figure 1 shows that turnover rates increase linearly with increasing CH4 pressure at 873 K on 0.8 wt % Ir/ZrO2; they were not influenced by CO2 pressures (10–300 kPa) for CH4–CO2 reactions. Similar CH4 and H2O dependences were observed in CH4–H2O reactions. In both re-forming reactions, CO or H2 addition influenced net turnover rates because of higher reverse rates as expected from thermodynamic considerations, but forward turnover rates were unaffected by CO or H2 pressures. These data indicate that Ir surfaces remain essentially uncovered by CH4-derived intermediates or by product reactions, because co-reactant or product concentrations would have otherwise influenced forward rates. H2 and CO desorb from Ir (111) at 380 K (0.5-L exposure) and 510 K (1-L exposure), respectively.[12,13] CO adsorption enthalpies (150 kJ mol−1) would lead to CO coverages below 0.1 % at 873 K, even at equilibrium CH4 conversions (for equimolar CH4–CO2 reactants, 100 kPa); thus, no inhibition by chemisorbed CO is expected or, indeed, detected.

The sole kinetic relevance of C–H bond activation on uncovered Ir surfaces leads to similar turnover rates for CH4–CO2 and CH4–H2O reactions at a given CH4 pressure (Table 1). Thus, the identity of the co-reactants, with the consequent implications for their reactivity, does not influence rates because both H2O and CO2 react with CH4-derived intermediates rapidly relative to C–H activation steps. These re-forming rates are also similar to initial rates for CH4 decomposition, a stoichiometric noncatalytic reaction that forms carbon and H2(g) on Ir catalysts (Table 1). These similarities in rate constants and turnover rates remain throughout a wide temperature range (823–1023 K), and as such the activation energies are also similar for these reactions (Table 1). Measured preexponential factors (Table 1) are about 10 times larger than those predicted from transition state theory (5.5 × 101 s−1 kPa−1) assuming immobile activated complexes, but they approach experimental values when activated complexes are allowed modest two-dimensional mobility.

The kinetic relevance of C–H bond activation was confirmed by similar kinetic isotopic effects (1.70–1.81) measured for CO2 re-forming, H2O re-forming, and decomposition reactions (0.8 wt % Ir/ZrO2; 873 K). The fast and quasi-equilibrated nature of co-reactant activation was dem-

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**Table 1**: Forward CH4 turnover rates, rate constants, activation energies, and pre-exponential factors for CH4 reactions on 0.8 wt % Ir/ZrO2 (873 K, 20 kPa CH4, 25 kPa CO2 or H2O, balance Ar).

<table>
<thead>
<tr>
<th>Co-reactant</th>
<th>Turnover rate [s−1]</th>
<th>Rate constant [s−1 kPa−1]</th>
<th>Activation energy [kJ mol−1]</th>
<th>Pre-exponential factor [s−1 kPa−1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>13.0</td>
<td>0.65</td>
<td>86</td>
<td>9.1 × 104</td>
</tr>
<tr>
<td>H2O</td>
<td>12.4</td>
<td>0.62</td>
<td>87</td>
<td>9.9 × 104</td>
</tr>
<tr>
<td>None</td>
<td>11.2</td>
<td>0.56</td>
<td>81</td>
<td>3.9 × 104</td>
</tr>
</tbody>
</table>

[a] Initial CH4 rate.
Demonstrated by the identical $^{13}$C content in the CO and CO$_2$ leaving a catalyst bed used to react CO$_2$/CH$_4$/$^{13}$CO (1:1:0.4) mixtures.

The uncovered nature of Ir surfaces and the persistence and catalytic relevance of Ir dispersions measured before reaction were confirmed by measuring rates of CO oxidation, a structure-insensitive reaction,[15] before and after re-forming reactions. CO turnover rates at 363 K on 1.6 wt% Ir/ZrO$_2$ were similar before and after CH$_4$–CO$_2$ or CH$_4$–H$_2$O reactions (Figure 2). Thus, Ir atoms are not covered by unreactive carbon residues or lost by sintering during CH$_4$ re-forming at 873 K. Re-forming and CO oxidation rates did not change with time, indicating that Ir surfaces are stable for extended periods of time under CH$_4$ re-forming conditions.

The simple kinetic equation $r = kP_{CH_4}$ accurately describes measured CH$_4$ re-forming and decomposition kinetics on Ir. CO$_2$ and H$_2$O co-reactants and H$_2$ and CO products do not influence rates. This expression is accurate for all catalysts throughout the temperature range examined (823–1023 K). These conclusions and the dispersion effects discussed below appear to be generally applicable to Pt,[21] Ru,[24] and Rh[25] clusters.

CH$_4$ re-forming and decomposition turnover rates increased with increasing Ir dispersion (Figure 3), as it varied with metal content (0.2–1.6 wt %) or support. These data contradict the lack of dispersion effects reported for CO$_2$–CH$_4$ reactions on Ir/Al$_2$O$_3$,[21] but they are consistent with coordinative unsaturation requirements inferred from theoretical and experimental studies on model surfaces.[4,18-24] Density functional theory showed that CH$_4$ binds 18–22 kJ mol$^{-1}$ more strongly on kink sites than on Ir (111).[21] C$_2$H$_4$ dissociates with ~20 kJ mol$^{-1}$ lower activation energies on Ir (110)-(1x2) than on Ir (111).[22,23] Ir (110)-(1x2) activates C$_2$–C$_n$ alkanes, whereas Ir (111) does not.[22,23] Similar trends are apparent from the reactivity of defect sites on Ir (111)[24] and of Ir (110) relative to Ir (111).[4,20]

We note that activation energies on model surfaces are much lower than those measured on Ir clusters in this study. Very active sites could form unreactive carbon, leaving less reactive sites to catalyze CH$_4$ conversion turnovers. Figure 2 shows unequivocally that CH$_4$ re-forming reactions do not change the number of exposed Ir atoms. We cannot rule out the presence of minority sites (<5% of exposed Ir atoms) with remarkable reactivity for activation of C–H bonds. We can conclude, however, that such sites do not react and are thus not relevant to catalysis. These issues illustrate the essential requirement that experiment and theory rigorously address catalytic cycles, and not merely the stoichiometric steps presumably involved in such cycles.

Support effects have been attributed to co-reactant activation sites, without rigorous assessment of the concomitant effects of the support on metal dispersion or transport artifacts.[25] We measured similar turnover rates on Ir/Al$_2$O$_3$ and Ir/ZrO$_2$ (Figure 3), as also found for other metals with a wider range of supports.[2,16,17] Co-reactant activation on supports, even if it occurred, could not influence CH$_4$ turnover rates, because such steps are not kinetically relevant. Thus, previously reported support effects[25] cannot be compared with our data or with our mechanistic conclusions. The absence of support effects agrees with a previous study of re-forming reactions catalyzed by Ir,[26] whose kinetic character is, however, equivocal, because of near-equilibrium conversions.

In summary, C–H bond activation is the only kinetically relevant step in CH$_4$ activation on supported Ir clusters, the reactivity of which increases with increasing dispersion. Kinetically relevant C–H bond activation steps and consequently, overall CH$_4$ re-forming rates are unaffected by the chemical identity of the support.

**Experimental Section**

Ir/Al$_2$O$_3$ and Ir/ZrO$_2$ were prepared by incipient wetness impregnation of Al$_2$O$_3$ or ZrO$_2$ with aqueous IrCl$_3$·3H$_2$O. Ir dispersions were
measured by using volumetric methods to determine uptakes of strongly chemisorbed H2 at 313 K. The high-pressure reactor system was described elsewhere.\[2\] Reactant and product concentrations were measured with a HP 6890 gas chromatograph. Catalysts (20 mg) diluted with quartz powder (500 mg) were used in CH4 decomposition kinetic measurements. Chemical composition was measured by on-line mass spectrometry. Ir/ZrO2 (1.6 wt %; 5 mg) was used to measure CO oxidation reaction rates at 363 K and 0.19 kPa CO and O2 pressures.

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