

Methane Activation**Structural and Mechanistic Requirements for Methane Activation and Chemical Conversion on Supported Iridium Clusters*****Junmei Wei and Enrique Iglesia**

Chemical conversion of CH₄ into larger molecules is practiced by initially forming H₂-CO mixtures over metal catalysts. These reactions use CO₂ or H₂O as co-reactants in processes which also produce H₂, that is then used in refining and petrochemical processes and in fuel cells. The strong bonds in CH₄ (439 kJ mol⁻¹^[1]) and the endothermic nature of reforming reactions call for high temperatures and stable catalysts.^[2-4] Supported Ir clusters catalyze CO₂-CH₄ 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 CO₂ or H₂O co-reactants.^[6,7]

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C–H bond dissociation controls CH₄ conversion rates on many metal clusters,^[2–4] 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 reaction products, 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

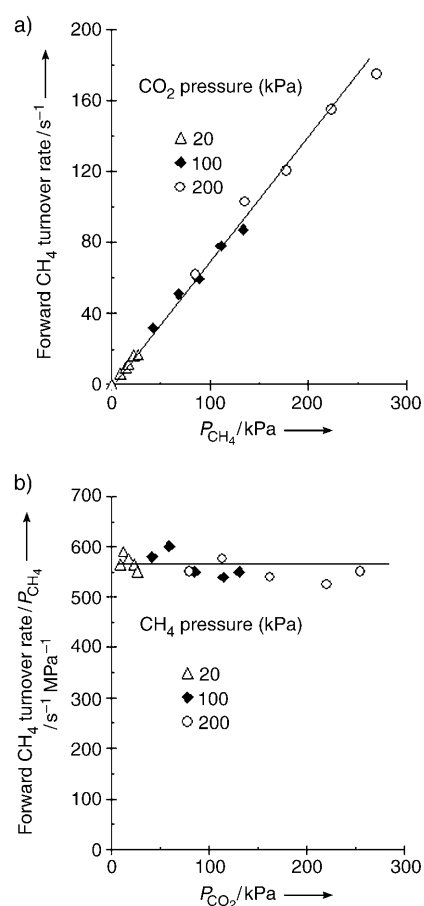


Figure 1. Effects of CH₄ (a) and CO₂ (b) pressure on forward CH₄ turnover rates for CH₄–CO₂ reactions on 0.8 wt % Ir/ZrO₂ (873 K, balance He, average pressure is the average of inlet and outlet pressures within the reactor; The unit for turnover rate is molecules/surface atom measured by H₂ chemisorption per second).

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).

Co-reactant	Turnover rate [s ⁻¹]	Rate constant [s ⁻¹ kPa ⁻¹]	Activation energy [kJ mol ⁻¹]	Pre-exponential factor [s ⁻¹ kPa ⁻¹]
CO ₂	13.0	0.65	86	9.1 × 10 ⁴
H ₂ O	12.4	0.62	87	9.9 × 10 ⁴
None	11.2 ^[a]	0.56	81	3.9 × 10 ⁴

[a] Initial CH₄ rate.

reactions (Table 1). Measured preexponential factors (Table 1) are about 10 times larger than those predicted from transition state theory ($5.5 \times 10^3 \text{ s}^{-1} \text{ kPa}^{-1}$) 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-

onstrated by the identical ^{13}C content in the CO and CO_2 leaving a catalyst bed used to react $\text{CO}_2/\text{CH}_4/^{13}\text{CO}$ (1:1:0.4) mixtures.^[14]

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/ZrO₂ were similar before and after CH₄-CO₂ or CH₄-H₂O reactions (Figure 2). Thus, Ir atoms are not covered by unreactive

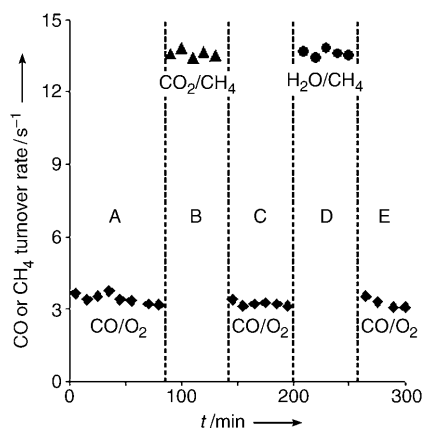


Figure 2. CO oxidation and forward CH₄ re-forming turnover rates on 1.6 wt% Ir/ZrO₂ (A, C, E, CO oxidation turnover rates, 363 K, 0.19 kPa CO and O₂; B, D, forward CH₄ turnover rates for CH₄-CO₂ and CH₄-H₂O reactions, 873 K, 25 kPa CH₄ and 25 kPa CO₂ or H₂O; The unit for turnover rate is molecules/surface atom measured by H₂ chemisorption per second).

carbon residues or lost by sintering during CH₄ 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 CH₄ re-forming conditions.

The simple kinetic equation $r_f = kP_{\text{CH}_4}$ accurately describes measured CH₄ re-forming and decomposition kinetics on Ir. CO₂ and H₂O co-reactants and H₂ 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,^[2] Ru,^[16] and Rh^[17] clusters.

CH₄ 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 CO₂-CH₄ reactions on Ir/Al₂O₃,^[5] 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 CH₄ binds 18–22 kJ mol⁻¹ more strongly on kink sites than on Ir (111).^[21] C₂H₆ dissociates with ~20 kJ mol⁻¹ lower activation energies on Ir (110)-(1×2) than on Ir (111).^[22,23] Ir (110)-(1×2) activates C₂-C₇ 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]

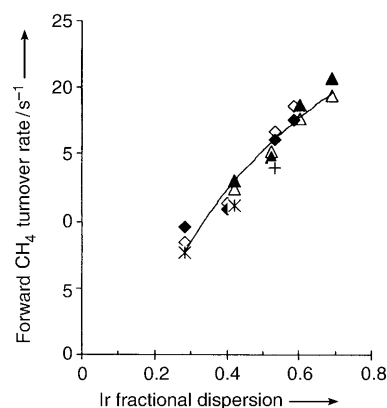


Figure 3. Forward CH₄ turnover rates for CH₄-CO₂ (solid symbol), CH₄-H₂O (open symbol), and CH₄ decomposition reactions as a function of Ir dispersion (873 K, 20 kPa CH₄, (◇) Ir/ZrO₂, (▲) Ir/Al₂O₃, (×) CH₄ decomposition on Ir/ZrO₂, (+) CH₄ decomposition on Ir/Al₂O₃). (The unit for turnover rate is molecules/surface atom measured by H₂ chemisorption per second).

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 CH₄ conversion turnovers. Figure 2 shows unequivocally that CH₄ 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/Al₂O₃ and Ir/ZrO₂ (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 CH₄ 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 CH₄ activation on supported Ir clusters, the reactivity of which increases with increasing dispersion. Kinetically relevant C–H bond activation steps and consequently, overall CH₄ re-forming rates are unaffected by the chemical identity of the support.

Experimental Section

Ir/Al₂O₃ and Ir/ZrO₂ were prepared by incipient wetness impregnation of Al₂O₃ or ZrO₂ with aqueous IrCl₃·3H₂O. 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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