Methane Activation

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

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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_2O 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} [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_2O co-reactants.[6,7]

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C–H bond dissociation controls CH_4 conversion rates on many metal clusters,[2–4] but CH_4 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 CH_4–CO_2, CH_4–H_2O, and CH_4-decomposition reactions on Ir.

CH_4 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 (Al_2O_3, ZrO_2).

CH_4 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 CH_4, H_2O, and CO_2 pressures on reaction rates were measured at 823–1023 K and 100–1000 kPa for reactant ratios (CO_2, H_2O)/CH_4 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 CH_4 pressure at 873 K on 0.8 wt% Ir/ZrO_2; they were not influenced by CO_2 pressures (10–300 kPa) for CH_4–CO_2 reactions. Similar CH_4 and H_2O dependences were observed in CH_4–H_2O reactions. In both re-forming reactions, CO or H_2 addition influenced net turnover rates because of higher reverse rates as expected from thermodynamic considerations, but forward turnover rates were unaffected by CO or H_2 pressures. These data indicate that Ir surfaces remain essentially uncovered by CH_4-derived intermediates or by reaction products, because co-reactant or product concentrations would have otherwise influenced forward rates. H_2 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 CH_4 conversions (for equimolar CH_4–CO_2 reactants, 100 kPa); thus, no inhibition by chemisorbed CO is expected or, indeed, detected.

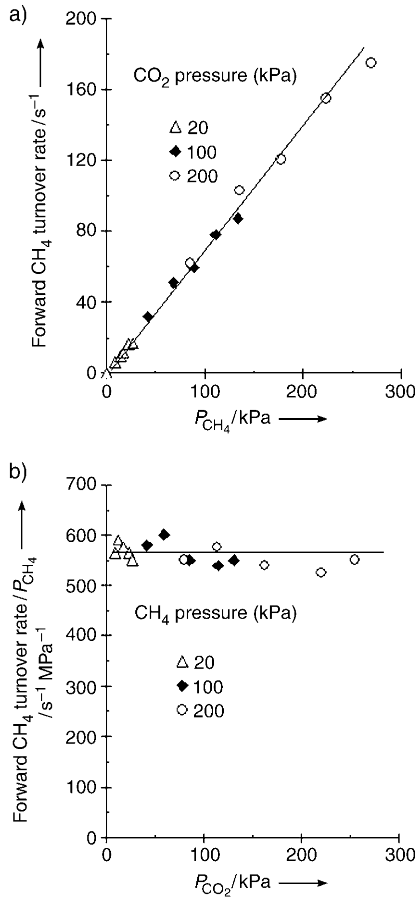

Figure 1. Effects of CH_4 (a) and CO_2 (b) pressure on forward CH_4 turnover rates for CH_4–CO_2 reactions on 0.8 wt% Ir/ZrO_2 (873 K, balance He, average pressure is the average of inlet and outlet pressures within the reactor; The unit for turnover rate is molecules/surface atom measured by H_2 chemisorption per second).

Table 1: Forward CH_4 turnover rates, rate constants, activation energies, and pre-exponential factors for CH_4 reactions on 0.8 wt% Ir/ZrO_2 (873 K, 20 kPa CH_4, 25 kPa CO_2 or H_2O, 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_2O	12.4	0.62	87	9.9×10^4
None	11.2[a]	0.56	81	3.9×10^4

[a] Initial CH_4 rate.

The sole kinetic relevance of C–H bond activation on uncovered Ir surfaces leads to similar turnover rates for CH_4–CO_2 and CH_4–H_2O reactions at a given CH_4 pressure (Table 1). Thus, the identity of the co-reactants, with the consequent implications for their reactivity, does not influence rates because both H_2O and CO_2 react with CH_4-derived intermediates rapidly relative to C–H activation steps. These re-forming rates are also similar to initial rates for CH_4 decomposition, a stoichiometric noncatalytic reaction that forms carbon and H_2(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 (5.5×10^3 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 CO_2 re-forming, H_2O re-forming, and decomposition reactions (0.8 wt% Ir/ZrO_2; 873 K). The fast and quasi-equilibrated nature of co-reactant activation was 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.[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/ZrO_2 were similar before and after CH_4–CO_2 or CH_4–H_2O 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.

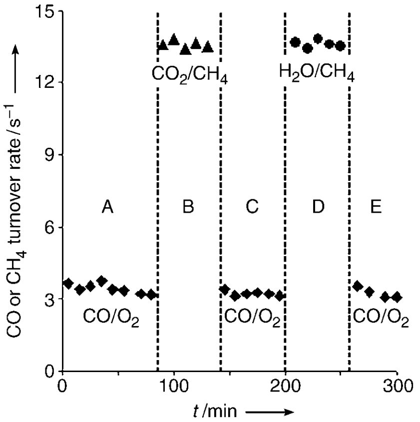

Figure 2. CO oxidation and forward CH_4 re-forming turnover rates on 1.6 wt% Ir/ZrO_2 (A, C, E, CO oxidation turnover rates, 363 K, 0.19 kPa CO and O_2; B, D, forward CH_4 turnover rates for CH_4–CO_2 and CH_4–H_2O reactions, 873 K, 25 kPa CH_4 and 25 kPa CO_2 or H_2O; The unit for turnover rate is molecules/surface atom measured by H_2 chemisorption per second).

The simple kinetic equation $r_f = kP_{CH_4}$ accurately describes measured CH_4 re-forming and decomposition kinetics on Ir. CO_2 and H_2O 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,[2] Ru,[16] and Rh[17] 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_2O_3,[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 CH_4 binds 18–22 kJ mol^{-1} more strongly on kink sites than on Ir (111).[21] C_2H_6 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 C_2–C_7 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]

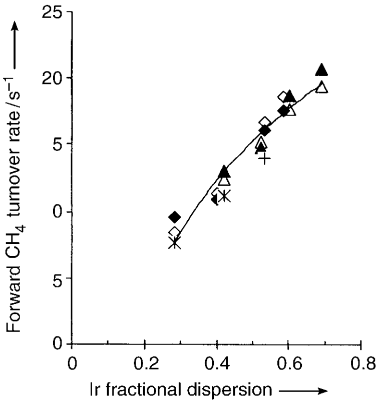

Figure 3. Forward CH_4 turnover rates for CH_4–CO_2 (solid symbol), CH_4–H_2O (open symbol), and CH_4 decomposition reactions as a function of Ir dispersion (873 K, 20 kPa CH_4, (◇◆) Ir/ZrO_2, (▲△) Ir/Al_2O_3, (*) CH_4 decomposition on Ir/ZrO_2, (+) CH_4 decomposition on Ir/Al_2O_3). (The unit for turnover rate is molecules/surface atom measured by H_2 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 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_2O_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_2O_3 and Ir/ZrO_2 were prepared by incipient wetness impregnation of Al_2O_3 or ZrO_2 with aqueous $IrCl_3 \cdot 3H_2O$. Ir dispersions were measured by using volumetric methods to determine uptakes of strongly chemisorbed H_2 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 CH_4 decomposition kinetic measurements. Chemical composition was measured by on-line mass spectrometry. Ir/ZrO_2 (1.6 wt %; 5 mg) was used to measure CO oxidation reaction rates at 363 K and 0.19 kPa CO and O_2 pressures.

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