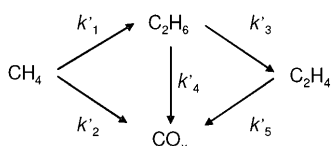


# Rate and Selectivity Enhancements Mediated by OH Radicals in the Oxidative Coupling of Methane Catalyzed by Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>\*\*

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The oxidative coupling of methane (OCM) proceeds via complex primary and secondary pathways involving coupled heterogeneous and homogeneous reactions. These reactions form higher hydrocarbons, predominantly ethane and ethene, but also undesired CO<sub>x</sub>.<sup>[1,2]</sup> Such pathways, which are described in Scheme 1, limit attainable C<sub>2</sub> yields<sup>[3–5]</sup> because



**Scheme 1.** Simplified scheme showing the OCM reaction network and pseudo-first-order rate constants for the respective steps.

of sequential reactions of C<sub>2</sub> products that are more reactive than CH<sub>4</sub><sup>[2]</sup> at the temperatures required to activate the C–H bonds in CH<sub>4</sub>.<sup>[2]</sup> Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalysts are chosen here because of their high selectivity and stability during OCM reactions at such temperatures.<sup>[6–10]</sup>

Several studies have described homogeneous (gas-phase) and heterogeneous (surface-catalyzed) OCM reaction networks.<sup>[3–5,11,12]</sup> These networks capture most features of the measured rates and selectivities, but contain limited (or phenomenological) descriptions of the surface-mediated steps, often limited to C–H bond activation in CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub> using active oxygen species.<sup>[3–5,11,12]</sup> The remaining inconsistencies between measurements and models have been attributed to other surface-mediated pathways (e.g. quenching of unselective radicals, such as HOO•),<sup>[5,12]</sup> reversible CH<sub>4</sub> activation steps,<sup>[12]</sup> or to transport restrictions.<sup>[12]</sup>

Herein we report the marked effect of H<sub>2</sub>O on OCM rates and selectivities caused by the catalytic generation of OH radicals, which react further to activate CH<sub>4</sub> in gas-phase reactions without net H<sub>2</sub>O consumption. The high reactivity of these OH radicals weakens the sensitivity of H-abstraction rates on C–H bond energies, as suggested earlier.<sup>[13]</sup> The

formation of OH radicals from O<sub>2</sub>/H<sub>2</sub>O mixtures on La<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> materials that also catalyze OCM has been observed<sup>[14,15]</sup> and is proposed to influence OCM rates without concomitant effects on selectivity.<sup>[16]</sup> Two patents have described the effect of water on OCM rates and C<sub>2</sub> selectivities on MnO<sub>x</sub>-based catalysts, although without mechanistic comment or interpretation.<sup>[17]</sup> Herein we rigorously describe the kinetic and mechanistic consequences of H<sub>2</sub>O in OCM reactions and provide chemical and isotopic evidence for the involvement of OH radicals in H-abstraction and for the marked consequences of these pathways on attainable C<sub>2</sub> yields. We also comment more generally on the free-energy relations that cause more reactive H-abstractors to weaken the effects of C–H bond energies on reaction rates.

Figures 1a and 1b show differential CH<sub>4</sub> conversion rates as a function of contact time and C<sub>2+</sub> selectivities as a function of CH<sub>4</sub> conversion, respectively, for Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalysts in gradient-less batch reactors. The CH<sub>4</sub> conversion rates increased with contact time and then decreased as O<sub>2</sub> was depleted in experiments where H<sub>2</sub>O was neither added with the reactants nor removed as it formed (“steady state reaction”; Figure 1). The C<sub>2+</sub> selectivities remained nearly constant up to around 10% CH<sub>4</sub> conversion but decreased at higher conversions (Figure 1b). These rate enhancements do not reflect the temperature gradients generally found for exothermic reactions in flow reactors,<sup>[10]</sup> which was ruled out by the lack of kinetic effects upon diluting the catalyst with inert solids (50:1). Recirculation minimizes transport effects by ensuring gradient-less operation and low CH<sub>4</sub> conversion per pass (< 1%).<sup>[18,19]</sup>

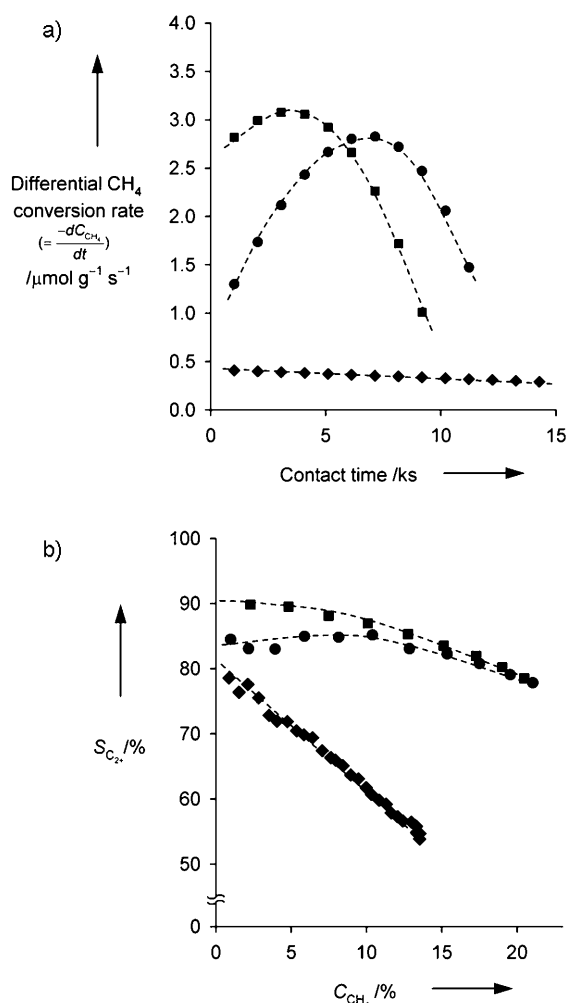
Rate enhancements with contact time may reflect the kinetic effects of products as they are formed, or of reactants as they are depleted, in gas-phase or surface reactions, or catalyst-structure and site-accessibility changes. Structural changes are inconsistent with the identical rates observed when the reaction mixtures were replaced with fresh CH<sub>4</sub>/O<sub>2</sub> reactants. The kinetic effects responsible for rate enhancements may, however, reflect a negative kinetic order in CH<sub>4</sub> or O<sub>2</sub> or a positive order in one or more products (C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CO<sub>x</sub>, H<sub>2</sub>O).

The CH<sub>4</sub> conversion rates, as measured by extrapolation to zero conversion in a flow-reactor, were found to be proportional to CH<sub>4</sub> pressure and the square root of the O<sub>2</sub> pressure; these data rule out reactant depletion as the cause of the observed rate enhancements and agree with previous reports.<sup>[9]</sup> These kinetic data are consistent with the kinetic relevance of CH<sub>4</sub> activation by dissociated oxygen atoms (O\*), which are formed by quasi-equilibrated O<sub>2</sub> dissociation as shown in the elementary steps (1)–(5), where \*, M, and [O<sub>2</sub>] denote sites, “third bodies” required to dissipate energy

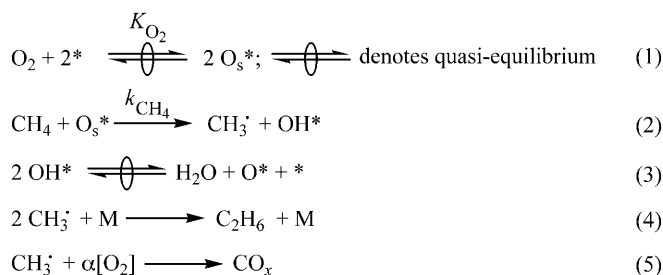
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**Figure 1.** Plots of differential CH<sub>4</sub> conversion rate vs. contact time (a) and C<sub>2+</sub> selectivity vs. CH<sub>4</sub> conversion (b); S: selectivity, C: conversion. ♦: H<sub>2</sub>O removed; ●: steady state reaction; ■: H<sub>2</sub>O added (0.02 g, 1073 K, unit volume: 275–650 mL, 10.7 kPa CH<sub>4</sub>, CH<sub>4</sub>/O<sub>2</sub> 6:1, 0.4 kPa H<sub>2</sub>O (when added), 101 kPa total pressure, balance He).



during radical recombination, and active oxygen atoms involved in CO<sub>x</sub> formation (which may differ from O\*), respectively. The CH<sub>4</sub> conversion rates are given by Equation (6) at low O\* coverages, which is consistent with the measured rates.

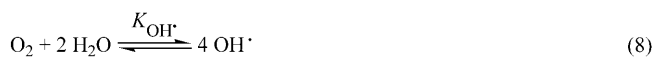
The C<sub>2</sub> products may cause rates to increase with increasing conversion by initiating homogeneous chain

$$r_{\text{CH}_4} = k' P_{\text{CH}_4} P_{\text{O}_2}^{1/2} \quad (6)$$

cycles, and <sup>13</sup>CH<sub>4</sub>/O<sub>2</sub>/<sup>12</sup>C<sub>2</sub>H<sub>6</sub> or <sup>13</sup>CH<sub>4</sub>/O<sub>2</sub>/<sup>12</sup>C<sub>2</sub>H<sub>4</sub> mixtures gave CH<sub>4</sub> conversion rate constants (*k*<sub>1</sub>, *k*<sub>2</sub>) identical to those without C<sub>2</sub>H<sub>6</sub> or C<sub>2</sub>H<sub>4</sub>. Thus, C<sub>2</sub> products cannot account for the observed rate enhancements. <sup>12</sup>CH<sub>4</sub> was not detected at any <sup>13</sup>CH<sub>4</sub> conversion, which is consistent with the irreversible nature of the steps involving hydrocarbons in Scheme 1.

Water may influence OCM reactions via OH-mediated pathways produced by H<sub>2</sub>O activation on oxide surfaces.<sup>[16]</sup> This proposal was tested by removing H<sub>2</sub>O as it formed (“H<sub>2</sub>O removed” in Figure 1) and by adding H<sub>2</sub>O to CH<sub>4</sub>/O<sub>2</sub> reactant mixtures (“H<sub>2</sub>O added”). The removal of H<sub>2</sub>O eliminated rate enhancements with conversion and led to rates that decreased with contact time because of depletion of CH<sub>4</sub> and O<sub>2</sub> (Figure 1a). The C<sub>2</sub> selectivities decreased markedly as CH<sub>4</sub> conversion increased when H<sub>2</sub>O was removed (Figure 1b). In contrast, adding H<sub>2</sub>O to CH<sub>4</sub>/O<sub>2</sub> reactant mixtures increased initial conversion rates and C<sub>2</sub> selectivities markedly and weakened the effects of contact time on rates (Figures 1a and 1b).

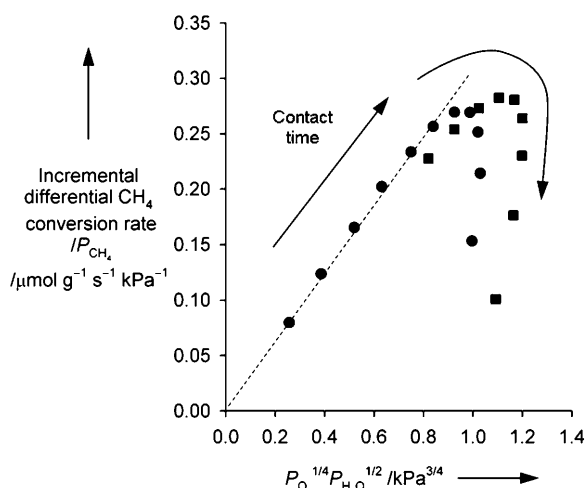
H<sub>2</sub>O/O<sub>2</sub> mixtures form OH radicals on La<sub>2</sub>O<sub>3</sub>-based OCM catalysts in a similar manner to CH<sub>3</sub>• radicals [step 2 above; Eq. (7)],<sup>[16]</sup> where OH• and OH\* denote radicals and chemisorbed species, respectively, and O<sub>s</sub>\* forms via step 1. The quasi-equilibria of steps 1, 3, and 7 mean that the equilibrium OH radical concentrations at 1173 K on La<sub>2</sub>O<sub>3</sub> reflect the thermodynamics of the overall reaction [Eq. (8)].<sup>[15]</sup> We suggest here that H<sub>2</sub>O increases OCM rates via OH-mediated homogeneous steps that abstract H-atoms from CH<sub>4</sub> [Eq. (9)].



The incremental rate (via step 9) using the OH radicals formed in step 8 is given by the second term in Equation (10)

$$r_{\text{CH}_4} = k' P_{\text{CH}_4} P_{\text{O}_2}^{1/2} + k'' P_{\text{CH}_4} P_{\text{O}_2}^{1/4} P_{\text{H}_2\text{O}}^{1/2} \quad (10)$$

with *k'* = *k*<sub>CH<sub>4</sub></sub>*k*<sub>O<sub>2</sub></sub><sup>1/2</sup> and *k''* = *k'*<sub>CH<sub>4</sub></sub>*K*<sub>O<sub>2</sub></sub><sup>1/4</sup>. Figure 2 shows the expected linear dependence on *P*<sub>O<sub>2</sub></sub><sup>1/4</sup>*P*<sub>H<sub>2</sub>O</sub><sup>1/2</sup> at short contact times (obtained from measured differences in rates with and without H<sub>2</sub>O). The observed decrease in CH<sub>4</sub> conversion rate (Figure 2) reflects O<sub>2</sub> dissociation (step 1) steps that are no longer in equilibrium, as O<sub>2</sub> is depleted and H<sub>2</sub>O concentration increases with increasing conversion. As a result, the rate of formation of O\* decreases, and this species is scavenged more effectively by reactions with CH<sub>4</sub> via OH-mediated pathways that deplete O\* to replenish OH as it reacts.



**Figure 2.** Plot of incremental differential  $\text{CH}_4$  conversion rate (obtained from measured differences in rates with and without  $\text{H}_2\text{O}$ ) vs.  $P_{\text{O}_2}^{1/4} P_{\text{H}_2\text{O}}^{1/2}$ .  $\bullet$ : steady state reaction;  $\blacksquare$ :  $\text{H}_2\text{O}$  added. The arrows indicate the increase in contact time (0.02 g, 1073 K, unit volume: 550–650 mL, 10.7 kPa  $\text{CH}_4$ ,  $\text{CH}_4/\text{O}_2$  6:1, 0.4 kPa  $\text{H}_2\text{O}$  (when added), 101 kPa total pressure, balance He).

The quasi-equilibrated nature of step 8 would lead to weak kinetic isotope effects (KIE) for  $\text{CH}_4/\text{O}_2/\text{H}_2\text{O}$  and  $\text{CH}_4/\text{O}_2/\text{D}_2\text{O}$  mixtures because OH activation precedes kinetically relevant steps. The measured  $\text{H}_2\text{O}/\text{D}_2\text{O}$  KIE value was 1.1. The  $\text{CH}_4/\text{CD}_4$  KIE values for surface-catalyzed and homogeneous OH-mediated paths (steps 2 and 9) were found to be similar to each other and larger (1.3–1.4) than the  $\text{H}_2\text{O}/\text{D}_2\text{O}$  isotope effects, which is consistent with the involvement of C–H bonds in kinetically relevant steps and quasi-equilibrated formation of OH radicals via fast  $\text{H}_2\text{O}$  activation, even though the O–H bonds in  $\text{H}_2\text{O}$  (497  $\text{kJ mol}^{-1}$ ) are stronger than the C–H bonds in  $\text{CH}_4$  (439  $\text{kJ mol}^{-1}$ ).<sup>[20]</sup> These trends reflect the stronger adsorption of  $\text{H}_2\text{O}$  than  $\text{CH}_4$  on the vacant sites prevalent on oxides during OCM catalysis.

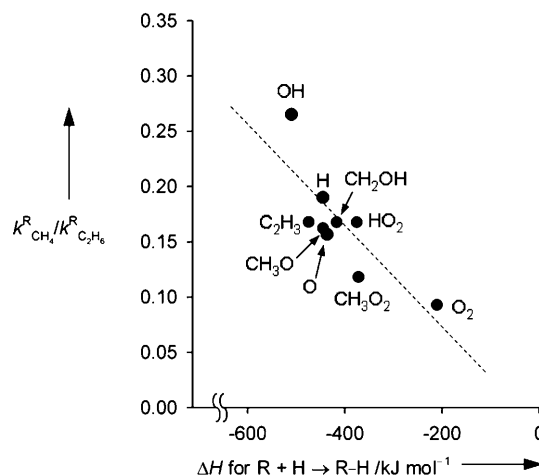
OH radicals, however, also activate C–H bonds in  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$ ; yet,  $\text{H}_2\text{O}$  leads to higher  $\text{C}_2$  selectivities (Figure 1b), apparently because OH radicals activate C–H bonds in  $\text{C}_2$  molecules with less specificity (relative to  $\text{CH}_4$ ) than oxide surfaces.  $^{13}\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6$  and  $^{13}\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_4$  mixtures allowed accurate estimates for all rate constants in Scheme 1 ( $k'_1$ – $k'_5$ ) with and without  $\text{H}_2\text{O}$  to be obtained (Table 1). All rate constants were larger when  $\text{H}_2\text{O}$  was present, although those for  $\text{CH}_4$  activation showed the largest increase. As a result of these OH-mediated activation pathways, the  $k'_1/k'_1$  ratios decreased for all species, thus causing the observed increase in  $\text{C}_2$  selectivities and yields with  $\text{H}_2\text{O}$ .

Figure 3 gives the rate constant ratios reported for H-abstraction from  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  ( $k_{\text{CH}_4}^{\text{R}}/k_{\text{C}_2\text{H}_6}^{\text{R}}$ ) in homogeneous reactions with various abstractors (R).<sup>[5,21]</sup> This ratio increases as the RH products become more stable ( $\text{R} + \text{H} \rightarrow \text{R-H}$ , more exothermic). These abstraction reactions become less sensitive ( $k_{\text{CH}_4}^{\text{R}}/k_{\text{C}_2\text{H}_6}^{\text{R}}$  is larger) to differences in energy between the C–H bonds in  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  ( $\text{CH}_4$ : 439  $\text{kJ mol}^{-1}$ ;  $\text{C}_2\text{H}_6$ : 423  $\text{kJ mol}^{-1}$ )<sup>[20]</sup> as the abstraction products become more stable, as is also the case for the relative

**Table 1:** First-order rate constants ( $\mu\text{mol g}^{-1} \text{s}^{-1} \text{kPa}^{-1}$ ) for the steps shown in Scheme 1 (0.02 g, 1073 K, 10.7 kPa  $^{13}\text{CH}_4$ , 1.7 kPa  $\text{O}_2$ , 0.4 kPa  $^{12}\text{C}_2\text{H}_6/^{12}\text{C}_2\text{H}_4$ , 0 or 0.4 kPa  $\text{H}_2\text{O}$ ).

Rate constant	Surface-mediated	OH-mediated <sup>[a]</sup>
$k'_1$	0.05	0.16
$k'_2$ ( $k'_2/k'_1$ )	0.01 (0.25)	0.02 (0.11)
$k'_3$ ( $k'_3/k'_1$ )	1.7 (33)	1.1 (6.8)
$k'_4$ ( $k'_4/k'_1$ )	0.14 (2.7)	0.12 (0.73)
$k'_5$ ( $k'_5/k'_1$ )	0.22 (4.3)	0.10 (0.63)
$(k'_1 + k'_2)/(k'_3 + k'_4)$	0.03	0.14

[a] Calculated from rate differences with and without  $\text{H}_2\text{O}$ ; [b] calculated from  $^{13}\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6/(\text{H}_2\text{O})$  mixtures; [c] calculated from  $^{13}\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_4/(\text{H}_2\text{O})$  mixtures.

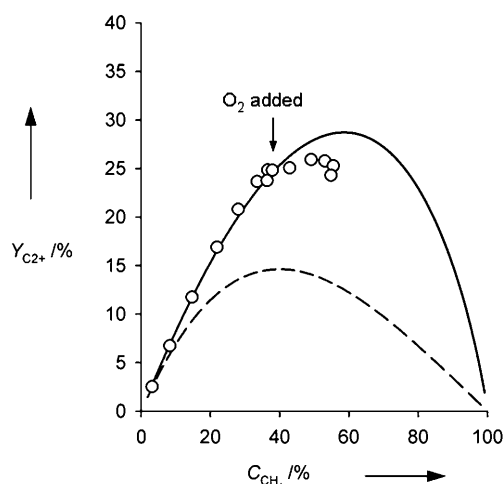


**Figure 3.** Ratios of rate constants  $k_{\text{CH}_4}^{\text{R}}/k_{\text{C}_2\text{H}_6}^{\text{R}}$  for H-abstraction from  $\text{CH}_4$  relative to  $\text{C}_2\text{H}_6$  for various abstracting entities (R) vs.  $\Delta H$  for the recombination reaction  $\text{R} + \text{H} \rightarrow \text{R-H}$  at 1073 K.

rates of  $\text{HCHO}$  and  $\text{CH}_4$  oxidation via homogeneous pathways.<sup>[22]</sup> OH radicals lead to very exothermic H-abstraction reactions and to the highest  $k_{\text{CH}_4}^{\text{R}}/k_{\text{C}_2\text{H}_6}^{\text{R}}$  ratios (Figure 3). Consistent with this, the involvement of OH radicals in H-abstraction increases the  $\{(k'_1 + k'_2)/(k'_3 + k'_4)\}$  ratios markedly, from 0.03 for surface-mediated pathways to 0.14 for OH-mediated pathways (Table 1).

$\text{H}_2\text{O}$  also leads to lower  $k'_5/k'_1$  ratios (4.3 without  $\text{H}_2\text{O}$ ; 0.63 for OH-mediated pathways; Table 1), which is consistent with the preferential enhancement of  $\text{CH}_4$  over  $\text{C}_2\text{H}_4$  activation rates by OH-mediated routes. Surfaces oxidize  $\text{C}_2\text{H}_4$  ( $k'_5$ ) more effectively than  $\text{CH}_4$  ( $k'_2$ ) or  $\text{C}_2\text{H}_6$  ( $k'_4$ ), in spite of the strong C–H bonds in  $\text{C}_2\text{H}_4$  (463  $\text{kJ mol}^{-1}$ ),<sup>[20]</sup> apparently because  $\text{C}_2\text{H}_4$  is strongly adsorbed.<sup>[23]</sup> OH-mediated pathways do not involve adsorption and lead to  $k'_5/k'_1$  values below unity (0.63). These ratios faithfully reflect the stronger C–H bonds in  $\text{C}_2\text{H}_4$ , without compensation by adsorption energies. In fact, these previously unrecognized OH-mediated pathways are essential to achieving the maximum  $\text{C}_2$  yields reported (up to 26%), which could not be reached with contributions from surface-mediated pathways only.

We have achieved  $\text{C}_{2+}$  yields of 26% by replenishing  $\text{O}_2$  after it is depleted in order to avoid explosive reactant mixtures (Figure 4). These yields match the highest values



**Figure 4.** Plot of  $C_{2+}$  yield vs.  $CH_4$  conversion for experimental data and pseudo-first-order kinetic models using the rate constants shown in Table 1. (0.02 g, 1073 K, unit volume: 550 mL, 4.0 kPa  $CH_4$ , 1.3 kPa  $O_2$  (initial), 1.5 kPa  $O_2$  (added) 101 kPa total pressure, balance He). -----: the "dry" model; —: the "wet" model.

reported previously.<sup>[6]</sup> A kinetic model based on Scheme 1 and rate constants for surface- and OH-mediated pathways (Table 1; see the Supporting Information for further details) accurately describes the measured yields and predicts a maximum possible  $C_2$  yield of 29%. Figure 4 shows that the rate constants for surface-mediated pathways, which prevail in the absence of  $H_2O$ , cannot account for observed  $C_2$  yields and predict maximum values of only 15%.

In summary, this study provides mechanistic evidence that OH-mediated C–H bond activation pathways are essential for attaining practical yields and describing the evolution of  $C_2$  yields during catalytic reactions. The ability of oxide catalysts to generate equilibrium OH-radical concentrations provides opportunities to exploit pathways mediated by such radicals in related chemistries. Our data provide compelling evidence for the benefits of using more reactive species (or higher temperatures) to weaken the sensitivity of H-abstraction reactions to C–H bond energies, a challenge and hurdle that limits the maximum attainable yields of the desired products in most practical applications of oxidation catalysis.<sup>[24]</sup>

### Experimental Section

$SiO_2$  (Davison chemical, Silica Gel Grade 57) was impregnated with aqueous  $Mn(NO_3)_2$  (50 wt. %, STREM Chemicals;  $2\text{ mL g}^{-1}$  of  $SiO_2$ ) and the mixture dried in ambient air at 403 K for 5 h.<sup>[8]</sup> This sample was then impregnated with an aqueous solution of  $Na_2WO_4 \cdot 2H_2O$  (99%, Sigma–Aldrich,  $2\text{ mL g}^{-1}$  of  $SiO_2$ ) to give a sample containing 2 wt. % Mn and 5 wt. %  $Na_2WO_4$ . This sample was dried at 403 K for 5 h and then heated in flowing dry air (Praxair, UHP,  $0.167\text{ mL s}^{-1}$ ) at 1173 K (temperature increase:  $0.033\text{ K s}^{-1}$ ) for 8 h. The samples were sieved to retain 0.25–0.35-mm aggregates.

OCM rates and selectivities were measured in flow or recirculating batch reactors using a U-shaped quartz cell (4 mm I.D.).<sup>[18]</sup> Samples (0.02 g) were mixed with quartz powder (0.5 g; Fluka,  $SiO_2$ , 0.25–0.35 mm) and held onto quartz wool. The temperature was

maintained with a Watlow controller (Series 982) coupled to a resistively heated furnace and measured with a type K thermocouple set outside the catalyst bed.  $CH_4$  (Praxair, 99.999%) and  $O_2$  (Praxair, 99.999%) were introduced with He (Praxair, 99.999%) as diluent. In batch experiments, the recirculation loop (275–650 mL) was evacuated to  $<0.1\text{ Pa}$  before introducing the reactants, which were circulated with a graphite gear micropump ( $>2.5\text{ mL s}^{-1}$ ).  $H_2O$  was removed from the reactor loop using a dry ice/acetone trap, which does not condense other products. Reactant and product concentrations were measured with an HP5890 gas chromatograph using a Carbosieve SII packed column (Supelco,  $3.2\text{ mm} \times 2\text{ m}$ ) with thermal conductivity detection and a HP-PLOT Q capillary column (Agilent,  $0.32\text{ mm} \times 30\text{ m}$ ) with flame ionization detection. Differential rates were obtained from time-derivatives of  $CH_4$  concentration profiles vs. time measured in batch reactors after regression to a polynomial fit. Selectivities are reported on a carbon basis as cumulative (integral) values.

$CD_4$  (Isotec, 99 atom % -D) and  $D_2O$  (Cambridge Isotope Laboratories, Inc., 99.9%) were used to measure kinetic isotope effects. Tracer studies used labeled  $^{13}CH_4$  (Isotec, 99 atom % - $^{13}C$ ) in the presence of  $^{12}C_2H_6$  (Praxair, 99.999%) or  $^{12}C_2H_4$  (Praxair, 99.999%). These isotopic measurements were carried out in a batch recirculating reactor equipped with two HP5890 gas chromatographs, with combined thermal conductivity, flame ionization and mass selective detectors. The latter was connected to an HP-PLOT Q capillary column used for isotopic detection.

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- [1] G. E. Keller, M. M. Bhasin, *J. Catal.* **1982**, 73, 9–19.
- [2] J. H. Lunsford, *Catal. Today* **2000**, 63, 165–174.
- [3] a) J. A. Labinger, K. C. Ott, *J. Phys. Chem.* **1987**, 91, 2682–2684; b) J. A. Labinger, *Catal. Lett.* **1988**, 1, 371–376.
- [4] a) S. C. Reyes, E. Iglesia, C. P. Kelkar, *Chem. Eng. Sci.* **1993**, 48, 2643–2661; b) S. C. Reyes, C. P. Kelkar, E. Iglesia, *Catal. Lett.* **1993**, 19, 167–180.
- [5] C. A. Mims, R. Mauti, A. M. Dean, K. D. Rose, *J. Phys. Chem.* **1994**, 98, 13357–13372.
- [6] A. Palermo, J. P. H. Vazquez, A. F. Lee, M. S. Tikhov, R. M. Lambert, *J. Catal.* **1998**, 177, 259–266.
- [7] X. Fang, S. Li, J. Lin, J. Gu, D. Yang, *J. Mol. Catal. (China)* **1992**, 6, 427.
- [8] D. Wang, M. P. Rosynek, J. H. Lunsford, *J. Catal.* **1995**, 155, 390–402.
- [9] S. Pak, P. Qiu, J. H. Lunsford, *J. Catal.* **1998**, 179, 222–230.
- [10] S. Pak, J. H. Lunsford, *Appl. Catal. A* **1998**, 168, 131–137.
- [11] A. J. Colussi, V. T. Amorebieta, *J. Catal.* **1997**, 169, 301–306.
- [12] Y. S. Su, J. Y. Ying, W. H. Green, *J. Catal.* **2003**, 218, 321–333.
- [13] J. A. Labinger, *J. Mol. Catal. A* **2004**, 220, 27–35.
- [14] L. C. Anderson, M. Xu, C. E. Mooney, M. P. Rosynek, J. H. Lunsford, *J. Am. Chem. Soc.* **1993**, 115, 6322–6326.
- [15] K. B. Hewett, L. C. Anderson, M. P. Rosynek, J. H. Lunsford, *J. Am. Chem. Soc.* **1996**, 118, 6992–6997.
- [16] K. B. Hewett, M. P. Rosynek, J. M. Lunsford, *Catal. Lett.* **1997**, 45, 125–128.
- [17] a) A. M. Gaffney, US Patent, 4788372, **1988**; b) D. W. Leyshon, US Patent, 4801762, **1989**.
- [18] E. Iglesia, J. E. Baumgartner, G. L. Price, K. D. Rose, J. L. Robbins, *J. Catal.* **1990**, 125, 95–111.

- [19] J. A. Roos, S. J. Korf, R. H. J. Veehof, J. G. van Ommen, J. R. H. Ross, *Appl. Catal.* **1989**, 52, 131–145.
  - [20] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, 36, 255–263.
  - [21] GRI-Mech v.3.0. G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner, Jr., V. V. Lissianski, Z. Qin, [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/).
  - [22] J. M. Zalc, W. H. Green, E. Iglesia, *Ind. Eng. Chem. Res.* **2006**, 45, 2677–2688.
  - [23] J. A. Dumesic, D. F. Rudd, L. M. Aparicio, J. E. Rekoske, A. A. Treviño, *The Microkinetics of Heterogeneous Catalysis*, American Chemical Society, Washinton, DC, **1993**.
  - [24] a) C. Batiot, B. K. Hodnett, *Appl. Catal. A* **1996**, 137, 179–191;  
b) A. Costine, B. K. Hodnett, *Appl. Catal. A* **2005**, 290, 9–16.
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