Comment on “Selective anaerobic oxidation of methane enables direct synthesis of methanol”

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Sushkevich et al. (Reports, 5 May 2017, p. 523) report on the use of water to oxidize methane to methanol. This seems problematic because the reaction of CH₄ and water to generate methanol and H₂ is highly unfavorable at any temperature (ΔG of reaction ≈ +28 kcal/mol at 200°C, equilibrium constant K ≈ 10⁻¹²). Consequently, even if the reaction is separated into two steps, it seems inconceivable to carry out such a net reaction in a practical manner.

Sushkevich et al. (1) report the net conversion of methane to methanol and H₂ using water as a “soft” oxidant. The reaction is carried out using a two-step “looping” reactor system where methane is oxidized with a CuO species to generate methanol and reduced Cu species in one step, which is then reoxidized with water to generate H₂ and the CuO species in the other step. They note that use of O₂ is problematic, as it leads to unselective reaction by overoxidation of methanol. Instead, they considered that water could act as a “soft,” more selective “oxidant,” as was reported in (2).

The authors analyzed for CH₃OH by mass spectrometry and infrared spectroscopy; H₂ was observed by mass spectrometry. There are fundamental challenges to interpreting this work that relate to the thermodynamics of the various reactions in the report. The discussion below pertains only to thermodynamics, which is path-independent, and makes no assumption of the kinetic feasibility of the various reactions. First, as shown in Eq. 1, published thermodynamic data (3) indicate that the overall reaction in the gas phase is highly unfavorable (ΔG ≈ +28 kcal/mol) at 200°C (473 K), where the reactions were examined. Assuming no other energy inputs or coupled chemical reactions that would change this net stoichiometry, this value (which is independent of how the reaction is carried out) means that the maximum yield of CH₃OH and H₂ from such an overall reaction would be quite low because the equilibrium constant is very small, K ≈ 10⁻¹² at 200°C.

CH₄ + H₂O → CH₃OH + H₂
ΔG₁ ≈ +28 kcal/mol at 200°C or K ≈ 10⁻¹²
ΔG₁ ≈ +28 kcal/mol at 900°C

The authors suggest that this overall conversion, Eq. 1, can be accomplished by carrying out the reaction in two steps in a so-called “looping” reactor. In one step, a zeolite-supported CuO species reacts with methane to generate gaseous CH₃OH and a reduced Cu species, followed by oxidation of the Cu species with gaseous H₂O to regenerate the CuO species and H₂. These two reaction steps are represented as shown in Eqs. 2 and 3, where pure solid CuO (a Cu(I)O species) and Cu₂O (a Cu(I) species) are used as models of the actual species in the study because accurate, experimentally obtained thermodynamic data (3) are available for these materials. This is an approximation, as the thermodynamics for these two reactions could be different in the reported system. However, as discussed below, this does not change the fundamental challenge of interpreting the results in this report because the thermodynamic parameters of these model steps must sum to the overall thermodynamic parameters of Eq. 1, for which there are accurate data (i.e., ΔG₁ = ΔG₂ + ΔG₃). This is important because as one reaction becomes more favorable (e.g., ΔG₂ becomes more negative), the other, ΔG₃, must become less favorable (more positive) in accord with the ΔG₃ = ΔG₁ - ΔG₂ relation. Of course, if other materials not considered in Eq. 1 are net consumed or generated (i.e., the net reaction is not given by Eq. 1), then these thermodynamic values do not apply. However, the authors claim that they can develop a process based only on the overall reaction shown in Eq. 1; they imply that there is no net consumption of Cu-zeolite or other materials.

2CuO + CH₄ → CH₃OH + Cu₂O
ΔG₂ ≈ -3 kcal/mol at 200°C or K ≈ 27
ΔG₂ ≈ +31 kcal/mol at 200°C or K ≈ 10⁻¹²

Cu₂O + H₂O → 2CuO + H₂
ΔG₃ ≈ +31 kcal/mol at 200°C or K ≈ 10⁻¹²

Net (ΔG₂) + (ΔG₃):
CH₄ + H₂O → CH₃OH + H₂
ΔG₁ ≈ +28 kcal/mol

These thermodynamic data show, consistent with this and other reports, that the oxidation of methane with solid CuIIO is favorable (spontaneous, ΔG < 0, K > 1) under the reaction conditions. Consequently, the observation of methanol in this work would be reasonable. However, the high reaction selectivity observed is unusual, as any oxidant competent for reaction with methane should be expected to react with methoxy species. It is possible, as the authors suggest, that the CH₃OH species are tightly coordinated to Cu(I) cations and that this could minimize over-oxidation. The observation of lower selectivity when the Cu(II) species is generated from O₂ is more consistent with the general expectation in the field. However, although the high selectivity is surprising, it is not the major issue in this report.

The more fundamentally challenging aspect of this work is to rationalize the use of water as a “soft” oxidant for the oxidation of Cu(I) to Cu(II) and H₂. As can be seen in Eq. 3, this model reaction is even less favorable (+31 kcal/mol) than the overall reaction shown in Eq. 1 (+28 kcal/mol). This is expected because, as discussed above, ΔG₃ = ΔG₁ - ΔG₂ = +28 + (−3) = +31. This makes intuitive sense, because if CuO is a strong enough oxidant to oxidize methane, the resulting reduced Cu species, Cu₂O, must be a weaker reductant than methane. Consequently, the reduction of H₂O by CuO [i.e., the oxidation of Cu(I) by H₂O] to give Cu(II) and H₂ would be expected to be less favorable than reduction of H₂O by methane (i.e., oxidation of methane with H₂O) to generate CH₃OH and H₂. Given the small equilibrium constant of H₂ and Cu(II) expected from Eq. 3 (K ≈ 10⁻¹²), it would likely be almost impossible to detect any H₂ or Cu(II) from this reaction. This is quite inconsistent with the authors’ observation of H₂ and, more important, their observation of >40% Cu(II) yield upon treatment of Cu(I) with H₂O.

In this regard, we note that the authors’ precedent (reference 25 in their report) for considering water as a “soft” oxidant, the aqueous oxidation of silanes to silanols (2), is not directly relevant to the oxidation of methane. A model for the reactions carried out in that reference is shown in Eq. 4. The thermodynamic value for this model reaction is based on experimental data (4). As can be seen, unlike the reaction of methane and water, this reaction is highly favorable and spontaneous at 25°C or above. This is because silanes are indeed strong reductants, not because water is a strong oxidant. These terms are, of course, relative. The point is that water can only be considered an oxidant if the species undergoing reactions with it is strongly reducing (e.g., elemental Na or silanes); CH₄, unlike a silane, R₂SiH, is not a sufficiently strong two-electron reductant. Consequently, their precedent (2) provides little basis for the use of water as an oxidant for methane.

(CH₃)₃SiH + 1/2H₂O →
1/2(CH₃)₃SiOSi(CH₃)₃ + H₂
ΔG₃ ≈ -25 kcal/mol or K ≈ 10³ at 25°C

The reader may make a connection between this work and the use of water in methane reforming,
Eq. 5, where water may be seen as an “oxidant.” However, this reaction is favorable ($\Delta G < 0$) only at >600°C. This explains why commercial reforming is carried out at ~900°C. This change in the thermodynamics with increasing temperature for methane reforming occurs because the reaction is entropically driven as the number of molecules increases from two (CH$_4$ and H$_2$O) to four (CO and three H$_2$). However, this possibility is not available for the overall reaction claimed in this report, Eq. 1, because the number of molecules in the reactants (CH$_4$ and H$_2$O) and products (CH$_3$OH and H$_2$) remains unchanged at two. Consistent with this, the oxidation of methane with water to methanol and hydrogen remains unfavorable, $\Delta G = +28$ kcal/mol, even at 900°C (Eq. 1).

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$$

$$\Delta G \approx +25 \text{ kcal/mol at } 200^\circ\text{C},$$

$$-1 \text{ kcal/mol at } 640^\circ\text{C},$$

$$-16 \text{ kcal/mol at } 900^\circ\text{C}$$

The authors may consider that running Eq. 3 with excess water or under vacuum could be sufficient to shift the equilibria. Although this is theoretically possible, it is impractical because enormous excesses of H$_2$O would be required, and even then, only traces of H$_2$ would be generated that would be effectively impossible to separate from the excess H$_2$O. The time under vacuum and the amount of H$_2$O used in the report are not consistent with these possibilities.

The authors’ density functional theory calculations also seem to point to a dilemma. The reaction coordinate in their Fig. 3 starts at 0 kJ/mol and ends at 0 kJ/mol. In a catalytic or looping reaction scheme where the Cu(II) is consumed and regenerated, the overall thermodynamics must correspond to those shown in Eq. 1. I would expect these values to start at 0 kJ/mol and end at +117 kJ/mol (+28 kcal/mol), assuming reaction at 200°C.

As discussed above, reaction of CH$_4$ with CuO (Eq. 2) is favorable. Consequently, it is plausible and has indeed been reported that CH$_3$OH can be generated in this reaction. If one considers the possibility that not all the CuO is consumed by CH$_4$ in the methane treatment step in the report and that H$_2$ is not actually generated in step 2, then it is possible that each “cycle” merely continues Eq. 2. This scenario would require an error to have occurred in the authors’ H$_2$ analysis. This is because if the CuO were not fully consumed by CH$_4$, it would be highly unlikely to generate H$_2$ under these conditions, as any H$_2$ would be expected to react with the excess CuO between reaction cycles.

Even if the authors’ observations are accurate, it is important that the authors address the concerns above regarding the thermodynamics of the overall reaction. The fundamental challenge with the existing commercial methane conversion technology is not selectivity, but rather the high capital costs that stem from the expensive equipment required to carry out the process. The overall yield of methanol from methane in the commercial process is high at ~70% (5). The high capital costs ensue from the high heat input necessary to drive the endothermic reforming reaction (Eq. 5) that is the basis for the current technology. Direct or partial oxidation of methane to methanol would ideally avoid the high costs associated with carrying out endothermic reactions that require large energy inputs. Independent of how the authors carry out their proposed reaction in Eq. 1, at least a similar energy cost to reforming must be paid, as that overall reaction is also similarly endothermic. Consequently, this chemistry likely would not address the major disadvantage of the current technology, namely the high capital costs. It is true that the authors’ process avoids the need for two steps in the commercial process, but the second step (CO/H$_2$ reduction to CH$_3$OH) is not the major cost.

REFERENCES
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