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

Vitaly L. Sushkevich,1* Dennis Palagin,1 Marco Ranocchiari,1 Jeroen A. van Bokhoven1,2*

Periana argues that the stepwise reaction of methane with water is thermodynamically unfavorable and therefore impractical. We reply by presenting an in-depth thermodynamic analysis of each step in the process and show that the surface concentrations of the reactants and products as well as the stabilizing effect of additional water molecules, as discussed in the original paper, fully support the feasibility of the proposed reaction.

In the Technical Comment, Periana (1) presents a thermodynamic analysis of two transformations in the oxidation of methane to methanol with water. Whereas the reaction of copper (II) oxide with methane (the first step in chemical looping) was accepted as being thermodynamically possible (Eq. 1, \( \Delta G^{473K} = -12 \) kJ/mol), the reaction of copper(I) oxide with water (the second step in chemical looping) was concluded to be thermodynamically impossible (Eq. 2, \( \Delta G^{473K} = +121 \) kJ/mol). The conclusions reached by Periana about the thermodynamics of bulk oxides were then projected to the CuI-CuII sites that interact with water in the mordenite zeolite.

\[
\begin{align*}
2\text{CuO} + \text{CH}_4 &\rightarrow \text{Cu}_2\text{O} + \text{CH}_3\text{OH} \quad (1) \\
\text{Cu}_2\text{O} + \text{H}_2\text{O} &\rightarrow 2\text{CuO} + \text{H}_2 \quad (2)
\end{align*}
\]

The thermodynamics represented in Eqs. 1 and 2 are correct under standard conditions; however, the models of the two reaction steps, the conditions, and the reactive species described by Periana are not representative of the material, nor do they fully represent the reaction steps in the chemical looping system described in our paper. The following assumptions were made by Periana, which led to erroneous conclusions:

1) Bulk crystalline copper oxides were used to model the copper sites in mordenite zeolite.
2) Gibbs free energy for the system in equilibrium, with total pressure of 1 bar for each component, was applied.
3) Specific adsorption of reacting and formed molecules over the surface of the copper-exchanged mordenite zeolite (CuMOR) material was not considered.
4) Enthalpic stabilization of intermediate species by water molecules was not taken into account.
5) An activation step, including the dehydration of the material, was omitted. We present the thermodynamic analysis of each of the sub-reactions, taking into account the adsorption phenomena typical of heterogeneous systems. We estimate the Gibbs free energy under the conditions given in our paper, in contrast to the standard \( \Delta G \).

Taking into account the experimental details of chemical looping over the CuMOR material, our simplified reaction scheme consists of two main steps (Eqs. 3 and 4), each of which is required for the reaction to occur. The Cu–O–Cu mono-μ-oxo sites are assumed to be active sites responsible for such transformations. Equation 3 corresponds to the interaction of activated CuMOR with methane at 7 bar and 473 K. Equation 4 represents the continuous flowing of water vapor at 473 K followed by desorption of methanol and the formation of hydrogen with the reoxidation of the copper sites. All these observations are based on experimental evidence. The standard Gibbs free energy was calculated by density functional theory, and Fig. 3 in (2) presents all the intermediates with respect to the initial Cu–O–Cu site, without taking into account the composition of the gas phase. Therefore, the energy of the regenerated site was zero. The overall free energy change in the methane oxidation reaction is calculated as +121 kJ/mol, in addition to the energy of the regenerated site.

Our analysis here includes the relation between the thermodynamic constant and the Gibbs free energy in order to estimate the likelihood of each step under the reaction conditions, taking into account the properties of CuMOR and the reacting molecules. The first step corresponds to the reaction of the copper(II) active sites with methane at 473 K, leading to the formation of the methoxy species and the reduced CuI species:

\[
\begin{align*}
\text{CuO} + \text{CH}_4 &\rightarrow \text{CuO} + \text{CH}_3\text{O} ÷ +58 \text{ kJ/mol} \quad (3)
\end{align*}
\]

For this reaction, the change in free energy \( (\Delta G^{473K} = -54 \text{ kJ/mol}) \) at a methane pressure of 7 bar is given by

\[
\Delta G = -RT \ln P_{\text{CH}_4} + \Delta G^{473K}
\]

High methane pressure will result in an even more negative \( \Delta G \) value and make the thermodynamics of this step more favorable. The second step is the addition of water and desorption of molecular methanol and hydrogen with \( \Delta G^{473K} = +121 - (-54) - 117 = 58 \text{ kJ/mol} \):

\[
\begin{align*}
\text{CuO} + \text{H}_2\text{O} &\rightarrow \text{CuO} + \text{H}_2\text{O} ÷ +58 \text{ kJ/mol} \quad (4)
\end{align*}
\]

As mentioned in the original paper, water plays a dominant role in the stabilization of the formed mono-μ-oxo copper core by introducing an enthalpic effect in addition to the entropic effect. Periana considers only the latter as a possibility for driving the reaction. As shown in fig. S11 in (2) (structure II0), the formation of copper bis-μ-oxo species provides an additional 117 kJ/mol of stabilization energy. Without this stabilization, the formal \( \Delta G^{473K} \) would not favor the formation of hydrogen. The strong interaction of the CuI oxidic species with water in zeolites is a unique feature that helps to thermodynamically drive the reaction. Additional water molecules might lead to further stabilization. We carried out additional calculations, probing the free energy of the chemisorption reaction of several water molecules on the Cu–(OH)2–Cu center (Fig. 1). The adsorption of the additional water molecules further lowers the required energy, which effectively drives the reaction thermodynamically downhill, leading to the formation of methanol and hydrogen as well as a hydrated Cu–(OH)2–Cu fragment, the end product of the first cycle. Thus, the \( \Delta G^{473K} \) of 58 kJ/mol is an upper limit (Eq. 4).

This reaction is not feasible with bulk oxides, as illustrated by Periana on the basis of Eqs. 1 and 2. Our experiments also revealed the inactivity of the bulk oxides; the transition from CuI to CuII was incomplete. The incomplete reoxidation suggests that there are multiple species exhibiting variable stabilization properties (Fig. 1).

Using the standard Gibbs free energy discussed above, the Gibbs free energy in Eq. 4...
under the reaction conditions described in our paper is given by

$$\Delta G = RT \ln \frac{\Theta_{H_2} \Theta_{CH_3OH}}{\Theta_{H_2O}} + \Delta G^{273K}$$

where $\Theta_{H_2}$, $\Theta_{H_2O}$, and $\Theta_{CH_3OH}$ represent the surface coverage of hydrogen, water, and methanol, respectively. According to the Langmuir isotherm, at low pressure the coverage is described by the adsorption coefficient $\alpha$:

$$\Theta \approx \alpha P$$

During the continuous-flow interaction of water with the methane-reacted CuMOR, the water pressure is significantly higher (26 mbar) than the hydrogen pressure (estimated to be <1 mbar) [Fig. 2B in (2)]. As hydrogen is purged from the system, its local concentration within the zeolite pores decreases further:

$$26 = P_{H_2O} \gg P_{H_2} \approx P_{CH_3OH} < 1$$

and for a spontaneous reaction:

$$\frac{\alpha_{H_2} \alpha_{CH_3OH}}{\alpha_{H_2O}^2} < 2.7 \times 10^{-4}$$

As discussed in the original paper, there was no observable adsorption of hydrogen on the surface during the interaction of CuMOR with water vapor, and the hydrogen signal was detected by mass spectrometry before the signal of water became visible [Fig. 2B in (2)]. This is common for zeolites; they are hydrophilic and do not adsorb nonpolar inert gases at low pressure and high temperature. For instance, the typical heat of adsorption of water for zeolites is in the range of 40 to 70 kJ/mol (3, 4), whereas for hydrogen the value is about 5 kJ/mol (5). We assume, therefore, that

$$\alpha_{H_2O} \approx \alpha_{CH_3OH} \gg \alpha_{H_2} \approx 0$$

Thus, despite the positive standard $\Delta G$ value (the upper limit of $\Delta G^{273K} = +58 \text{ kJ/mol}$), we conclude that Eq. 4 is driven by the water stabilization effect, the conditions of the reaction, and the low adsorption of hydrogen with respect to water on the active sites of the CuMOR material.

However, although strong adsorption of water helps to drive the reaction of water with CuI, it leads to poisoning of the active sites of CuMOR competing with the reaction of methane. To specifically address this issue, removal of water should be considered as the last step in the whole process:

$$\text{Cu} \cdot \text{O} \cdot \text{Cu} + +80 \text{ kJ/mol} \quad \text{at } 673K$$

To remove excess water after the reaction, we purged the CuMOR material in dry helium at a high temperature of 673 K. This step is similar to the first activation of an as-made Cu-zeolite at elevated temperature, where hydrated CuI species are activated at high temperature to generate the active sites in the reaction in Eq. 3 (6, 7). In those cases, there is competition between water adsorption driven by exothermicity and desorption driven by the absence of water. Furthermore, at 673 K, the $\Delta G$ value of the dehydration process will be lower than that calculated at 473 K. We estimate this to be $+80 \text{ kJ/mol}$, which is relatively high. However, poisoning of the copper active sites is not detrimental to methane activation, provided that the conditions are suitable.

After high-temperature activation and exposure to high-pressure methane, methanol forms. During activation, water is removed from the active site, which may occur by transformation of Cu-($\text{OH})_2$-Cu to a Cu-O-Cu species with chemisorbed water molecules as an intermediate step. As described in the original paper, the active sites that are poisoned with water can still interact with methane at high pressure [Fig. 2A in (2)], aided by the negative Gibbs energy of this reaction (Eq. 3). An increase in the methane pressure then drives the reaction, resulting in higher methanol yields [Fig. S10 in (2)]. Water poisoning is not detrimental to methane activation, consistent with other studies on the role of water molecules as methane reacts with zeolites (4); hence, the above values of $\Delta G$ in the reactions in Eqs. 4 and 5 are the upper limit. It is possible to use the above-mentioned inert treatment to remove fractions of water molecules step by step, thus effectively reducing the strong endotherm to a set of weaker effects that occur only in the absence of water in inert gas atmosphere.

It is well established that chemical reactions can be driven by the removal of specific products. For instance, a reverse water-gas shift reaction has a positive $\Delta G$ of 29 kJ/mol but can be driven by adsorption effects and can be applied on a large scale (8). Goto et al. (9) and Imai et al. (10) studied the dehydrogenation of cyclohexane to benzene and hydrogen with a mixture of platinum on an alumina catalyst with a hydrogen scavenger, CaNi-5, in the reactor at $+35 \text{ kJ/mol}$ at 473 K. Fanelli et al. (11) showed that the addition of titanium to the catalyst during the dehydrogenation of isobutane leads to isobutene/isobutene ratios up to 20 at 641 K at $+45 \text{ kJ/mol}$. Similarly, after saturation with water, zeolites that work as adsorbents can be dried in a flow of dry gas, despite the positive value of the standard $\Delta G$ (12). Numerous reactions, including water splitting on the surfaces, are inhibited by standard values of $\Delta G$ but are nonetheless feasible (13).

Periana suggests the possibility of an interaction of some of the formed hydrogen with residual CuII species because the reaction of CuO with hydrogen is favorable. We agree that if CuO is present, then it will react with H2. However, our experimental data show that in the case of anaerobic activation of CuMOR, autoreduction of some of the copper species occurs and the number of residual CuIII sites is too small to interact with hydrogen. On the contrary, for an oxygen-activated sample, which has only CuII sites, hydrogen is not observed in the interaction of

Fig. 1. Additional stabilization of the active center with water. Adding water molecules further stabilizes the active copper oxide centers through the formation of hydrogen bonds, thus helping to overcome endothermic effects. The zeolite structure is omitted for the sake of clarity. Color code: gray, silicon atoms; pink, oxygen atoms of the zeolite framework; red, oxygen atoms of the active site and adsorbed water molecules; brown, copper atoms; white, hydrogen atoms.
water with the methane-reacted material. As suggested by Periana, any hydrogen that would have formed is likely to react with these additional CuII sites. Similarly, the higher selectivity to methanol for the helium-activated sample is explained by the partial oxidation of CuI with water and the autoreduction of some of the CuII to CuI species in the absence of oxygen, leading to a lower concentration of active CuII species that overoxidize methoxy species. Oxidation of all the copper to CuII species in the presence of oxygen during activation is responsible for overoxidation and the formation of the larger amounts of formates and carbon monoxide on the surface of CuMOR (figs. S2 and S5 in (2)).

The thermodynamic feasibility of the process, as described in the paper, is further supported by the analysis of the methanol yield after five consecutive loops. After five cycles, our data reveal that the total methanol yield amounts to 0.142 + (0.204 × 4) = 0.958 mol(MeOH)/mol(Cu), which is twice as high as the theoretical yield of methanol because of the stoichiometric ratio between the copper sites and reacted methane. Therefore, the oxidation of CuI sites must occur during one of the steps in each cycle.

In the original paper (2), we reported an approach that suggests the possibility of converting methane directly to methanol in the absence of oxygen. Although it may have its drawbacks, it is too early to estimate the financial costs of this process and to doubt the possibility of its commercialization. We hope that our work will motivate further research in the field, eventually making industrial implementation of novel routes for the direct conversion of methane to methanol possible.
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