Answer to reviewer comments

Dear Prof. Luo,

Thanks very much for your letter with two reviewers’ comments. We highly appreciate the very useful comments and suggestions from the reviewers. We have revised our manuscript accordingly and our responses to the comments are enclosed.

Best regards,

Chuanming Wang
Hu et al. performed a systematic theoretical study of syngas to methanol conversion on Cr2O3 with first principles calculations and microkinetic modelling. Overall, I think it deserves for publication as the following comments are addressed.

1. As shown in Fig. 5, at 673K, the reaction of CO+H2 to methanol over all facets becomes endothermal? Why it can take place in experiments? The net reaction rate should be methanol decomposition.
   **Response:** Thank this reviewer for this useful suggestion. It should be noted that the free energies of reactants and product in gas phase at 673 K is calculated at 1 atm, and the reaction is endothermic, agreeing with the data taken from CRC handbook. While in experiments, the reaction is carried out at higher pressures (e.g., 3 MPa) and is thus exothermic at the reaction conditions including higher pressure or lower temperature. The following sentence is added in the caption of FIG.5 of the revised manuscript. “The free energies of reactants and product in gas phase at 673 K is calculated at 1 atm.”

2. Based on the intrinsic activity (TOF) over different facets, can we estimate by fraction of facets and calculate the apparent activity, which is more interesting for experiments.
   **Response:** Thank this reviewer for this interesting suggestion. While it is of great challenge in computational catalysis. In this work, only two most stable surfaces were studied and the (001) surface is much less active compared to (012) surface. We further demonstrated that the reducibility of the active (012) surface would be more significant. Such findings we believe would be instructive for experiments to focus on the reduced Cr2O3(012) surface. The direct comparison between computation and experiment on real catalyst particles is highly challenging, and we hope this reviewer understand this.

3. Overall, the local structures of these adsorbates and transition states on these surfaces are not clearly shown, I suggest to show the local structures only, while blur other atoms at the bottom or shown in slim line.
   **Response:** Thank this reviewer for this useful suggestion. We have carefully considered this reviewer’s suggestion and re-drawn some figures according to this reviewer’s suggestion. However, in the slim line mode, the bonding between the surface atoms and the bottom atoms are difficult to recognize (for example, the following comparison), especially on the (012)-8H and (012)-4Ov. As a result, it may be better to keep the original displaying style to meet our taste.
4. In Fig. 1, the top and side views should be shown separately.

Response: Thank this reviewer for this useful suggestion. We have revised Fig. 1 as below in the revised manuscript.
5. *What CO methanation is not considered for comparison? Methane is the major product instead of methanol as oxide used only, instead with the bifunctional oxide-zeolite catalysts.*

**Response:** Thank this reviewer for this point. Methane is one important by-product in bifunctional catalysts composed of oxides and zeolites. While this work is mainly focused on the conversion of Cr2O3 for syngas conversion in bifunctional catalysis. We thus computationally studied the formation of methanol, key intermediate bridging oxide and zeolite components, on Cr2O3 surfaces. The findings on the surface structures and reactivity of Cr2O3 we believe are useful in bifunctional catalysis. CO methanation, on the other hand, would be important to construct complete reaction picture, and would be another issue for study.
Reviewer: 2

In this manuscript, the authors computationally investigated the reaction mechanisms of the syngas to methanol process on the stable Cr2O3 (001), (012), (012)-8H, and (012)-4Ov surfaces using DFT+U based microkinetics. The novel concerted hydrogenation mechanism was discovered on the Cr2O3(012)-4Ov surface. The theoretical results unravel that surface reducibility is a crucial factor governing the yield of methanol. This theoretical paper contains a staggering amount of work. The paper could be publishable in Chinese Journal of Chemical Physics but the authors need to consider the following issues:

1. The paper is strictly theoretical. Could the authors provide some experimental results to support their conclusions?

Response: Thanks very much for this useful comment. The methanol synthesis from syngas by Cr2O3 is the initial process in bifunctional catalysts including Cr2O3/ZSM-5 for syngas to aromatics reaction. The experimental studies on the individual methanol synthesis process on Cr2O3 oxide is very few and only the following related article can be found (Ref. 28, ACS Catal., 2019, 9, 895), in which the conversion of CO2 to aromatics by Cr2O3/ZSM-5 was studied. They found that Cr2O3 catalyst achieved methanol and DME selectivity up to 97% with 29.1% of CO under 350 °C and 3.0 MPa, and which has been introduced in the Introduction section. No atomic insights in experimental articles can be found, and it is unlikely to directly compare our calculations to experiments. We hope this reviewer understand this.

2. For the microkinetics results, the rate-determining step should be obtained by the degree-control calculation. The authors should provide the related data and the imaginary frequency of the transition state of each elementary step.

Response: Thanks very much for this useful comment. The calculated degree of rate control (DRC) values for the transition states and intermediates are listed in Table 2, and the imaginary frequencies are added in FIG. 5 of the revised manuscript.

3. The authors should provide more discussion on the reason why the reducible surface could promote the activity of syngas to methanol.

Response: Thank this reviewer for this useful suggestion. More discussion was added in section III. C. Microkinetic modeling analysis in the revised manuscript as bellow.

“...It seems that the higher activity of the reduced (012) surface may originate from the additional states near the fermi energy level (see FIG. 4). Both additional occupied and unoccupied states..."
exist on the (012)-4O_v surface, and the dissociated H* + H^+ pairs are more active for the subsequent reaction. This is also confirmed by DRC analysis (see Table 2), indicating that the step of H2 dissociation becomes more important on the (012)-4O_v surface than on other three surfaces.”

4. For Fig. 5, the figure caption or the figure should provide the definitions of black and red energy profiles. The notation for the energy profile is not clear as well.

Response: Thanks very much for this useful comment. Additional notes related to black and red energy profiles were added in figure caption of the revised manuscript.

5. The English still needs to be improved and carefully checked. A few typos could be found in the paper.

Response: Thanks very much for this useful comment. We tried our best to go through the manuscript, and some spelling and grammar mistakes were corrected.