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Doctoral dissertation evaluation report

Author of the thesis: Mariia Lemishka
Title of the thesis: Binuclear transition metal ion centers in zeolites: Their preparation, characterization, and catalytic properties
Thesis evaluator: prof. David Kubička, Ph.D., University of Chemistry and Technology Prague, Czech Republic

The doctoral thesis of Mariia Lemishka is a systematic study of binuclear transition metal ion centers in zeolites that looks at their potential applicability in the direct oxidation of methane to methanol. The thesis is based on six published articles in renowned journals (e.g. ACS Catalysis, Applied Catalysis B, Chemical Communications, and others). She is the first author of only of these articles (although in one of the articles a joint first-authorship is claimed). Therefore, the contribution of Mariia Lemishka to each of the articles should be explicitly stated in the thesis.

Overall, the dissertation is of very high scientific relevance and quality as reflected by the top journals in which the research findings were published. The quality of the dissertation can be compared to the quality of theses at top European universities I had the privilege to review. From the formal point of view, the thesis is well organized, easy to read with a minimum number of typos using good English. My only concern is the absence of the experimental section which is unfortunate as this is an experimental thesis. Important details need to be looked up in the articles which is not very convenient for the reader.

There are several points I would like to raise:

1. Can you be please specific in which isomerization, carbonylation and cracking reaction FER is used? (page 15). Also, in case of MOR, the refining and petrochemical processes should be specified as are the other applications (page 16).
2. Moreover, it should be strictly distinguished between industrial applications and research use of the zeolites. For instance, many applications for BEA are given (page 16), but is BEA used in any of them industrially?

3. It is said (page 17) that from environmental perspective there has been a great deal of interest in the chemical utilization of CH₄. Why is that? If we left it underground we would limit its emissions dramatically, which would be desirable from the environmental point of view.
4. Converting methane to methanol to be used as chemical commodity might certainly be of interest, but would it really make sense to make methanol from methane for energy applications, i.e. methanol as energy carrier which you mention on page 18? A similar statement “The CH₃OH produced from CH₄ oxidation has the dual potential of serving as both an energy carrier and a key chemical raw material...” is on page 20. What would be the advantage (economical and environmental) to convert an established energy carrier (i.e. methane) to methanol to be then used as an energy carrier?
5. Also, please explain, why direct oxidation is the most promising way to transform CH₄. Currently, partial oxidation and/or steam reforming of methane are commercially used. They allow to produce a wide range of commodities via the so-called syngas.
6. Table 1 should show also conversion of methane at which the results were obtained. The conversion of methane should be actually always explicitly given, i.e. also in the other tables in the thesis.
7. On page 24 it is said “Furthermore, the selective oxidation of CH₄ by the α-O on Fe-zeolites is terminated after the formation of methoxy groups strongly bound to the catalyst. Subsequently, extraction of the methoxy groups by a water or water-organic medium is necessary to desorb the oxidation products from the Fe-zeolite catalysts” while on page 28 it is claimed “Recently, Tabor et al.⁷¹ reported a new feature of Fe-zeolites that revealed the cooperation of two (binuclear) Fe(II) centers in O₂ activation. In addition, the stabilized oxygen species (α-O) formed after O₂ splitting selectively oxidized CH₄ to CH₃OH at RT”. Does this mean that methanol was really formed in the latter case or was that one also terminated by formation of methoxy species?
8. Generally, it is not clear which of the numerous activities were performed by the student and which were done by her colleagues – e.g. theoretical study is mentioned on page 32. Did the student perform the calculations herself?
9. In Table 2, being a surface technique is given as a limitation of FTIR spectroscopy. Please explain in what way is this a limitation?
10. It is reported that “the CH₃OH productivity obtained at 220°C varied over the three subsequent redox cycles between 0.20 and 0.38 μmol/gcat”, but I miss the information on the fed amount of methane. How much methane was fed and what was the methane conversion?
11. With respect to previous comment, Figure 21 shows that the productivity of CO₂ is 10 times larger than that of methanol. What is the mechanism of methane interaction with the active sites (i.e. is it adsorbed directly from the gas phase)? What are the other products (CO, H₂O, CH₂O, etc.?) and what are their yields?
12. It is suggested that excellent activity in methane oxidation with excellent selectivity to methanol can be achieved already at room temperature (sentence of the abstract), but at the same time it seems that higher than room temperature is necessary to desorb methanol from catalyst surface. In the example presented in Figure 21, the temperature was as high as 220°C, which led to a significant deterioration of the selectivity. Could you please present the desorption of the formed methanol as a function of temperature? In other words, what are the requirements for spontaneous desorption of methanol from the catalyst surface?
13. Also, from the mechanism point of view, when methoxy species are formed from methane, what happens to the fourth hydrogen atom? Where does it adsorb on the catalyst?

14. The formation of binuclear center seems to be a key parameter. Why the comparison in chapter 3.2 discusses only Co, Ni and Mn? In other words, why was Fe not added in this comparison here (e.g. Figure 22, Table 3)?
15. As experimental part is missing in the thesis, it is not easy to follow the experiments. Nonetheless, it appears, that the catalysts need to be first pre-oxidized by oxygen and only after that methane is introduced / fed. From a practical point of view, could methane and oxygen be co-fed so that the active oxygen species on the catalysts surface are continuously restored? Or is this not possible?
16. It is reported that “The yields of methanol produced by N₂O dissociation over M-FERs were twice as high as the yields of methanol produced by O₂ splitting”. What is the reason? Do the active sites differ?
17. What is the methanol productivity that needs to be achieved for the catalyst to be attractive for an industrial application?

In summary, even though I have raised several points for discussion, the doctoral dissertation of Mariia Lemishka is of top quality and I strongly recommend the dissertation for public defense.

Prof. David Kubička 