

Referee report on the doctoral thesis “High pressure CO and methanol oxidation study over nanopowders Rare Earth Oxides and platinum thin film catalysts” by Mgr. Andrii Rednyk.

The submitted doctoral thesis reports on the reactivity of rare earth oxides and platinum-based catalytic systems towards CO oxidation and methanol reforming/oxidation under high pressure conditions. The corresponding reactions play an important role in numerous catalytic processes for production of hydrogen from renewable resources.

The thesis is organized into five chapters. In chapter 1, the authors describes the structure of the thesis but gives rather brief description of the goals and the objectives of the presented work. The experimental techniques are described in chapter 2 including details of the sample preparation. The experimental results are given in chapters 3 and 4 that start with the introductory subsections providing motivation and general aspects of the studied reactions and mechanisms. The conclusions are given in chapter 5.

The main disadvantage of the corresponding structure of the thesis is the absence of general Introduction sections summarizing previous knowledge about the reactivity of the investigated materials. For this reason it is difficult to estimate the novelty of the presented results.

Also, the thesis are cluttered by overly detailed description of similar results, multiple repetitive details of experimental procedures, and notations of the reaction equations without a need.

Among the advantages of the submitted thesis is very detailed study and comparison of different catalytic systems under similar experimental conditions accompanied by characterization of their structure and composition at various reaction stages. This unique approach allowed the author to establish the reaction mechanisms and to identify the active catalytic sites during CO oxidation. Additionally, well-controlled alteration of the reactant stoichiometry allowed to estimate the contributions of various elementary reactions steps at different stages of the methanol reforming/oxidation.

An important result of the thesis is the development of the preparation procedure for the efficient catalytic materials for partial oxidation of methanol.

The author have demonstrated ability to conduct an experimental work and communicate his results. The part of the reported results has been published in recognized journals.

Thereby, I recommend Mgr. Andrii Rednyk for awarding him the title PhD.

To the content of the Thesis I have following questions sorted in the order of their importance below.

More important:

- 1) Page 14. Section 3.1. The author mentioned “new sol-gel approach” in the preparation of rare earth oxides. What is the advantage of the “new” with respect to “old” approach?
- 2) Pages 19-20. Figure 15. How does the author define and determine the onset temperature for CO₂ production?
- 3) Page 20. Inset of Figure 15. Why does the author use the temperature region of 180-220 °C for determination of the activation energy also from TPR1 if the onset temperature here is above this region (240 °C)?

In general, what is the advantage of near-onset temperature region for determination of activation energy? The activation energy does not depend on temperature as long as the morphology of the surface is stable. More accurate values would be obtained by fitting the whole temperature region where the reaction occurs.

- 4) Pages 19-22. Figures 15-17. The activation energies are different on Pt/SiO₂, Pt/G-foil, and Pt/C/SiO₂ samples. Is it possible to correlate the change of the activation energy with the size of the supported Pt particles?
- 5) Pages 19-22. Figures 15-17. Why there is such a big difference (order of 10¹⁰) in CO₂ production on Pt/SiO₂ with respect to Pt/G-foil and Pt/C/SiO₂? Also, note that despite the difference, the same curves have comparable intensities when plotted in Figure 21a.
- 6) Page 25. The author suggests that on Pt/SiO₂ sample, the coalescence of platinum was not accompanied with uncovering the SiO₂ substrate. How this is possible?
- 7) Page 26. Unclear discussion of CO oxidation mechanism on PtO_x/SiO₂: The author first points out that PtO_x film decomposes to Pt⁰ under CO flux between 150 and 230 °C. Then later in the text he states that *“above 260 °C (and in the following TPR2 and TPR3), CO oxidation presumably proceeds via MvK mechanism where platinum layer is alternately reduced and re-oxidized, which leads to roughening of the surface of catalyst.”* This assumption seems unlikely, since platinum should be in metallic state above 260 °C and therefore should behave similar to Pt/SiO₂, i.e. the reaction should proceed via L-H mechanism as discussed before. However, later in the text, the author provides correct explanation assuming full reduction of PtO_x to metallic platinum.

The author should carefully check the corresponding discussion in the text and at the end of Section 3.3 and clarify the mechanism of CO oxidation on PtO_x/SiO₂.

- 8) Pages 27-33. Based on the results presented in Section 3.4, it is clear that Ce/Al AG have significantly higher CO conversion with respect to praseodymia, samaria, and terbia based materials. Therefore, it is not clear why samaria was selected as a perspective material for further studies presented in Section 3.5. The author should explain the importance of samaria in catalysis.
- 9) Chapter 4. The author plots relative concentrations of the reaction products (H₂, CO, CO₂) which is in range from 0 to 10⁻⁷ for SRM, from 0 to 10⁻⁴ for POM. What does these concentration relate to? How these concentrations were calculated?
- 10) Pages 43-48. The reactivity of all studied samples in SRM is generally very low. Considering very low product yields, the discussion of the mechanisms on these samples at the end of the section seems pointless. Also, the author mentioned the “active platinum” in Pt-CeO₂ without the explanation of its meaning.
- 11) Page 51. In the discussion of POM on PtO_x/SiO₂, the author states: *“above 260 °C we observed considerable increasing of CO concentration, which indicates starting the MD reaction (23).”* How did the author reach this conclusion?
- 12) Page 55. The assumption that “residual Pt²⁺ is responsible for the altered chemistry of the PtO_x catalyst” seems farfetched.
- 13) Page 59. According to the text, the author plotted XPS spectra obtained from PtO_x/a-C₁/SiO₂ sample in Figure 45 before and after TPR2. It is strange that sample contained Pt^{4+/2+} before TPR2. According to the behavior of the similar system described above, one would expect reduction of Pt^{4+/2+} already after TPR1.
- 14) Page 60. In the discussion of POM on PtO_x/a-C₁/SiO₂ sample, the author states that POM is accompanied by SRM and MD reaction at higher temperatures. However, from the comparison of the product intensities, the contribution of SRM appears rather small (compare the intensities in Figure 31, 33 and Figure 44a).
- 15) Page 60-61. The author associates non-uniform trend in H₂ desorption (Figure 43) with a switch from SRM to MD reaction during POM on PtO_x/a-C/SiO₂ and PtO_x/a-C₁/SiO₂ samples. Is it

possible that the change in the film morphology (reduction, coalescence) during TPR1 is responsible for the non-uniform shape of the plots similar to the situation observed during CO conversion discussed in Section 3.3?

- 16) Page 61. The author concludes that the main source of CO and CO₂ during TPR2 are SRM and MD reaction. Did the author considered carbon support as a possible source of these products?
- 17) Page 61. The author suggests that the use of carbonaceous materials as interlayer is a good option to improve the efficiency of thin films. However, comparison of the activity of PtO_x films prepared without carbon interlayer (Figure 34) and with carbon interlayer (Figure 44a) does not reveal a big difference.
- 18) Page 63. Repetitive explanation of POM mechanism on PtO_x/SiO₂ sample involving SRM and MD process. In addition to the point raised above (question 14), it appears that MD contribution to POM is also small (compare the intensities in Figure 46 and 49, also Figure 50a). Under these circumstances, H₂ is most likely formed due to WGS reaction. The author should estimate the contributions of SRM and MD reactions to the POM before discussing the sources of CO and CO₂ products.
- 19) Section 4.3.3. When discussing the POM under different stoichiometric ratios of CH₃OH and O₂, the author uses terms “*activity*” and “*selectivity*” to describe the relative yield the POM products. It would be more informative to use a ratio of H₂ product to the amount of CH₃OH in the feed and/or product ratios H₂/CO, H₂/CO₂.

Less important:

- 1) Page 2. “...precious control ...” should be “ ... precise control ...”
- 2) Page 3. “Inverse Pt/CeO₂ thin films” are not “inverse” if prepared as described.
- 3) Page 6. Repetition of two sentences: “SE and BSE ...topography of the samples.”
- 4) Page 19. The author states that “... grains sized 40 nm in diameter are surrounded by corresponding substrates”. Does it means that the grains are encapsulated by the substrate?
- 5) Page 26. Most likely the error in the sentence “... the highest CO₂ yield at TPR3 stages exhibited Pt/C/SiO₂ specimen (Fig. 21b).” The correct sentence should be “... the highest CO₂ yield at TPR3 stages exhibited PtO_x/C/SiO₂ specimen (Fig. 21b).”
- 6) Page 44. Inconsistent labeling of the samples in the text and in the Figure 29.
- 7) Page 43. The reactivity of Pt-CeO₂ is discussed in Section 4.2.1 without explanation of how this sample was prepared. The author refers to Section 4.3.4 for the preparation details which far behind the Section 4.2.1.
- 8) Page 55. Mismatch in sample labeling: Pt/SiO₂ versus Pt/Si.
- 9) Page 59. Figure 44a. Mismatch in symbol color between the legends and the plots.
- 10) Page 60. Figure 45. The author probably made a mistake in the figure caption. According to the text, the plotted data are obtained from PtO_x/a-C_t/SiO₂ sample and not from Pt/a-C_t/SiO₂.
- 11) Page 64. At the top of the page, CH₃OH:O₂ – 3:1, most likely should be CH₃OH:O₂ – 1:1.
- 12) Page 67. Figure 50b. The „x“ axis should be time and not temperature.

Erlangen, 5.02. 2016

Mgr. Yaroslava Lykhach, PhD.