



REFeree'S REPORT

on the PhD. Thesis of Mgr. JAKUB PASTVA

The submitted PhD. Thesis of Mgr. Jakub Pastva entitled "Preparation and characterization of new materials for metathesis and adsorption" ("Příprava a charakterizace nových materiálů pro metatéze a adsorpci" in Czech) is a work dedicated to studies of mesoporous materials. The author's goal was to synthesize several mesoporous molecular sieves and to achieve their modification by incorporating MgO and K₂CO₃ in their structures. These newly prepared systems were afterwards subjected to adsorption tests with the intent to examine their behaviour against CO₂. A major part of the work is dedicated to the study of anchoring ruthenium-based organometallic complexes, acting as metathetic catalysts for several variants of metathetic reactions. Thorough attention is paid also to adsorption tests of the newly prepared systems. The experimental part of the work is concluded with catalytic tests of the most active catalyst (labelled as **C05**) in elucidating whether the environmentally quite unfriendly toluene – used during previous tests – could be substituted by another friendlier alternative, which would inflict no major impairment on the catalyst's behaviour. Most of the experimental research was conducted at the Department of Synthesis and Catalysis, J. Heyrovsky Institute of Physical Chemistry of The Czech Academy of Sciences, *u.z.* in Prague.

The work is divided into several parts and starts with outlining the main scientific goals. Next follows a brief (albeit thorough) introduction to various topics, which are discussed more in detail during later parts of the work. The main part of the work consists of the presentation and discussion of results, which are then concluded by a summary of achievements accomplished by the candidate.

The research topic that the author has devoted himself during the course his studies is a natural continuation and extension of the research conducted at the Department of Synthesis and Catalysis of the J. Heyrovsky Institute. Nevertheless, the demanding character of this research calls for the cooperation of several scientific groups, a fact, which is reflected well in the presented Thesis.

Already if judging only the amount of work presented through the results in the evaluated Thesis, I am happy to conclude that the candidate has done a large amount of scientific work and has achieved several results that surely deserve attention. I shall refrain myself from listing all of these, as this will be surely done by the Thesis supervisor, who bears an in-depth knowledge about significance of the newly exploited systems in the context of the state-of-the-art knowledge about molecular sieves and homogeneous catalyst anchoring.

The amount of scientific results achieved by the candidate is best illustrated by the fact that his results have already been published in eight articles printed in prestigious international scientific journals, thus only a fraction of his results could find their way into the submitted Thesis. The topics discussed in the current Thesis have been reported in three papers whose reprints are included at the end of the work for reference. Such a conception of work facilitated also the task of the referee(s), since most of the text has already been subject to careful evaluation prior to publishing.

The text preceding the three reprints is conceived not only as an introductory part defining the most important terms used throughout the discussion, but serves simultaneously as a summarization of results achieved. The introduction surely deserves compliments from my side, since it provided a relatively short, but very readable route into the discussion of results. All the terms and methods used in interpreting the experimental results have been properly defined and have been explained clearly to the reader. I thus regard the work as very well written, although with a remark that the frequency of typos and grammatical inconsistencies was slightly higher than desired for such a work.

I have a few (mostly formal) remarks in conjunction with the text, listed below:

1. List of symbols: the molar concentration should probably be a lowercase “c”.
2. p.11. What did the author mean by the low energy of regeneration for MgO?
3. p.11. It would be highly desirable to provide in this section a detailed list of toxic chemicals employed in the preparation of MgO.
4. p.14. Schemes 2.6. & 2.7. are misleading in their current form. Their captions are providing explanation only for the processes pointing to the right side of the equations.
5. p.18. I strongly disagree with the author calling the electron transfer occurring from the occupied p orbital of the carbenic carbon to the metal as back donation. In addition, an explanation assuming the involvement of ligand π orbitals(s) would probably be much more appropriate.
6. p.30, Section 2.3.4.3. The phrasing of the whole paragraph is a little unfortunate and does not explain well the boomerang mechanism. Already the first sentence is fully self-evident and does not provide any useful information on its own.
7. p.48. I suspect there was no monochromator employed on the diffractometer. Even if I'm wrong, the author should specify anyway whether the monochromator was employed as an upstream or a downstream one. In addition, the correct spelling of the radiation detector is VANTEC-1.
8. p.56. The symbol *p6mm* designates a wallpaper group and probably *P6mm* was intended. In any case, the rotation axis is to be written with no italics.
9. Reference [24] is incomplete (no publication year and no ISBN).

Apart from the minor problems listed above, I have some further suggestions for the author to discuss upon the defence of his Thesis:

1. There is an apparent increase in the isosteric adsorption heat (Q_{st}) for SBA-15 for amounts of adsorbed gas ranging approximately from 13 cm³/g to 17 cm³/g. Can this be a signal of some structural changes in SBA-15 upon adsorption or are its reasons of different origin?
2. I could not understand the explanation for the possible catalyst deactivation for WHSV (weight hour space velocity) observed at 6 h⁻¹ for the RCM of 1,7-octadiene catalysed by **C01**. Also the corresponding graph in Fig. 4.27. lacks a smooth shape. Does this particular functional dependence bear any physical significance or is it an inconsistency only?
3. It would be highly desirable that the author specify his own contributions to the experimental material used to assemble the evaluated Thesis. For example, nobody has been credited for carrying out the metathetic tests, nor for measuring (and interpreting) solid-state NMR spectra. Are these all the author's own achievements?

Conclusion

The evaluated PhD. Thesis of Mgr. Jakub Pastva is a work well written, having clear scientific motivation and incorporating a substantial amount of results, all with clear scientific value. Both the amount of experimental work and the processing of results achieved meet the requirements imposed on doctoral theses. I am happy to provide the defence committee my unequivocal recommendation for the successful defence of this work.

Praha (Prague), 6/III/2017

Róbert Gyepes