

Evaluation of the PhD Thesis entitled
Ruthenium alkylidene
immobilized on mesoporous molecular sieves as catalysts for olefin
metathesis

presented by

M.Tech. Tushar Raghunath Shinde

to the Charles University in Prague, Faculty of Sciences,
Department of Physical and Macromolecular Chemistry

The Thesis of Mr. Tushar Shinde presents the results of his multidisciplinary study aimed at preparing new heterogeneous metathesis catalysts based on ruthenium complexes of the Zhang and Grubbs second generation types and, mainly, testing the activity, efficiency and selectivity of these catalysts in various metathesis reactions such as acyclic-diene metathesis polymerization (ADMET), ring-closing metathesis, ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), enyne metathesis, cross-metathesis of unsaturated natural compounds and ethenolysis of unsaturated compounds. The catalysts were anchored on mesoporous supports of various architecture and pore diameters and effects of these characteristics on the catalyst activity, selectivity and leaching were examined. The Rh catalysts anchored on a non-porous silica were used as the reference systems. Results and knowledge comprised in this Thesis has already been published in four original papers issued in impacted international scientific journals, of which Mr. Tushar Shinde is the first or second co-author.

The heterogenized catalysts studied by Mr. Tushar Shinde were prepared by direct anchoring of soluble homogeneous catalysts on unmodified or surface-modified mesoporous sieves. Analyses carried out by various experimental techniques as well as results of catalytic tests have shown that the active centers are mostly anchored by non-covalent interactions or by labile bonds that undergo equilibrium cleavage in polar solvents. This fact is not crucial but anyway important since it limits repeated usage of these new catalysts in such reaction surroundings. In spite of that, there are many useful transformations for which these catalysts have shown high activity and selectivity even in repeated use.

As far as the scientific content is concerned, the Thesis of Tushar Shinde can be ranked among the average ones. My evaluation of the formal aspects and clarity of presentation is quite good, since Mr. Tushar Shinde essentially followed general conventions codified in the Guidelines for preparing manuscripts for journals and his English is quite good.

Conclusions

The research presented in the Thesis of Tushar Shinde is based on good ideas and contains several points of valuable scientific novelty. The author namely succeeded in preparing new effective heterogeneous catalysts that can be repeatedly used in non-polar solvents, in which he proved the stability of anchoring the active centers on mesoporous supports was demonstrated. He has shown that despite limitations restricting a repeated use of the catalyst to non-polar environments, these new catalyst might be utilized in a wide scope of useful chemical transformations. The results he obtained are discussed in a fully competent way though some mostly formal weak points can be found in Thesis.

My final statement is that the Thesis of Tushar Shinde fulfils all conditions required for a doctorate degree and thus He should be allowed to defend the Thesis.

Prague, February 20, 2015

Prof. Jiří Vohlídal

Questions to discussion

- 1) The stability of the active species anchoring on a support without depriving them their selectivity is the key point of developing of new efficient and really productive heterogenized catalysts. One possible way meeting these demands is introduction of groups capable of covalent anchoring on the support as the end-capping groups of side chains of one or more ligands of the active central atom. This approach has not been examined within the Thesis, however, is there a successful example of such anchoring described in the metathesis related literature?
- 2) The supports used were of the siliceous class. Is something known about anchoring the metathesis catalysts on alumino-siliceous supports?
- 3) How long would be the spacer between the support and central atom of the active species for the catalyst selectivity be not influenced by anchoring ?
- 4) If you will take into account overall costs of the homogeneous and heterogenized (including cost of work to prepare the support and linker), is some of your heterogenized catalyst able to compete with the free homogeneous catalyst ?