

## **Ruthenium alkylidenes immobilized on mesoporous molecular sieves as catalysts for olefin metathesis**

The Thesis was aimed in the synthesis of ruthenium complexes immobilized various variants of mesoporous molecular sieves, testing the obtained heterogeneous catalysts in model metathesis reactions and their application on transformation of cardanol into commercially applicable products.

In the first short part the author summarizes individual objectives of the Thesis: synthesis and characterization of heterogeneous catalysts, study of the role of support properties, testing and optimization of selected metathesis reactions and application obtain results in metathesis of cardanol.

Theoretical part covers known information about alkene metathesis, ill- and well-defined metathesis catalysts, various variants of immobilization of homogeneous ruthenium catalysts, industrial applications of metathesis and industrial applications of cardanol. It thus covers quite wide area of various branches of chemistry, but is written in a clear and concise manner with minimum of errors. Nevertheless, I have several comments: 1) why strange citation format [<sup>n</sup>] was used; 2) on page 3 the author speaks about three broad categories of metathesis reactions but does not specify them; 3) for general introduction, references to reviews on the given topics would be more productive than to their first appearance; 4) historically first well-defined Ru catalysts of low activity need not to be included; 5) Grubbs 2<sup>nd</sup> generation catalyst cannot directly bind to silica, ligand exchange has to be used (p. 9); 6) Hoveyda-Grubbs catalysts typically initiate more slowly than Grubbs catalysts (p.11); 7) I am missing the discussion regarding the role of initiation in metathesis, as the catalysts used are in principle precatalysts from which active catalytic form is formed and how this influences potential recycle of metathesis catalyst; 8) In contradiction to author statement, Ref. [76] contains no information about metathesis of cardanol.

The Experimental part is written in a way characteristic for the area of heterogeneous catalysis and without larger errors. The description of heterogenization of catalysts and their characterization is clear. However, the organic part, especially the description of some metathesis experiment and the details of the analysis of the products is in some cases insufficient. The first issue I am missing is the role of stirring. Most experiments were heterogeneous and hence they should be sensitive to the stirring rate. Was this studied? Some of the experiments do not bring sufficient data, masses and volumes of individual components are often not given (e.g. in exp. 3.5.1.2, 3.5.2) and require tedious deduction from the reader. In exp. 3.5.6 the final volume of the reaction mixture is given, but the starting solvent volume is missing. The composition of the reaction mixtures, amounts of products and the details of the assignment of individual products is mostly missing.

The Results and discussion part follows individual objectives of the Thesis. The first part thus describes synthesis and characterization of heterogeneous catalysts. My main problem as organic chemist was here to understand the connection between text on pages 43 to 46 and related Figures 4.1 to 4.5. I will appreciate more detailed explanation what information can be deduced from Figures and how is this related to  $S_{\text{BET}}$ ,  $V$  and  $d$  values. The second question is: in all cases, theoretical loading of Ru was 1%, but for all catalysts the values found were exactly 0.93%. Does this mean that 0.07% was in all cases lost in the solvent used during heterogenization?

As the key part of characterization of the catalyst, the leaching into solvent was studied briefly and to my opinion deserved more attention. On page 49, NMR spectra of

organics washed from heterogeneous catalyst are claimed to be identical to the parent complex, but there is no explanation of large signals at 7.1, 2.5, 2.4 and 1.4 ppm. To which compound they belong and how this influenced reported 76% of Ru recovered? The choice of THF for leaching test was not ideal as it decomposes ruthenium metathesis catalysts and is thus not common solvent of choice. Hence, it is probable that 24% of catalyst not removed by THF in leaching experiments probably decomposed, as was also confirmed by metathesis experiments after leaching. The author should discuss solubility of Zhan catalyst in cyclohexane and other common metathesis solvents (toluene, dichloromethane). From the brief results the leaching seems to reflect polarity of the liquid phase (solvent, reactants and products) and thus probably solubility, limiting significantly the applicability of the catalyst (normally, dichloromethane and toluene are preferred solvents for metathesis).

For the catalyst **G.II/SBA15**, it is possible that part of it was not attached covalently, but by chemisorption in analogy to **ZC/...** catalysts. Was this checked, e.g. on the base of amount of PCy<sub>3</sub> released by ligand exchange? Complexes **K1a** and **K1b** were prepared as a mixture. Using excess of Me<sub>3</sub>SiOK, it should be possible in analogy to analogous literature information to obtain only **K1a**. Was this tested and if not, why? The characterization of complexes **K1a** and **K1b** (by <sup>1</sup>H NMR only) is insufficient, no data are given in the Thesis. Regarding the activity of the **K2** catalyst, it should be expected and addressed that catalytic centres based on **K1b** should be significantly more active than those based on **K1a**.

In the second part, obtained heterogeneous catalysts were tested on a broad spectrum of metathesis substrates and display well the advantages of heterogeneous catalysts used. However, most experiments concentrated on easily proceeding metathetic reaction and (in analogy to many similar works including heterogeneous catalysts) I am missing standard tests of more demanding metatheses as allylmethyl- or dimethyl malonates forming tri- or tetrasubstituted double bond indicating the limits of activity and stability of the catalyst. In this sense, study of metathesis of citronellene is probably most valuable, special attention deserves observation that heterogeneous catalysts led to complete conversion while significantly more active homogeneous catalyst **ZC** ceased to be active at 90 % conversion. This is quite surprising and should be explained or at least commented. As possible explanation, slow releasing of protected catalytic sites into solution, limiting thus decomposition of catalyst, could be one explanation, higher stability of Ru=CH<sub>2</sub> catalytic intermediate on heterogeneous support the other. With the exception of metathesis experiments claimed to proceed with 100% selectivity, I am missing full description of results obtained from other metathesis experiments. I do not understand well what means 100% selectivity for metathesis of methyl oleate, when the mixture of three products was probably formed. The description of results based only on TON is here again too brief. In ADMET of 1,9-decadiene, the description of dimers/trimers formation is highly interesting, but I am missing again data about the composition of the mixtures formed. Attention deserve the tests of cross enyne metathesis of vinylcyclopentane with modified phenylacetylenes, which are significantly more descriptive than those with octyne and long alkenes, as its products could not be well identified. Here, if the structures could not be assigned, how the author knows they are isomers (p. 66)? Assignment of side-products of the former enyne metathesis based only on GC/MS is rather optimistic. Also, full data about the preparative experiment (yield of crude product, yield of product after CC) are missing. Of course, it is hard to analyze the structure of polymers, but nevertheless in Fig. 4.25 c) the structures are speculative. Moreover, first structure in Fig. 4.25 a) is probably incorrect (should be vinylbornene, cf. the paper of the author?)

The third part is devoted to metathesis of cardanol and was highly interesting and supports the quality of the Thesis. The reference to recent paper dealing with identical theme (Julis et al., Green Chem. **2014**, *16*, 2846) should be given. For all experiments, I am again

missing tables containing the results of analysis of the reaction products, the authors mostly speak only about TON, conversion and selectivity. The problem of isolation of compound **13** could be solved by appropriate protection of the free OH group (ester, not ether as stated was probably formed).

To evaluate the Thesis as a whole, it is very well written and contains only few typos. I appreciated broad range of chemistry the author successfully coped with and huge amount of experimental work included. The results of PhD. Thesis have been published in four papers in international peer-reviewed journals with high impact factors. The student unequivocally reached the targets posed in the Thesis.

Due to abovementioned reasons, I **recommend** to accept the PhD. Thesis of M. Tech. Tushar Raghunath Shinde as the basis for defending the **Ph.D.** title.

In Prague, 28.10.2014

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