



Budapest University of Technology and Economics  
Faculty of Chemical Technology and Biotechnology  
George Oláh Doctoral School

**Mounir Chamam**

**Preparation of bimetallic catalysts by  
CONTROLLED SURFACE REACTION:**

**Physical-chemical and catalytic characterisation of Ge-Rh and Sn-Rh**

Ph. D. Thesis

*Scientific Supervisor:* **Prof. Zoltán Paál**

*Consultant:* **Dr. Attila Wootsch**

Université de Poitiers, LACCO UMR 6503,  
Laboratoire de Catalyse par les Métaux

Hungarian Academy of Sciences Institute of Isotopes,  
Department of Catalysis and Tracer Studies



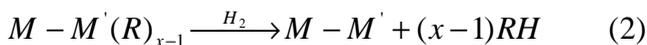
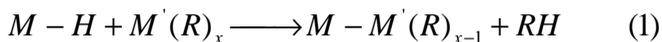
Budapest, 2007.

## 1. Introduction, aims

The rise of modern chemical can be attributed mainly to the development of catalytic processes. Development of heterogeneous catalysts and understanding of their behaviour is one of the most challenging tasks of researchers.

In practice, mono- and multi-metallic catalysts are used widely. Adding a second metal modifies substantially the activity, stability and selectivity. The preparation method used determines, however, the properties of catalysts [1]. Classical methods of preparation of multi-metallic catalysts (e.g.: co-precipitation, subsequent impregnation, etc...) can be reproduced and controlled with difficulty. In order to avoid this problem, preparation by the so-called “controlled surface reaction” (CSR) has been developed [1], during which the second metal can be deposited selectively on certain surface sites. In the early studies, the difference of the electrode potential of the two metals has been used to develop bimetallic systems [2].

Because of the limited possibilities of the redox method, in 1984, three research groups proposed independently [3-5] the preparation of bimetallic catalysts by grafting organometallic compounds. The essence of the method, that hydrogen preadsorbed on the surface of monometallic catalyst is reacted with an organometallic compound, and than the “primary surface complex” (PSC) formed subsequently is decomposed by hydrogen [3-5]:



*M*: first metal; *M'*: second metal; *R*: alkyl group.

The method has been considerably developed since the first publication, and also more and more reactions are described in which catalysts prepared by this methods behaves advantageously. Nevertheless, the selection of preparation conditions and the nature of metal-metal interactions (e.g. modification of the electronic structure or a geometric effect) is not clarified. Further, it is a question if the modifying metal is exclusively located on the surface, or “bulk” bimetallic particles can also be formed.

Modification of Pt by organometallic grafting has been examined most frequently. For instance, the cooperative research of the Institute of Isotopes (Budapest, Hungary) and the LACCO (Poitiers, France) could show the specific behaviour of Pt-Ge catalysts prepared by organometallic grafting, in 2002 [6]: in the case of addition of adequate amount ( $1/8$  monolayer =  $1/8$  Ge/Pt<sub>surface</sub>) of Ge, the selectivity of saturated C<sub>6</sub> isomers increased. This could be explained by the selective blocking of high coordination (i.e. low Miller-index) sites.

The use of Rh catalyst became more widespread recently (e.g.: in three way automotive catalysts, TWC) Modification of Rh by organometallic grafting method is seldom examined, and the studies are usually limited to selective hydrogenation reactions [7]. Monometallic Rh catalysts were studied in the transformation of methylcyclopentane in the Institute of Isotopes. It was found among others that the particle size of Rh influences the reaction mechanism [8]. On small particles (dispersion, D>70%) C<sub>1</sub>-C<sub>5</sub> fragments can be produced from any adsorbed surface intermediate, whereas in the case of big particles (D<70%), fragments are exclusively formed from the adsorbed 2-methyl-pentane intermediate.

The aim of my PhD thesis was the preparation of Rh-based bimetallic catalysts by organometallic grafting method and their characterization by physical and chemical methods.

My primary aims were to optimize the conditions of preparation, determine the structure of bimetallic catalysts prepared, and to examine the catalytic behaviour in methylcyclopentane test reaction. Methylcyclopentane was proved to be a good test molecule for Rh catalysts [8]. My further aim was to disclose the reaction mechanism and to describe the interaction of reactants and catalyst surface on bimetallic catalysts.

The doctoral work has been carried out in the Institute of Isotopes Hungarian Academy of Sciences) as well as in the LACCO research laboratory at the University of Poitiers. I performed the catalyst preparation as well as some physical characterization in France.

#### References:

- [1] V. Ponec, G.C. Bond, *Catalysis by Metals and Alloys*, *Stud. Surf. Sci. Catal.*, **95**, Elsevier, Amsterdam, 1995.
- [2] S. Szabó, F. Nagy, D. Móger, *Acta Chim. Acad. Sci. Hung.* **93**, 33 (1977).
- [3] J.L. Margitfalvi, M. Hegedűs, S. Góboldós, E. Tálas, P. Szedlacsek, S. Szabó, F. Nagy, Proc. 8<sup>th</sup> Int. Congress on Catalysis, Vol. 4, p. 903, Berlin, 1984.
- [4] C. Travers, J.P. Bournonville, G. Martino, in: Proc. 8<sup>th</sup> International Congress on Catalysis, Vol. 4, p. 891, Berlin, 1984.
- [5] R.G. Nuzzo, L.H. Dubois, N.E. Bowles, M.A. Trecocke, *J. Catal.* **85**, 267 (1984).
- [6] A. Wootsch, L. Pirault-Roy, J. Leverd, M. Guérin, Z. Paál, *J. Catal.* **208**, 490 (2002).
- [7] J.P. Candy, B. Didillon, E.L. Smith, T.B. Schay, J.M. Basset, *J. Mol. Catal.* **86**, 179 (1994).
- [8] D. Teschner, K. Matusek, Z. Paál, *J. Catal.* **192**, 335 (2000).

## 2. Catalyst modification, experimental methods

First, I prepared monometallic 1% Rh/Al<sub>2</sub>O<sub>3</sub> catalysts with different dispersion (D=20-80%) and then I modified them by grafting of organometallic complex (GeR<sub>4</sub> or SnR<sub>4</sub>, where R=butyl-group). The bimetallic catalysts were prepared in an apparatus developed for this purpose. Steps of the procedure:

- 1) Reduction of monometallic catalysts (T=673 K, 2 hours, H<sub>2</sub> stream), then cooling to room temperature, purging with argon and addition of heptane solvent with exclusion of air (under Ar) Hydrogen adsorption (T=295 K, 30 min bubbling with H<sub>2</sub>), subsequently another purging with Ar (30 min).
- 2) Grafting of the organometallic complex: calculated amount of organometallic complex in heptane solution (air-free, because previously purged with Ar) is added to the heptane suspension of monometallic catalysts during bubbling of the *grafting gas*. The temperature is T= 343 K for Ge and T=323 K for Sn.
- 3) In-situ washing of the catalyst with heptane (at temperature of grafting) than drying at T=393 K.
- 4) Hydrogenolysis of the alkyl radical: reduction of the bimetallic catalyst at 473 or 673 K with H<sub>2</sub> for 4 hours.

Several parameters were modified during preparation: type of second metal (Ge or Sn), amount of second metal (1/8-2 monolayer), type of *grafting gas* (Ar or H<sub>2</sub>), and temperature of hydrogenolysis (T=473 or 673 K). The effect of preparation method has been studied by blank preparation (same method without addition of the organometallic complex) and characterization of the catalysts received. During my PhD work I prepared and examined 42 different catalysts.

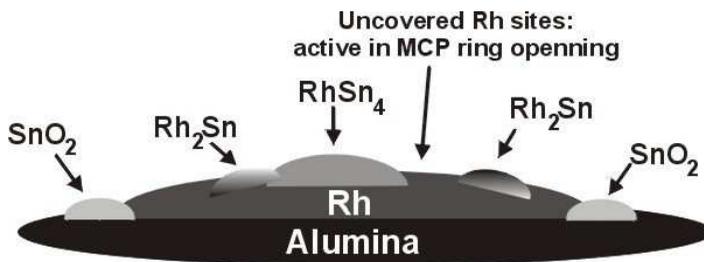
The structure of the catalysts was examined by the following physical methods: the size of active metal surface (metal dispersion) by measuring H<sub>2</sub> adsorption capacity, the size and shape of particles by transmission electron microscopy, the structure of the Rh surface by Fourier transformation infrared spectroscopy of CO adsorption (CO-FTIR). In the case of tin containing samples, the valence of tin was measured by <sup>119</sup>Sn-Mössbauer spectroscopy.

The catalytic properties of the samples prepared were examined in transformation of methylcyclopentane (MCP, 1.3 kPa) in the presence of hydrogen, at different hydrogen pressures (16-64 kPa) and temperatures (T=478-513 K). Product mixture was analyzed by on-line gas chromatography.

### **3. New results, thesis points**

1. *By the organometallic grafting method applied in the thesis, Ge and Sn can be deposited selectively on the surface of Rh of Rh/Al<sub>2</sub>O<sub>3</sub>. I proved that deposition of the second metal on the alumina surface is negligible. In the case of Sn chemical interaction of tin and alumina could not be detected even after high-temperature treatments.*
2. *The preparation procedure without addition of the second metal (blank preparation) caused increasing Rh particle size due to sintering. Sintering was hindered in the presence of the second metal. Sintering could be further reduced if H<sub>2</sub> was used as grafting gas instead of Ar.*
3. *The efficiency of grafting procedure decreases with increasing amount of the second metal. Actually, more than 1 monolayer of the second metal cannot be deposited on the Rh surface by organometallic grafting in the presence of Ar. The grafting procedure is a reaction between the pre-adsorbed hydrogen and the organometallic precursor.*

4. *By the method applied, the second metal is not always exclusively located on Rh surface, but, as opposed to the literature, under certain conditions forms “bulk” bimetallic compounds are produced. Accordingly, I classified the bimetallic catalysts prepared by organometallic grafting into two groups: “surface bimetallic catalysts” and “bulk bimetallic catalysts”. In the case of addition of low amount of Ge or Sn (<1/2 monolayer) in the presence of Ar, “surface bimetallic catalysts” were obtained. In this case, the decrease in the dispersion value measured by H<sub>2</sub> adsorption was proportional to the amount of Ge or Sn added, which proves that the second metal is essentially situated on the surface of Rh. Increasing amount of the second metal resulted in “bulk bimetallic catalysts” In the case of Sn-Rh catalysts, the formation of inter-metallic compounds could be identified by Mössbauer spectroscopy (point 5.), while in the case of Rh-Ge catalysts “bulk” bimetallic phases could only be suggested in the case of a catalysts containing large particles (D=20 %), based on micro-diffraction analysis. The formation of Rh<sub>5</sub>Ge<sub>3</sub> seems likely. The formation of “bulk bimetallic catalysts” could be revealed by the shift in CO-FTIR bands (wavenumber decrease), and by studying the catalytic activity, too.*
  
5. *In the case of Rh-Sn catalysts three different RhSn phases is formed after reduction: SnO<sub>2</sub>, “Sn-poor” (most probably Rh<sub>2</sub>Sn alloy) and “Sn-rich” (most probably RhSn<sub>4</sub> alloy). The role of SnO<sub>2</sub> is, most probably, stabilization of small Rh (bimetallic) particles. Among the Rh-Sn phases, RhSn<sub>4</sub>, and Rh<sub>2</sub>Sn are not active in the ring opening of MCP, but Rh<sub>2</sub>Sn is active in hydrogen adsorption. Inactive Rh-Sn phases located on certain surface sites (for example low Miller-index – see point 6) influence the catalytic behaviour (Figure).*



6. *By the method applied, addition of small amount ( $\leq 1/4$  monolayer) of both second metals in the presence of Ar on parent catalysts with high dispersion ( $D > 60\%$ ) resulted in their selective deposition on high coordination (low Miller-index) planes. The selective deposition on these planes is proved by both the decreasing intensity of the CO band adsorbed in bridged form (CO-FTIR) and the catalytic measurements. On such catalysts, the addition of second metal increased the catalytic activity in the selective ring opening reaction of MCP and decreased the selectivity towards fragmentation products ( $< C_6$ ). The phenomenon was explained by the hindrance of strong adsorption of MCP on planes. In the case of both second metals, addition of nominally  $1/4$  monolayer (for Ge actually 1150 ppm, for Sn actually 2200 ppm) is optimal.*
7. *Addition of large amount ( $> 1$  monolayer) of the second metal in the presence of Ar on parent catalysts with high dispersion ( $D > 60\%$ ) decreased the catalytic activity. Further, if the amount of tin added is high (in our case 2 monolayers, 1,72%), the catalyst was completely inactive in the cleavage of the C-C bond. The results can be explained by penetration of second metal and formation of alloy phases (see points 4 and 5). Adding large amounts of Ge did not result in such pronounced activity decrease, thus the bulk-like Rh-Ge phases (e.g. Rh<sub>5</sub>Ge<sub>3</sub>) are catalytically not inactive.*

8. *If the particle size of the parent catalyst is large, i.e. the dispersion is low, selective deposition of the second metal could not be detected (neither by CO-FTIR, nor by catalytic reaction).*
9. *At low temperature the second metal is preferentially located on the Rh surface, while at higher temperature it is located in the inside of the Rh particles, as revealed from studying the effect of the temperature (473 or 673 K) and the gas atmosphere (Ar or H<sub>2</sub>) of the grafting procedure in the case of the preparation of Rh-Ge catalysts. In the latter case, CO-FTIR and catalytic studies indicated strong Rh-Ge “bulk” interaction, which does not block surface Rh atoms, but increases their activity. If H<sub>2</sub> was applied instead of Ar as grafting atmosphere, the probability of the formation of three dimensional (multi-layer) Ge species increased, which can stabilize the size of Rh particles (point 2), but decrease the catalytic activity, due to their spatial effect.*

In summary, our results confirm the co-existence of electronic and geometric effects, i.e., the surface modifying geometric effects and metal-metal chemical interactions cannot be separated.

#### **4. Possible application of the results**

I developed a method for the modification of Rh/Al<sub>2</sub>O<sub>3</sub> catalysts by using tin- and germanium-alkyl compounds. I succeeded in disclosing the effect of parameters applied during catalyst preparation and also their effect of the catalytic behaviour in the methylcyclopentane ring opening reaction.

I found that high coordination sites (low Miller index) can be blocked selectively if the dispersion of the monometallic Rh catalyst is high ( $D > 60\%$ ) and the amount of the second metal added is low ( $\leq 1/4$  monolayer). By this method, catalysts containing mainly low coordination (high Miller-index) metal sites, i.e. edges and corners, can be prepared. These catalysts can catalyse selectively not only the examined ring opening of the C<sub>5</sub> ring, but also different – industrially important – reactions, e.g. selective hydrogenation of unsaturated aldehydes to allyl-alcohols, of nitriles to primary amines, etc.... Selective blockage of metal planes can prevent strong adsorption of deeply dehydrogenated intermediates from hydrocarbons, which are precursors of carbonaceous deposits, thus by our method the resistance of catalysts against deactivation can be increased. Accordingly, some undesired by-products, like aromatics and fragments are also formed via unsaturated intermediates, mainly on high coordination sites, the blocking of which can suppress their formation.

The experiences obtained in catalyst preparation and characterization would allow us to prepare catalyst with two metals different from those used in our study (e.g. two active ones) or multi-metallic catalysts and to examine them in transformation of hydrocarbons. For example, it is possible to prepare Pt-Ir catalyst by controlled method, which is widely used in refinery, or to modify Rh with e.g. Au.

## 5. References

### Publications

1. M. Chamam, A. Wootsch, L. Pirault-Roy, I. Boghian, Z. Paál: Methylcyclopentane transformation on Ge-Rh bimetallic catalysts prepared by organometallic grafting, *Catal. Comm.* 8, 686–692 (2007).
2. D. Teschner, E. Vass, M. Hävecker, S. Zefeiratos, P. Schnörch, H. Sauer, A. Knop-Gericke, R. Schlögl, M. Chamam, A. Wootsch, et al. Alkyne Hydrogenation over Pd Catalysts: A New Paradigm. *J. Catal.* 242, 26-37 (2006).
3. M. Chamam, A. Wootsch, K. Lázár, Z. Paál, C. Bourry, I. Boghian, L. Pirault-Roy, Structural properties and catalytic tests in methylcyclopentane ring opening reaction of Rh-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by organometallic grafting, in “*Sampling Catalysis Research in the Pannonian Region*” (István Pálinkó, Ed.), Hungarian Zeolite Association, 2006, Szeged, ISBN: 963 06 0138 9, p. 310-315.
4. M. Chamam, K. Lázár, L. Pirault-Roy, I. Boghian, Z. Paál, A. Wootsch, Characterization and catalytic properties of Rh-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by organometallic grafting, *Appl. Catal. A*, 332, 27-36 (2007).

### Oral presentations:

1. **A. Wootsch**, N. Győrffy, M. Chamam, L. Pirault-Roy, S. Szabó, I. Bakos, Z. Paál, Hydrocarbon transformation as a tool for the disclosure of the surface state on metal catalysts, *Proceeding of the 7<sup>th</sup> Pannonian International Symposium on Catalysis*, Srní, Czech Republic, 12-16 September 2004.
2. **M. Chamam**, Ródium katalizátorok készítése fémorganikus komplex felhasználásával. Budapest, *BME doktori konferencia*, 24 November 2004.
3. **M. Chamam**, M., Rh-Sn fizikai tulajdonságai elemzése, H<sub>2</sub>-adszorpció, TEM, CO-FTIR és <sup>119</sup>Sn-Mössbauer-spektroszkópia ill. kémiai tulajdonságai meghatározása MCP átalakulásában. *BME doktori konferencia*, 7. February 2005.

4. **M. Chamam**, Preparation of bimetallic Rhodium catalysts by using organometallic complexes. Université de Poitiers, 5 May 2005.
5. **M. Chamam**, Etude comparative des performances de catalyseurs Rh-Ge et Rh-Sn préparés par voie organométallique pour la réaction d'ouverture du cycle méthylcyclopentane, *Master Recherche Deuxième Année*, Poitiers, 21 June 2005.
6. **M. Chamam**, Ródium katalizátorok készítése fémorganikus komplex felhasználásával, *Katalízis Munkabizottság*, Szeged, 26 October 2006.
7. **M. Chamam**, Ródium katalizátorok készítése fémorganikus komplexek felhasználásával, Rh-Ge és Rh-Sn katalizátorok összehasonlítása MCP átalakulásában, *Intézeti beszámoló*, 4. June 2007.
8. **D. Teschner**, R. Schlögl, S. D. Jackson, M. Chamam, A. Wootsch, et al., Pd-C surface phase as an essential parameter of selective alkyne hydrogenation, *SYMPOSIUM ON APPLIED CATALYSIS*, Glasgow, UK, 18-20 July 2007.
9. **D. Teschner**, E. M. Vass, M. Hävecker, S. Zafeiratos, P. Schnörch, A. Knop-Gericke, J. Borsodi, M. Chamam, A. Wootsch, R. Schlögl, Pd-C surface phase as an essential parameter of selective alkyne hydrogenation: a high-pressure XPS study, *8th EUROPACAT*, Turku, Finland, 26-31 August 2007.

Posters:

1. **M. Chamam**, A. Wootsch, K. Lázár, C. Bourry, I. Boghian, L. Pirault-Roy, Z. Paál, Characterization of tailor-made Rh-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts by <sup>119</sup>Sn-Mössbauer spectroscopy and methylcyclopentane ring opening reaction, *7<sup>th</sup> EUROPACAT*, 28 August – 1 September 2005. Sofia, Bulgaria
2. **M. Chamam**, A. Wootsch, K. Lázár, Z. Paál, C. Bourry, I. Boghian, L. Pirault-Roy, Structural properties and catalytic tests in methylcyclopentane ring opening reaction of Rh-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by organometallic grafting, *8<sup>th</sup> Pannonian Symposium on Heterogeneous Catalysis*, 4-7. July 2006. Szeged.

3. **M. Chamam**, A. Wootsch, K. Lázár, L. Pirault-Roy, Z. Paál, Methylcyclopentane transformation on Rh-M (M = Ge, Sn) catalysts prepared by organometallic grafting, *1<sup>st</sup> European Chemistry Congress*, 27-31. August 2006, Budapest.