

## Comparison of different preparation methods of PtIr, PtIrSn and PtIrGe catalysts for hydrocarbon transformation.

Laurence Pirault-Roy<sup>1\*</sup>, Christophe Poupin<sup>1,2</sup>, Camille La Fontaine<sup>1</sup>, Mounir Chaman<sup>2</sup>, Zoltan Paál<sup>2</sup> and Attila Wootsch<sup>2</sup>

<sup>1</sup>LACCO, UMR 6503 CNRS-Univ. de Poitiers, 40 Av. R. Pineau, 86022 Poitiers (France)

<sup>2</sup>Institute of Isotopes, Hung. Acad. Sci., Budapest P. O. Box 77, 1525, (Hungary)

\*laurence.pirault@univ-poitiers.fr

### Introduction

Heterogeneous catalysts are employed in 80 % of industrial catalytic processes with multimetallic formulations which enhance the performances of catalysts [1]. Nowadays, an increased attention has been paid to preparation methods using “Controlled Surface Reactions (CSR)” [2, 3]. These catalysts are rather active and selective in various reactions, for example in hydrocarbon transformation [3, 4]; promisingly result in cleaner products and safer processes producing less wastes. The full characterization of such catalysts requires a combination of physico-chemical methods with catalytic tests. Our aim was to investigate bimetallic Pt-Ir catalysts prepared by two different methods, namely classical successive impregnation and by organometallic grafting [2, 4] as well as to study the effect of a third metal (Ge or Sn) added in both cases by organometallic grafting method.

### Materials and Methods

A 1 wt.-% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (**Pt**) (BET<sub>Alumina</sub>= 100 m<sup>2</sup> g<sup>-1</sup>, D=50 %) was modified (i) by adding 0.2 % Ir by a second impregnation of Ir(acetyl-acetonate)<sub>3</sub> in toluene (**PtIr-IS**) and (ii) by organometallic grafting of Ir(acetyl-acetonate)<sub>3</sub> nominally corresponding to 1/2 monolayer (2460 ppm) of Ir in toluene (**PtIr-GS**). These catalysts were further modified by adding Ge and Sn in amounts corresponding nominally to 1/4 monolayer in the case of **PtIr-IS**, noted **PtIrGe-IS** and **PtIrSn-IS**, as well as to 1/5 and 1/8 monolayers, respectively, for **PtIr-GS** resulting in **PtIrGe-GS** and **PtIrSn-GS**. A monometallic 0.25 wt.-% Ir/Al<sub>2</sub>O<sub>3</sub> sample (**Ir**) was tested for comparison purposes. The catalysts were characterized by TEM and EDX, hydrogen chemisorption and evaluated in transformation of methylcyclopentane (MCP) in hydrogen excess at T=543 to 603 K.

### Results and Discussion

Both Pt and Ir are active in hydrogenative ring opening of methylcyclopentane [5] producing ring opening products (ROP): hexane, 2-methyl-pentane and 3-methyl-pentane. Beside ROPs, Ir also forms considerable amount of C<sub>1</sub>-C<sub>5</sub> fragments, at a much lower conversion level (Table 1). Addition of 0.2 wt.-% Ir to **Pt** catalyst resulted in slight activity decrease parallel to an increase in the fragmentation selectivity and decrease of ROP activity. Therefore, **PtIr-IS** catalyst shows a combined behavior of **Pt** and **Ir** monometallic samples. On the other hand, when Ir was added by organometallic method, the activity is twice fold as compared to **Pt**, while fragment selectivity increased only slightly. Iridium located on the surface of Pt can fragment carbonaceous deposits and thus increase the ROP activity of Pt sites. Consequently, in the case of **PtIr-IS**, separate Pt and Ir particles on the alumina surface can be suggested while in the case of **PtIr-GS**, Ir is exclusively attached to Pt, as ensured by

the organometallic grafting method, as described previously [4] (Table 1). Addition of Ge or Sn to the catalyst prepared by organometallic grafting resulted in activity decrease and very small effect in the selectivity pattern (cf. **PtIr-GS**, **PtIrGe-GS**, **PtIrSn-GS**). It confirms that in the case of strong Pt-Ir interaction the third metal is located on the surface of the bimetallic particle and thus blocks both metals to the same extent. On the other hand, when the third metal was added to **PtIr-IS**, Ge- and Sn-based samples resulted in different types of modification. The presence of Ge enhanced the activity of Ir sites, i.e. increased fragmentation activity, while Sn – even slightly loaded – increased activity of Pt function (Table 1). Further, the effect of different pretreatments (both oxidative and reductive) and the catalyst structures (TEM) were studied on all samples, and they confirmed the model indicated above.

**Table 1.** Selectivity of different products (alkanes not shown) at T=603 K, p(MCP):p(H<sub>2</sub>)=1.3:64 kPa

Catalysts	Metal amount /wt.-%	Metallic accessibility	Conversion /%	Selectivities /%			
				ROP	Fragments	Benzene	Others
Pt	1	50	40	96	4	0	0
Ir	0.2	50	14	27	64	6	3
PtIr-IS	Pt 1 - Ir 0.2	40	10	63	29	7	1
PtIrGe-IS	Pt 1 - Ir 0.2 - Ge 0.2	7	24	42	43	14	1
PtIrSn-IS	Pt 1 - Ir 0.2 - Sn 0.2	11	26	68	23	8	1
PtIr-GS	Pt 1 - Ir 0.2	10	82	80	15	5	0
PtIrGe-GS	Pt 1 - Ir 0.2 - Ge 0.2	10	53	73	19	8	0
PtIrSn-GS	Pt 1 - Ir 0.2 - Sn 0.13	16	57	79	14	6	1

Addition of Ir to Pt catalysts by successive impregnations or by organometallic grafting results in catalysts displaying different structures: separate Pt and Ir sites in the first case and bimetallic PtIr sites in the second case. This later catalyst shows very promising behavior with high selectivity for MCP ring-opening reactions even at high conversion.

### References

1. Ponec, V., and Bond, G.C., “Catalysis by Metals and Alloys”, *Stud. Surf. Sci. Catal.*, Elsevier, 1995.
2. Margitfalvi, J. L., Borbáth, I., Tfirst, E., and Tompos, A. *Catal. Today* 43, 29 (1998).
3. Coq, B., and Figuéras, F., *Coord. Chem. Rev.* 178, 1753 (1998)
4. Wootsch, A., Paál, Z., Györfy, N., Ello, S., Boghian, I., Leverd, J., and Pirault-Roy, L., *J. Catal.* 238, 67 (2006).
5. Paál, Z., and Tétényi, P. *Nature*, 267, 234 (1977).