

# Bimetallic Rh-Ge and Pt-Ge catalysts supported on TiO<sub>2</sub> for citral hydrogenation

## I. Preparation and characterization of the catalysts

T. Ekou, A. Vicente, G. Lafaye\*, C. Especel, P. Marecot

*Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503 Université de Poitiers,  
40 Avenue du Recteur Pineau, F-86022 Poitiers Cedex, France*

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### Abstract

Bimetallic TiO<sub>2</sub>-supported Rh-Ge and Pt-Ge catalysts were prepared by surface redox reaction between hydrogen activated on a parent monometallic rhodium or platinum catalyst and a germanium salt dissolved in water (catalytic reduction method). They were characterized by elemental analysis, transmission electronic microscopy (TEM), temperature-programmed reduction (TPR) and by their activity for the gas phase dehydrogenation of cyclohexane.

Elemental analysis of the bimetallic catalysts showed that germanium can effectively be deposited by the catalytic reduction method on titania-supported Rh and Pt catalysts. Moreover, the different characterization methods (TEM, TPR and cyclohexane dehydrogenation) proved that germanium is in great interaction with rhodium and platinum. Nevertheless, some germanium deposition occurred also separately on the titania support.

TEM and cyclohexane dehydrogenation results revealed that both rhodium and platinum particles were stable on titania support under the conditions of bimetallic catalyst preparation contrary to previous results obtained with silica or alumina supports. Effectively, no sintering has been observed when they were immersed in an aqueous solution under hydrogen bubbling (catalytic reduction protocol). Their catalytic performances for the cyclohexane dehydrogenation reaction indicate that all the catalysts reduced at high temperature (500 °C versus 300 °C) developed the strong metal–support interaction (SMSI) effect, which implied the formation of TiO<sub>(2-x)</sub> species. Whatever the nature of the parent metal (Rh and Pt), this effect was totally destroyed by air exposure of the samples at ambient temperature whereas one part of the TiO<sub>(2-x)</sub> moieties remained after immersion of the catalysts in an aqueous medium.

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### 1. Introduction

The preparation of unsaturated alcohols by selective hydrogenation of the corresponding  $\alpha,\beta$ -unsaturated aldehydes has a great industrial importance and constitutes a challenging task, since the hydrogenation of the C=C bond is thermodynamically favoured over the hydrogenation of the carbonyl group. Monometallic catalysts usually produce the saturated aldehyde, and it is necessary to modify them either by support effects [1–9] or by addition of a second metal [10–18] to

improve the selectivity towards the hydrogenation of the carbonyl bond. Recently, Reyes et al. [19,20] as well as Silva et al. [21,22] have combined these two effects, that is the addition of a second metal and the use of a reducible support, in order to enhance the reactivity towards hydrogenation of unsaturated alcohols.

We have previously reported our investigations concerning the liquid phase hydrogenation of citral over bimetallic Rh-Ge/silica and Rh-Ge/alumina catalysts prepared by a surface redox reaction, namely the catalytic reduction method [16,17]. We concluded that the main effect of germanium addition to rhodium catalysts was to improve the reaction selectivity toward unsaturated alcohols (nerol and geraniol), this effect being more obvious on alumina-supported catalysts. The

\* Corresponding author.

E-mail address: [gwendoline.lafaye@univ-poitiers.fr](mailto:gwendoline.lafaye@univ-poitiers.fr) (G. Lafaye).

present contribution is the continuation of the study on Rh-Ge systems prepared by catalytic reduction with a comparison to Pt-Ge systems prepared by the same technique. The important aspect is the influence of a reducible support, TiO<sub>2</sub>, on the surface and catalytic properties of these such prepared catalysts.

This paper deals with the preparation of the titania-supported bimetallic rhodium-germanium and platinum-germanium catalysts by the so-called catalytic reduction method and the effect of their reduction temperature. In this way, the different catalysts were characterized by chemical analysis and transmission electron microscopy (TEM). Temperature-programmed reduction (TPR) under hydrogen was also used to follow the reduction of the catalyst metallic phase. Their catalytic performances were measured for a model reaction, that is cyclohexane dehydrogenation (structure insensitive reaction) to evaluate the interaction between germanium and the active phase.

The hydrogenating properties of these catalysts for the selective hydrogenation of citral will be discussed in Part II of this paper.

## 2. Experimental

### 2.1. Catalyst preparation

The TiO<sub>2</sub> support (Degussa P25, surface area = 50 m<sup>2</sup> g<sup>-1</sup>) was calcined in flowing air for 4 h at 500 °C. Prior to use, it was ground and then sieved to retain particles with sizes between 0.04 and 0.10 mm. Monometallic 1.0 wt.% Rh/TiO<sub>2</sub> and 1.0 wt.% Pt/TiO<sub>2</sub> catalysts were prepared by an ion exchange method using RhCl<sub>3</sub> and H<sub>2</sub>PtCl<sub>6</sub> as described elsewhere [16,23,24]. Both catalysts were dried at 110 °C overnight, followed by calcination for 4 h in flowing air at 300 °C for Rh/TiO<sub>2</sub> and at 400 °C for Pt/TiO<sub>2</sub>. Finally, they were reduced at 300 °C or 500 °C in flowing pure hydrogen for 4 h. Catalysts activated following the above temperatures are denoted in this manuscript as Rh(300), Pt(300) and Rh(500), Pt(500), respectively.

Bimetallic catalysts were prepared by surface redox reaction between hydrogen activated on metal parent (Rh or Pt) particles and the germanium salt (GeCl<sub>4</sub>) dissolved in water (“catalytic reduction” method). A known amount of the prereduced parent catalyst was introduced into a reactor [25] under nitrogen and was activated at the same temperature than its first reduction, i.e., 300 °C or 500 °C, for 1 h under hydrogen. Then the solution of the germanium precursor, previously degassed under hydrogen flow, was introduced onto the catalyst at room temperature. After 1 h reaction time under hydrogen bubbling, the solution was filtered out and the catalyst was dried overnight at 100 °C under hydrogen flow. Finally, the bimetallic catalyst was reduced under hydrogen flow either at 300 °C or at 500 °C for 1 h (2 °C min<sup>-1</sup> heating rate). Blank platinum and rhodium catalysts were prepared following the same procedure but the germanium salt was replaced by a hydrochloric solution of the same pH, that is pH = 1.

The elemental analysis of the platinum, rhodium, germanium and chlorine contents was determined by the atomic

Table 1  
Characteristics of monometallic and bimetallic catalysts

Catalyst/TiO <sub>2</sub>	T <sub>reduction</sub> (°C)	Ge (wt.%)	Cl (wt.%)	Average particle size <sup>a</sup> (nm)
Rh(300) parent	300	0.0	0.5	2.3
Rh(300) blank	300	0.0	0.5	2.4
Rh(300)-0.5Ge	300	0.5	0.5	–
Rh(300)-1.0Ge	300	1.0	0.5	–
Rh(300)-1.4Ge	300	1.4	0.5	–
Rh(300)-1.6Ge	300	1.6	0.5	2.8
Rh(300)-1.8Ge	300	1.8	0.5	–
Rh(500) parent	500	0.0	≤0.2	2.3
Rh(500) blank	500	0.0	≤0.2	2.4
Rh(500)-0.4Ge	500	0.4	≤0.2	–
Rh(500)-0.8Ge	500	0.8	≤0.2	–
Rh(500)-1.3Ge	500	1.3	≤0.2	2.9
Pt(300) parent	300	0.0	0.5	1.9
Pt(300) blank	300	0.0	0.5	1.8
Pt(300)-0.2Ge	300	0.2	0.5	–
Pt(300)-0.3Ge	300	0.3	0.5	–
Pt(300)-0.4Ge	300	0.4	0.5	1.9
Pt(300)-0.5Ge	300	0.5	0.5	–
Pt(300)-0.6Ge	300	0.6	0.5	–
Pt(300)-1.1Ge	300	1.1	0.5	–
Pt(500) parent	500	0.0	≤0.2	2.0
Pt(500) blank	500	0.0	≤0.2	2.1
Pt(500)-0.2Ge	500	0.2	≤0.2	–
Pt(500)-0.3Ge	500	0.3	≤0.2	–
Pt(500)-0.4Ge	500	0.4	≤0.2	2.3
Pt(500)-0.5Ge	500	0.5	≤0.2	–
Pt(500)-0.6Ge	500	0.6	≤0.2	–
Pt(500)-1.0Ge	500	1.0	≤0.2	–

<sup>a</sup> Deduced from TEM analysis.

absorption method. All the prepared catalysts are listed in Table 1 with their code name and metallic composition.

### 2.2. Transmission electron microscopy measurements

Transmission electron microscopy studies were performed on a Philips CM 120 instrument operating at 120 kV. All the samples were embedded in a polymeric resin (spurr) and cut into a section as small as 40 nm with an ultramicrotome equipped with a diamond knife. Cuts were then deposited on an Al grid previously covered with a thin layer of carbon. Average particle sizes were determined by measuring at least 100 particles for each sample analyzed, from at least 5 different micrographs.

### 2.3. Temperature-programmed reduction experiments

The TPR experiments were done with a 1.0 vol.% H<sub>2</sub>/Ar gas mixture. The temperature range was 25–500 °C with a ramp of 5 °C min<sup>-1</sup> and then maintained at 500 °C for 1 h. The hydrogen uptake was monitored by a thermal conductivity detector.

#### 2.3.1. Monometallic catalysts

Prior to the TPR, the monometallic rhodium and platinum catalysts were first pretreated in situ under oxygen for 30 min at

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