

Selective hydrogenation of citral on Rh-Ge/TiO₂ bimetallic catalysts: influence of the precursor salts

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Introduction

The preparation of unsaturated alcohols by selective hydrogenation of the corresponding α , β -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. Supported noble metal catalysts usually produce the saturated aldehyde, and it is necessary to modify them either by support effects or by addition of a second metal to improve the selectivity towards the hydrogenation of the carbonyl bond. We have previously reported our investigations concerning the liquid phase hydrogenation of citral (figure 1) over bimetallic Rh-Ge/silica, Rh-Ge/alumina and Rh-Ge/titania catalysts prepared by a surface redox reaction, namely the catalytic reduction method [1-4]. We concluded that the main effect of germanium addition to rhodium catalysts was to improve the reaction selectivity toward unsaturated alcohols (nerol and geraniol). The present contribution is the continuation of the study on Rh-Ge/TiO₂ catalysts prepared by catalytic reduction with the aim of determining the influence of the nature of the precursor salts for both Rh and Ge metals.

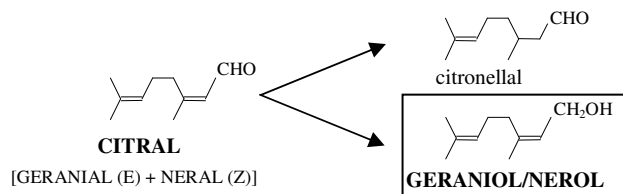


Figure 1. Simplified reaction scheme for citral hydrogenation.

Materials and Methods

Monometallic 1.0wt%Rh/TiO₂ catalysts were prepared by wet impregnation of the support using an aqueous solution of either RhCl₃ or Rh(NO₃)₃. Bimetallic Rh-Ge/TiO₂ catalysts were prepared by catalytic reduction, i.e. by surface redox reaction between hydrogen activated on rhodium particles and the germanium salt dissolved in water (figure 2). Two different germanium salts were used: GeCl₄ and GeO₂. Blank rhodium

catalysts were prepared following the same procedure but without the germanium salt introduced in solution.

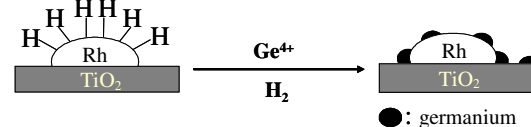
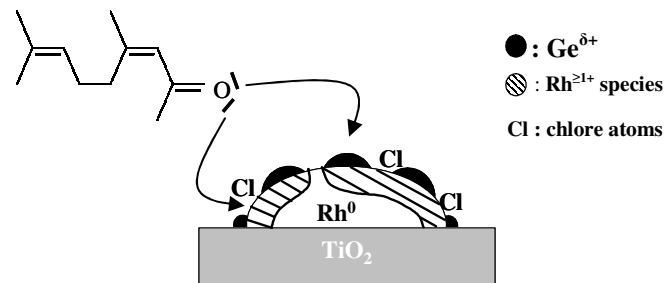


Figure 2. Schema of the preparation of Rh-Ge/TiO₂ by catalytic reduction.

The monometallic and resulting bimetallic catalysts were reduced at 300°C (heating rate = 2°C.min⁻¹) in flowing pure hydrogen for 1 hour. The catalysts were tested for the selective hydrogenation of citral at 70°C and at constant pressure of 7 MPa. They were characterized by transmission electron microscopy (TEM), electron diffraction spectroscopy (EDS) and by FTIR of adsorbed CO.

Results and Discussion

Among the Rh-Ge materials, the catalysts prepared from chloride precursors showed the highest activity and selectivity to the unsaturated alcohols (80%). In the literature, it is commonly admitted for selective hydrogenation of α , β - unsaturated aldehydes that the role of the modifier on the metallic surface and/or in its close vicinity is to act as Lewis acid sites (i.e. in a partially oxidized state) to activate the carbonyl group by interaction with a lone electron pair of oxygen. The different characterizations of Rh-Ge systems have provided further insight into this structure-selectivity relationship. Surprisingly, it appeared that the selectivity toward the unsaturated alcohols would be also linked to the presence of Rh^{≥1+} species. This study allowed us to propose the following schema which represents the active sites for C=O hydrogenation:



References

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