

Pd-Promoted Selective Gas Phase Hydrogenation of Butadiene over Alumina Supported Au Catalysts

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Introduction

Short alkenes, like propene or butenes can be used as raw materials for polymer synthesis. They are often contaminated by diolefins and alkynes, and the polymerization catalysts require a concentration lower than 10 ppm in diolefins and alkynes. Purification by catalysis is the most appropriate way to reach this goal. These catalysts must selectively hydrogenate them without hydrogenating olefins. Pd-based catalysts modified by a second metal, such as Ag, are currently used to remove these impurities. However, the catalytic performances are limited by the tendency of palladium to over-hydrogenate the desired olefins into alkanes.

Gold catalysts have recently shown the ability to selectively hydrogenate alkydienes or alkynes into alkenes [1-6]. However they are poorly active. The goal of this study was to investigate the catalytic behavior of gold-palladium catalysts with an at./at. Au/Pd ratio $\gg 1$ in the reaction of selective hydrogenation of butadiene in an excess of propene.

Materials and Methods

Bimetallic Pd-Au (1 wt% Au, Au/Pd $\gg 1$) catalysts were prepared by co-deposition-precipitation with urea (DP) (Au/Pd = 8, 20, 90 and >90 (< 50 ppm Pd)) and co-impregnation in excess solvent (IMP) (Au/Pd ~ 10 and 20), using Al_2O_3 as support. The samples were activated *in situ* in H_2 at 300 °C or 500 °C. The catalysts were characterized by TPR, H_2 chemisorption, TEM and DRIFTS combined with CO adsorption. The performances of these catalysts were tested in selective hydrogenation under the following reaction conditions: butadiene (0.3%), propene (30%), hydrogen (20%) in He at atmospheric pressure from RT to 300°C with a ramp of 1°C/min, in condition close to the equilibrium.

Results and Discussion

Figure 1 reports the curves of conversion of butadiene and production of alkanes (propane and butane) over monometallic Au-DP (1wt % Au) and Au/Pd-DP (1wt % Au, Au/Pd = 8, 20, 90 and >90 (50 ppm Pd)). It shows that the catalysts become more active as the Pd content increases, but less selective. However, for the Au/Pd ratio of 20, the 100% conversion of butadiene to butenes with 100% selectivity is obtained with a shift of 90 °C to lower temperature compared to $\text{Au}/\text{Al}_2\text{O}_3$.

DRIFTS measurements using CO as a probe molecule showed that in the case of the Au/Pd DP samples, the contribution of multi-bonded CO on Pd was reduced compared to Pd catalysts. A geometric effect, due to the formation of bimetallic Pd-Au nanoparticles and surface Au-Pd interaction (which is also attested by results of TPR and H_2 chemisorption), and resulting in a decrease in the size and/or the number of Pd ensembles required for multiple bonding can account for this response.

The catalytic behavior depends on the preparation method. Co-impregnation in excess solvent does not lead to performances as satisfactory as those obtained with DP

samples: (i) the activity is lower, either because the metal particles are larger, or because the samples contain large amount of chlorine; (ii) the selectivity is also lower, which can be related to the less bimetallic character of the particles, as attested by DRIFTS analyses. The temperature of activation is also an important parameter. *In situ* reduction at 500 °C leads to more active catalysts than reduction at 300 °C, which indicates that high temperature is required to obtain stable structure of bimetallic particles.

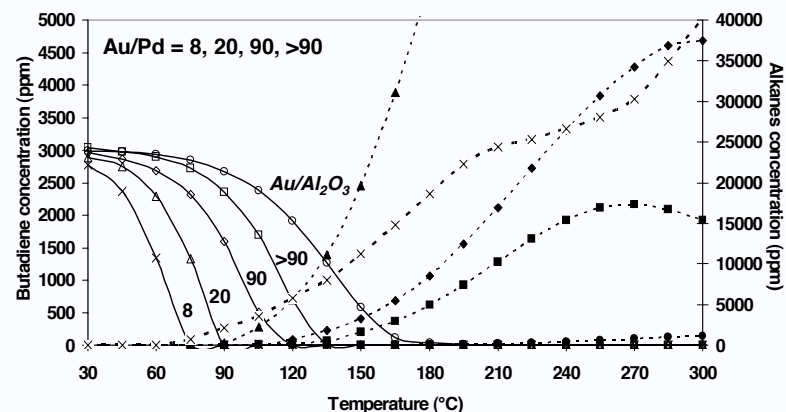


Figure 1. Conversion of butadiene (open symbols) and alkanes production (full symbols) over Au-DP (1wt % Au) and Au/Pd-DP (1wt % Au, Au/Pd = 8, 20, 90 and >90 (< 50 ppm Pd)).

In summary, when very low amount of Pd is added to gold catalysts, the high selectivity of gold catalysts can be maintained while the activity is improved. This makes this type of catalysts very promising, especially as catalysts for the ultimate stage of purification of alkenes.

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