Gold based catalysts performances in selective hydrogenation of butadiene in an excess of propene.

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Introduction

Short alkenes, like propene or butene are of major importance in petrochemical processes, and are used as raw materials for polymer synthesis. These olefinic feedstocks are often contaminated by diolefins and alkyenes in various amounts, and the polymerization catalysts have an extremely low tolerance towards these compounds, which imposes a concentration lower than 10 ppm in di-olefins and alkyenes. Classical methods of separation, such as distillation, are not able to separate totally these compounds, and purification by catalysis is the most appropriate way to reach this goal.

These catalysts must selectively hydrogenate diolefins and/or alkyenes without hydrogenating the olefin. Palladium-base catalysts are currently used to remove these undesirable impurities. These Pd catalysts are the subject of numerous researches, publications and patents. Even though improvements have been performed, e.g. by addition of a second metal, such as Ag, 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 alkenienes or alkyenes into alkenes [1-4]. The goal of this study was to investigate the catalytic behavior of several gold catalysts in the reaction of selective hydrogenation of butadiene in an excess of propene.

Materials and Methods

Gold catalysts (1 wt%) supported on titania and alumina were prepared by deposition-precipitation with urea [5]. They were characterized after activation by TEM. The selective hydrogenation ability was tested 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, i.e., at different temperatures in condition close to the equilibrium.

Results and Discussion

TEM analyses showed that the smallest gold metal particles, 1.7 nm on TiO2 and 2.1 nm on Al2O3, were obtained after activation of the catalysts under H2 at 300°C.

A typical set of catalytic results is reported in Figure 1. It shows that for temperatures higher than 170°C, 100 % conversion of butadiene into butenes are reached with very low hydrogenation of alkenes into alkanes. Even at 300°C, only 1000 ppm over the 30% of propene present in the feed are converted into propane, and the level of butane remains close to zero.

The nature of the support does not seem to have any influence on the catalytic behavior of gold. Non activated catalysts, i.e., catalysts containing Au11 precursor, are not active, except when the reaction temperature reaches that of gold reduction. Larger gold particles leads to less active catalysts, but the TOF expressed as the number of reaction cycles per second and per surface gold atom is rather constant.

If the percentage of propene in the gas stream is lowered, the catalytic activity increases, indicating that propene is acting as an inhibitor in the hydrogenation of butadiene (competition of adsorption). In contrast, the presence or absence of butadiene has no influence on the hydrogenation of propene, which occurs at high temperature only (Figure 1). The behavior of gold will be compared to that of palladium in the discussion.

The gold catalysts slowly deactivate at high conversion, probably due to surface oligomerization, but they can be regenerated by a thermal treatment under air.

![Figure 1](image-url)  
*Figure 1. Conversion of butadiene and propene on Au/TiO2 (1wt %) and selectivities as a function of the reaction temperature.*

Significance

The lower activity of gold compared to that of Pd is largely compensated by the fact that gold catalysts are much more selective. Within a large window of temperatures, the conversion of butadiene is 100% and the selectivity in alkenes is close to 100%.

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References