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Direct gas-phase epoxidation of propene over bimetallic Au catalysts

Aalbert Zwijnenburg, Mehdi Saleh, Michiel Makkee*, Jacob A. Moulijn

Faculty of Applied Sciences, Industrial Catalysis, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Abstract

Bimetallic Au catalysts have been prepared and tested for the direct gas-phase epoxidation of propene using hydrogen and oxygen. Modification of $Au/TiO_2/SiO_2$ catalysts with Pt is beneficial for both activity and selectivity. The water–propene oxide ratio decreases upon addition of Pt to a $Au/TiO_2/SiO_2$ catalyst, while the epoxidation activity is maintained. Hydrogenation of propene to unwanted propane does not occur at temperatures below 373 K.

Keywords: Selective oxidation; Propene; Gold catalysts

1. Introduction

The direct gas-phase synthesis of propene oxide, by the use of molecular oxygen, has long been desired. Highly dispersed Au/TiO_2 catalysts show an extraordinary selectivity in the oxidation of propene to the corresponding epoxide (>99%), using a combination of H_2 and O_2 as oxidation mixture [1]. Additional studies of the epoxidation reaction indicated several drawbacks of the Au/TiO_2 catalyst. Firstly, the low conversion (1–2%) obtained under typical reaction conditions (atmospheric pressure, 323–423 K) cannot be improved by increasing the reaction temperature, because this leads to extensive by-product formation. Secondly, the low efficiency of hydrogen (relatively large amounts of water are formed) is hard to prevent. Finally, significant deactivation of Au/TiO_2 catalysts within several hours on stream has been observed. Deactivation can be partly prevented by using dispersed TiO_2 supports, such as TiO_2/SiO_2 and titanium-silicalite-1 (TS-1) [2,3] and Ti-MCM [4,5]. For industrial applications the efficiency of hydrogen should be increased not only to favor process economics, but also decrease the amount of heat released in the reactor.

In recent literature [2,6], a hydroperoxide-like intermediate has been proposed to be responsible for the selective epoxidation. This oxidizing species is said to be formed over gold and subsequently used for epoxidation over the Ti-containing support. Although gold is known to catalyze the formation of hydrogen peroxide from H_2 and O_2—and this is also supported by theoretical predictions [7]—most patents describing H_2O_2 direct synthesis are based on bimetallic Pd and Pt catalysts (e.g. [8,9]). H_2O_2 formation from H_2 and O_2 and subsequent propene epoxidation has been shown by Hölderich and co-workers [10,11] for Pd/Pt supported on TS-1.

In this contribution catalytic concepts established from H_2O_2 direct synthesis have been applied to the gas-phase propene epoxidation to both improve hydrogen efficiency and gain insight into the epoxidizing

* Corresponding author. Tel.: +31-15-2781391; fax: +31-15-2784452.
E-mail address: m.makkee@tnw.tudelft.nl (M. Makkee).

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species. The addition of a second metal to the gold catalyst complicates the preparation and characterization. Consequently, several preparation routes have been assessed for their ability to yield active gold-only catalysts. The most promising preparations have been used to modify the gold with Pd or Pt.

2. Experimental

In a first series of experiments several gold catalyst preparation routes were assessed. Gold was deposited on a TiO_2/SiO_2 support [2] by deposition–precipitation (DP) [12], ion exchange (IE) [13], and via size-controlled gold colloids (SCG) [14].

For the DP preparation the support was dispersed in water (approximately 10 ml/g of support) to which ammonia was added to raise the pH to a value between 9 and 10. Over a period of 2 h the required amount of gold (in the form of $AuCl_3$ solution) was added dropwise to the support under vigorous stirring. The mixture was stirred for another half an hour after which it was centrifuged and washed with at least ten times its own volume of distilled water.

For the IE preparation, a $[Au(ethylenediamine)_2]Cl_3$ complex was made by the method of Block and Bailar [15]. A suspension of TiO_2/SiO_2 was heated to 343 K in aqueous ammonia of about pH 11. The $[Au(ethylenediamine)_2]Cl_3$ solution was added dropwise into the slurry of TiO_2/SiO_2. After addition of the solution, the slurry was maintained at 343–335 K for 1 h and then cooled to room temperature. The treated TiO_2/SiO_2 was centrifuged and washed with at least 10 times its own volume of distilled water.

In order to prepare Au stabilized as colloid, the sol preparation of Baiker and co-workers [14] was performed. The TiO_2/SiO_2 support was suspended in water at pH 2, and the appropriate amount of a H_2SO_4-treated solution (pH = 2) with gold colloids was added with stirring. After 10 min the suspension was filtered and washed three times with distilled water.

The samples prepared by DP, IE, or SCG were dried at 353 K for 2 h and calcined at 673 K for 4 h.

Steady-state experiments were performed in a micro-flow equipment. In this apparatus, nitrogen (70 vol.%), oxygen (10 vol.%), hydrogen (10 vol.%), and propene (10 vol.%) were continuously fed over a 10 ml fixed-bed reactor placed in a fluidized-bed oven. The analysis of the reaction products was performed using an automated sampling gas chromatograph, analyzing a gas sample every 12 min. The column used for analysis was a Poraplot Q 0.53 mm diameter, 25 m length capillary column, with He as carrier gas. A flame ionization detector (FID) was used for the analysis. This configuration was able to separate all oxygenated organic components relevant in this study. The hydrogen and oxygen consumption was measured on the same gas chromatograph using a Molsieve 5 Å, 2 mm diameter, 3 m length column and a TCD detector.

Transmission electron microscopy was performed using a Philips CM30T electron microscope with an LaB_6 filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

3. Results and discussion

Different preparation routes have been evaluated for their ability to yield active gold catalysts. The results are given in Table 1. It is shown that the highest yield of propene oxide (PO) was achieved with the catalyst prepared according to the DP method. On a TiO_2/SiO_2 support, the DP catalyst gives PO with a yield of 1.2% and no propane, while the IE catalyst gives mainly propane as a major product. TEM indicated for both DP and IE samples a homogeneous distribution of gold particles with sizes between 4 and 10 nm, with a mean particle size of 6 nm. Apparently, not only the gold particle size, but also the contact with the support might be important for epoxide selectivity. The stabilizer (tetrakis(hydroxymethyl)phosphonium chloride, THPC) used for the SCG method apparently dimin-

Table 1
Product yields at 373 K and WHSV = 0.71 $g_{propene}/g_{cat}$ h. Other products are ethanal, acrolein, propanal and acetone

Preparation	PO (%)	Propane (%)	H_2O/PO (–)	Other (%)
DP	1.2	<0.1	29	<0.01
IE	0.05	9.0	110	0.06
SGC	<0.01	3.5	∞	0.16

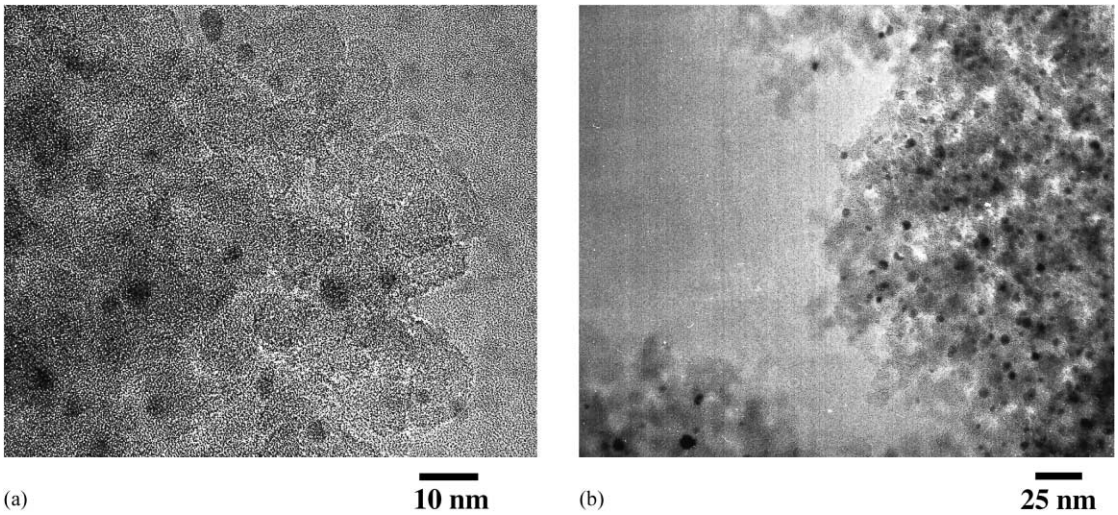

Fig. 1. TEM micrographs for: (a) 5:95 Pd–Au/TiO_2/SiO_2; (b) 5:95 Pt–Au/TiO_2/SiO_2 catalysts.

ishes the epoxidation activity. In the original paper [14] phosphorus was found to remain on the catalyst. Stangland et al. [6] investigated several preparation routes and concluded DP was the best to obtain active gold catalysts. As only the DP sample was found active for propene epoxidation, it was decided to use DP for the addition of promoting elements to the Au catalyst. Contrary to the IE preparation, which was originally proposed for obtaining well-mixed Pd–Au catalysts [13], the DP method does not necessarily give alloy formation [16].

The DP method was chosen for investigation of bimetallic catalysts. To the $AuCl_3$ solution the corresponding Pd or Pt salts were added (Pt:Au = 5:95). TEM micrographs are given in Fig. 1. Both catalysts show homogeneously distributed metal particles up to 5 nm. No separate Pt or Pd metal particles were found. XRF analysis confirmed the presence of Pd and Pt in the bimetallic samples. In Table 2, the hydrogenation and epoxidation activities are compared for the bimetallic catalysts obtained. Clearly, it can be seen that both Pt and Pd induce hydrogenation of propene to the unwanted propane. The Pd–Au catalyst made by DP only shows propene hydrogenation and no oxidation activity. This result is supported by claims in patent literature [3] that promotion by Pd is not to be applied for selective gas-phase propene epoxidation. Also the addition of Pt leads to the formation of propane at 373 K, but this catalyst exhibits less water formation compared to the Au-only catalyst. The ratio of H_2O to PO is 9 for the Pt-modified catalyst compared to 30 for the Au-only sample. It should be noted that the Pt sample shows no propene hydrogenation activity at temperatures below 373 K, while the PO yield is still high (1.1% at 348 K against 1.5% for the 1:9 Pt–Au at 373 K).

Table 2
Product yields for bimetallic catalysts compared to Au-only at 373 K

Metal	PO (%)	Propane (%)	H_2O/PO (–)
Au-only	1.2	<0.1	29
Pd–Au	<0.01	10	∞
Pt–Au	1.0	0.1	9.3

The effect of Pt concentration was further investigated and the results are given in Fig. 2. It can be seen that at even higher Pt concentrations the H_2O/PO ratio is again increased. This might be due to the formation of separate Pt particles that enhance the water formation reaction. The hydrogenation of propene does not occur below 373 K even with the highest Pt concentration investigated.

Based on the TEM characterization and reaction data Pt seems to be incorporated into the Au metal particles. Formation of the oxidizing species is more

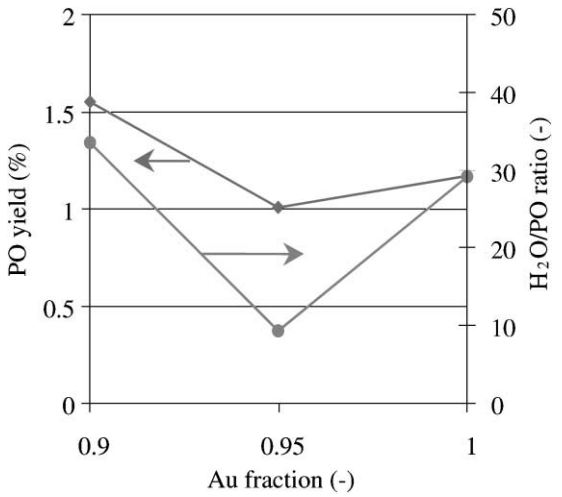

Fig. 2. Effect of Au fraction in Pt–Au bimetallic catalysts on PO yield and H_2O/PO ratio at 373 K, WHSV = 0.71 $g_{propene}/g_{cat}$ h.

efficient for these bimetallic samples compared to Au-only catalysts.

4. Conclusion

Our results show that DP is a good technique for obtaining active and selective epoxidation catalysts. However, upon addition of Pd or Pt this method is not expected to yield alloy metal particles. Based on the H_2O_2 direct synthesis literature and the proposed reaction scheme both Pd and Pt are interesting additives. However, the results for Pd–Au catalysts made by DP indicate that although Pd seems well dispersed over the support, hydrogenation of propene to unwanted propane occurs. This is probably due to the presence of monometallic Pd particles.

Results for Pt show an increase in the hydrogen and oxygen efficiency, combined with a stable yield in PO. Hydrogenation of propene to propane occurs at higher temperatures, but can be prevented by operating below 373 K.

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