Highly selective propene epoxidation with hydrogen/oxygen mixtures over titania-supported silver catalysts

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Received 9 November 2000; accepted 27 February 2001

Silver supported on titania was found to be active for propene epoxidation using hydrogen/oxygen mixtures at 50 °C. The dependence of the activity on the preparative method is pronounced, i.e., only catalysts prepared by using deposition–precipitation exhibit activity. Optimum performance was found for 2 wt% Ag/TiO_2 calcined at 400 °C. The propene epoxidation activity, the activity in the low-temperature CO oxidation, in propane oxidation and deactivation behavior of these silver catalysts strongly resemble the results obtained for the Au/TiO_2 catalysts developed by Haruta.

KEY WORDS: propene oxide; alkylene oxides; CO oxidation; epoxidation; silver; titania

1. Introduction

The direct oxidation of propene with oxygen is one of the most challenging tasks in catalysis. Recently, catalysts containing gold particles from 2 to 4 nm in size on various titanium-containing supports have been demonstrated to catalyze this reaction at low temperatures. In the presence of hydrogen and oxygen, propene is converted to propene oxide with a selectivity exceeding 99% [1,2]. Although bulk gold is considered as catalytically inert, well dispersed gold particles show a very rich and interesting catalytic chemistry, the origin of which is not fully understood [3]. To date, no other metals have been identified to be active and highly selective for this epoxidation reaction except to very recent reports in the patent literature [4,5]. Pd, Pt, Cu and Ag catalysts supported on TiO_2 were found to be totally inactive under the conditions used by Haruta et al. [2]. These findings were, in most cases, confirmed in our studies. However, it was discovered that silver supported on titania exhibits activities and selectivities comparable to those observed for gold catalysts, provided the silver is precipitated onto the support using sodium carbonate or hydroxide.

2. Experimental

2.1. Catalyst preparation

The titania-supported silver catalysts were prepared by deposition–precipitation of silver carbonate or hydroxide onto titania. This was achieved by suspending 1.5 g of the support (Hombifine N, Sachtleben Chemie, or Titiania P25, Degussa-Hüls AG) in 200 ml of a sodium carbonate solution (0.05 M), and subsequently adding 100 ml of a silver nitrate solution to the suspension under vigorous stirring. The concentration of silver nitrate was varied corresponding to the silver loading. The resultant pH was 11. Total precipitation of silver was proven by addition of a diluted solution of sodium chloride to the eluate after the subsequent filtration. Additionally Micro-EDX confirmed the loading and showed homogeneous dispersion of silver on the support. The slightly yellowish solid recovered after 1 h of stirring was repeatedly washed, dried at 90 °C, and then calcined by heating at a rate of 1 K min^{-1} and maintaining the final temperature, ranging from 250 to 450 °C, for 10 h.

For comparison, catalysts with a loading of 2.3 wt% silver were also prepared using impregnation and sol–gel procedures. For the incipient wetness impregnation, a solution of 30.2 mg silver nitrate dissolved in 600 μl water was added in small portions to 0.825 g titania (Hombifine N) while grinding. The resultant mixture was dried at 90 °C and calcined at 250 °C, as described above. The sol–gel synthesis was performed by dissolving 3.227 g $Ti(OCH_3)_4$ in 10 ml conc. nitric acid. To this solution 55 mg silver nitrate in 90 ml of water were slowly added. The resulting solution was transparent, indicating that no titania particles had formed upon hydrolysis. To this mixture a solution of 13.8 g of sodium carbonate dissolved in 200 ml of water was added over a 5 min interval. The resultant gelatinous mixture had a pH of 10–11 and was hard to filter. The precipitate was redispersed three times in 300 ml of water to remove sodium nitrate. After drying at 90 °C it was calcined at 250 °C using the same method as described above.

2.2. Catalyst characterization

Catalysts were characterized by XRD performed with a Θ/Θ-diffractometer (STADI P, STOE) and TEM (Hitachi HF 2000) equipped with a EDX-unit (Kevex Systems). TG-

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MS measurements of deactivated catalysts were conducted by using a TG/DTA (STA 449C, Netzsch) coupled with a MS (Thermostar, Balzers Instruments).

2.3. Catalytic tests

Propene and propane oxidation were performed in an open flow tubular reactor with an inner diameter of 4 mm at 50 °C and ambient pressure. Catalyst grit (125–250 μm) was placed on a steel frit. The catalysts were operated at a volume ratio of 10/10/10/70 ($C_3H_6/H_2/O_2/N_2$) and, except noted otherwise, at a space velocity of 4000 ml $g_{cat.}^{-1}$ h^{-1}. Analysis of the effluent gas stream was performed using a gas chromatograph (CE Instruments 8000 top) equipped with a methanizer and a flame ionization detector. Carbon mass balances closed within 1%, which was mainly determined by the precision of the propene peak integration. This means, that small amounts of carbon retained on the catalyst via oligomerization (see below) might not be accounted for, and the selectivities reported thus only hold strictly for the gas phase products. Hydrogen consumption was measured with a second gas chromatograph equipped with a thermal conductivity detector. For propane oxidation, the same conditions were used.

Low temperature CO oxidation, as well as preliminary high-throughput experiments in propene epoxidation, were carried out in a setup described elsewhere. For CO oxidation 100 mg of catalyst were operated in a gas atmosphere of 1% CO in air at a space velocity of 10000 ml $g_{cat.}^{-1}$ h^{-1} and the reaction temperature was varied. For propene epoxidation screening experiments, 100 mg of catalyst were operated under the conditions given above.

3. Results and discussion

Figure 1 shows the catalytic performance of differently synthesized catalysts with 2.3 wt% silver loading (WHSV 2000 ml $g_{cat.}^{-1}$ h^{-1}). Obviously, the samples prepared by either impregnation or sol–gel synthesis were totally inactive under the conditions of the reaction. However, catalysts synthesized by the deposition–precipitation method showed substantial activity for propene oxide formation. In addition, selectivities for propene oxide based on propene conversion were above 90% for all active catalysts. As the reaction temperature was increased, the selectivity to propene oxide drastically decreased, corresponding with an increase in total oxidation products. This is in agreement with literature data for gold-based catalysts [7,8]. Hydrogen consumption of the active catalysts could not reliably be assessed with the analytical equipment used, but was below 5% of the hydrogen fed into the system. As can be seen in figure 1, the support material is also influential to the performance of the catalysts. Hombifine N, an amorphous material which crystallizes upon calcination at 250 °C to microcrystalline anatase with a surface area of 140 m^2 g^{-1}, was consistently superior to P25, a rutile/anatase phase mixture with a specific surface area of 50 m^2 g^{-1}, for many different preparations. The

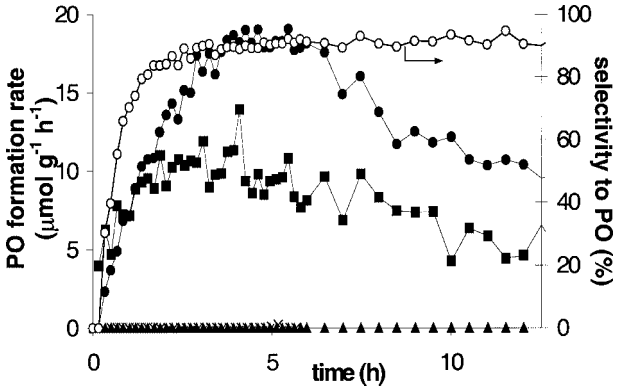


Figure 1. Propene oxide production rate of catalysts prepared by deposition–precipitation on Hombifine N (calc. 300 °C (•), PO-selectivity (○)), on P25 (calc. 250 °C (■)), by sol–gel route (×), by impregnation (▲).

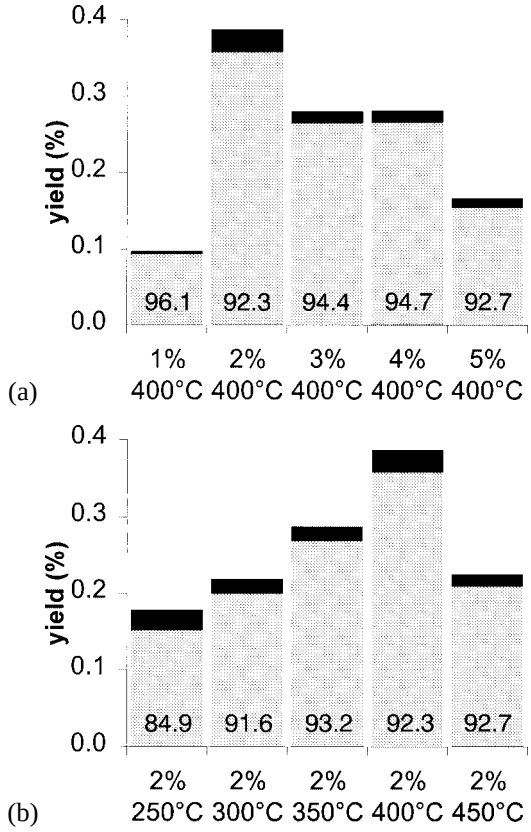
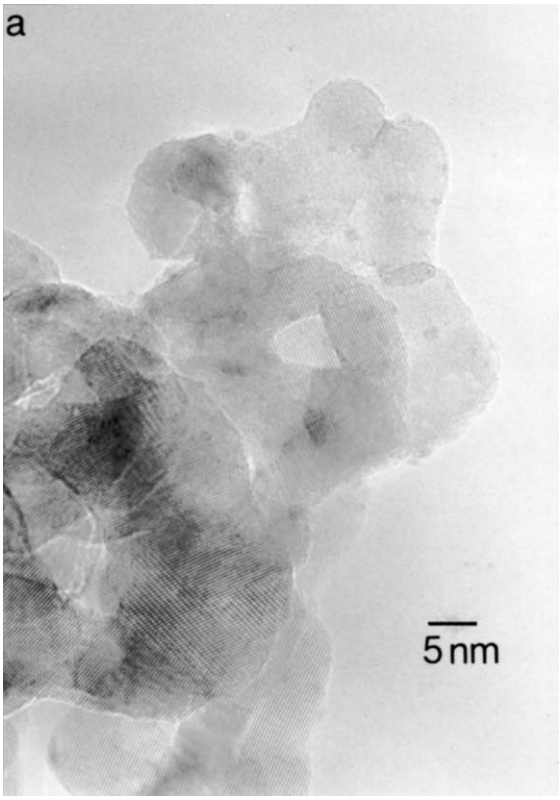
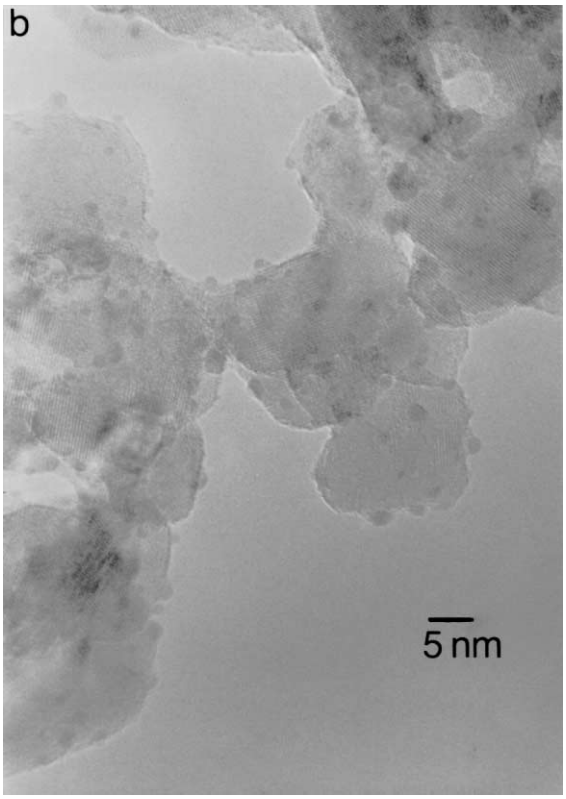


Figure 2. Propene oxide (▨) and carbon dioxide (■) yields of selected catalyst with (a) different loadings and (b) different calcination temperatures from the screening experiments yields based on propene consumption, inside bars: selectivity for propene oxide, WHSV 4000 ml $g_{cat.}^{-1}$ h^{-1}.

reason for this difference is not yet clear, but a strong dependence of catalytic performance upon the nature of the support has previously been reported [2,7–9]. The active catalysts showed a pronounced formation period of several hours under reaction conditions. During formation, the propene oxide concentration increased steadily, while the CO_2 concentration decreased. After the catalysts had reached maximum activity, CO_2 formation was very low, and selectivities to propene oxide exceeded 90%. The catalysts also deacti-





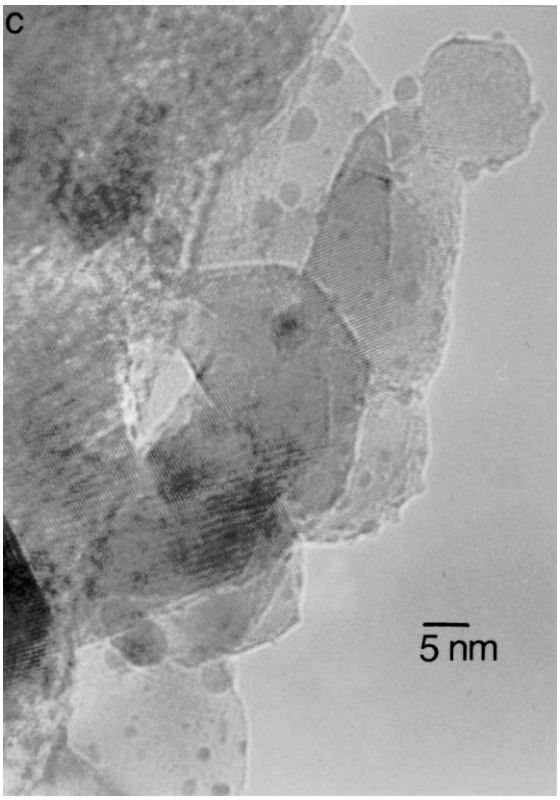


Figure 3. TEM micrographs of (a) 2 wt% Ag/Hombifine N calcined at 400 °C, (b) 5 wt% Ag/Hombifine N calcined at 400 °C and (c) 5 wt% Ag/Hombifine N calcined at 450 °C.

vate to about 10% of the initial activity over a period of three days.

For further optimization the loading as well as calcination temperature for the Hombifine N based Ag/TiO_2 catalysts were varied and the resulting catalytic performance measured in a high-throughput screening device. Results for selected catalysts are given in figure 2. A 2 wt% Ag catalyst calcined at 400 °C exhibited an optimum performance. The maximum conversion achieved so far was 0.4% propene to propene oxide at a space velocity of 4000 mln g^{-1} h^{-1}. An optimum silver loading appears to be around 2 wt% as can be seen in figure 2. With concentrations up to this value, the rate increases with silver loading and then reaches a plateau which extends to loadings of around 4 wt%. The silver catalysts described here reached approximately one third (0.07 mol g^{-1} h^{-1}) of the activities of the optimum Au/TiO_2 catalyst described by Haruta using an identical gas composition ($C_3H_6/H_2/O_2/N_2$ = 10/10/10/70) [2]. However, this does not seem to be the limit for the gold-based systems as substantially higher rates have very recently been reported [10].

The catalysts are very sensitive to the calcination conditions used, as can be seen in figure 2. At temperatures below 250 °C the propene oxide formation was negligible, whereas activation at temperatures between 250 and 400 °C yielded active catalysts, although calcination at 250 °C produced catalysts less selective for propene oxide. After calcination at higher temperatures, the propene oxide formation again sharply decreases especially for higher silver loading. In addition, catalysts supported on P25 seem to be thermally less stable. While Hombifine N materials can be calcined to 400 °C without loss of activity, a substantial loss of activity is observed for P25-based catalysts at a temperature above 300 °C.

Figure 3 shows transmission electron micrographs of three different catalysts. The difference of the two catalysts with 2 and 5 wt% silver loading, calcined at 400 °C, seems to be mainly in the density of particles on the support, although a slight particle size increase can be observed with higher loading. However, activity of 2 wt% samples was superior to 5 wt% samples and this might be explained in two alternative ways. Either the crystalllites visible in TEM analysis are not responsible for activity and an even higher dispersed silver species carries the activity, or a slight increase in particle size effects a strong decrease in activity. The pronounced increase in particle size with calcination at higher temperature corresponds to a strong loss of activity. Calcination at 400 °C results in silver particles in the range of 2 and 4 nm. Bigger particles around 5 nm are observed if calcination is carried out at 450 °C. For all catalysts no silver phase was detectable in XRD, probably because the most intense reflection of silver is close to one intense anatase reflection, and because of the low loading. This creates difficulties to measure these reflections which are expected to be broad and of low intensity anyway.

The pronounced deactivation is in line with the results of other groups for gold-based catalysts [7,9]. In TG/MS experiments performed on the deactivated catalysts, an initial desorption peak, corresponding to the mass of propene oxide, was observed at 250 °C. A second peak, corresponding to the release of hydrogen, acrolein and propene oxide, appears at 400 °C. This suggests that oligomeric or polymeric propene oxide species are responsible for the loss of activity. Correspondingly, the activity could be restored to more than 50% of the initial value by heating the deactivated catalysts at 400 °C in air.

The assumption that part of the propene oxide is converted to oligomeric species remaining on the catalyst is supported by the fact that the rates observed are strongly dependent on the residence times. At long residence times the apparent rates are lower, since some of the initial propene oxide formed is probably lost due to oligomerization. Here again strong similarities to the gold systems can be observed, where Nijhuis et al. [7] described the same phenomenon and attributed this effect to oligomerization of propene oxide over the catalyst.

The behavior of the silver catalyst described here is, in many respects, similar to that of small particle gold catalysts first described by Haruta. In order to check whether these similarities extend to other reactions, low temperature CO oxidation was carried out over the silver-based catalysts (table 1). Although the silver-based catalysts described here are not as active as the best gold catalysts in the CO oxidation, they are remarkably active compared to other silver catalysts. A CO conversion of 10% is observed even at room temperature. CO oxidation is essentially complete at temperatures of approximately 70 °C. Additionally, activity for propane oxidation could also be found. A 2 wt% Ag/TiO_2 catalyst yielded 0.01% acetone at 50 °C.

Table 1
Carbon dioxide yield (%) of different catalysts at increasing catalyst temperatures.

$T_{cat.}$ (°C)	CO_2 yield (%)				
	1% Ag 350 °C	2% Ag 300 °C	3% Ag 300 °C	4% Ag 350 °C	5% Ag 30 °C
27	0.0	2.5	6.6	12.0	11.0
70	9.0	28.4	52.7	62.9	70.1
130	53.5	96.7	100.0	100.0	100.0

The results presented here show that the special properties of small gold particles supported on suitable oxides are not unique, but can also be present in supported silver catalysts. Such unusual properties have also been reported for small silver particles in a hydrogenation reaction [11]. If one accepts the notion that the observed similar catalytic performance of gold and silver catalysts is related to the same underlying phenomenon, any explanation which is very specific for gold is most probably not fully correct.

Acknowledgement

We would like to thank B. Spliethoff for the TEM analysis and H. Kestenbaum for support in determining hydrogen efficiency. We would also like to thank Degussa-Hüls AG, Frankfurt, for providing P25 support materials and Sachtleben-Chemie GmbH, Duisburg, for providing Hombifine N.

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