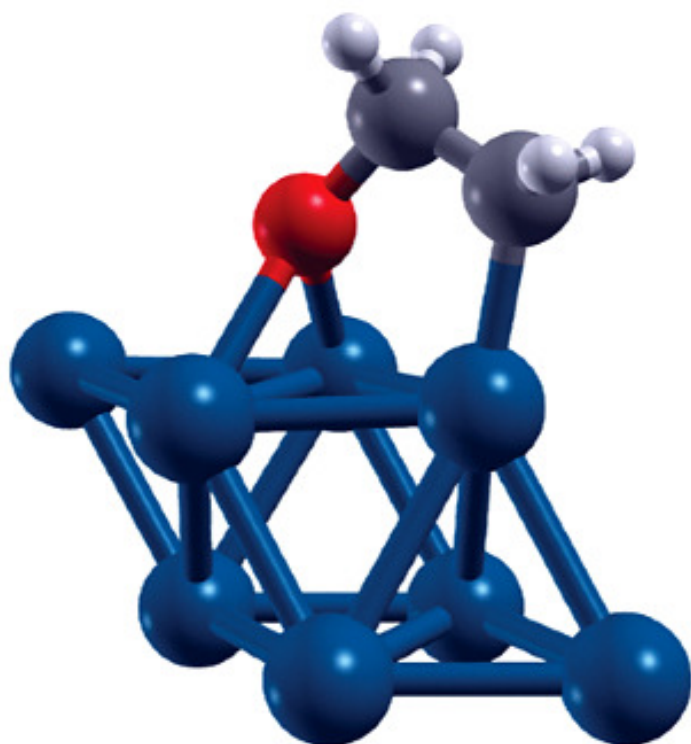
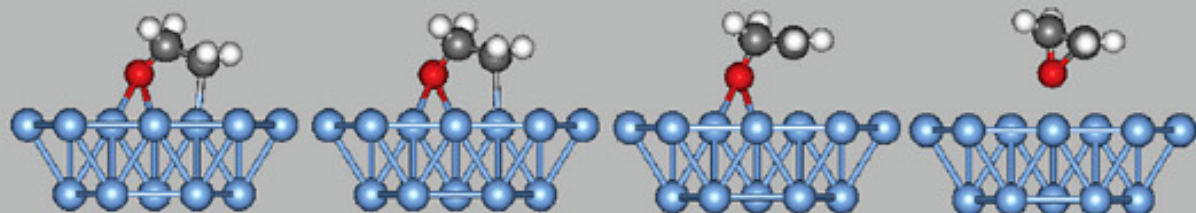




MECHANISMS IN HOMOGENEOUS AND HETEROGENEOUS EPOXIDATION CATALYSIS



EDITED BY
S. TED OYAMA



Mechanisms in
**HOMOGENEOUS
AND HETEROGENEOUS
EPOXIDATION
CATALYSIS**

Edited by

S. TED OYAMA

*Department of Chemical Engineering
Virginia Tech, Blacksburg, USA*



ELSEVIER

Amsterdam • Boston • Heidelberg • London • New York • Oxford • Paris
San Diego • San Francisco • Singapore • Sydney • Tokyo

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2008

Copyright © 2008 Elsevier B.V. All rights reserved

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at <http://elsevier.com/locate/permissions>, and selecting *Obtaining permission to use Elsevier material*

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN: 978-0-444-53188-9

For information on all Elsevier publications
visit our website at books.elsevier.com

Printed and Bound in Hungary

08 09 10 11 12 10 9 8 7 6 5 4 3 2 1

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER

BOOK AID
International

Sabre Foundation

The Epoxidation of Propene over Gold Nanoparticle Catalysts

T. Alexander Nijhuis,* Elena Sacaliuc,[†]
and Bert M. Weckhuysen[†]

Contents	1. Introduction	340
	2. Experimental	341
	2.1. Catalyst preparation	341
	2.2. Catalyst characterization	342
	2.3. Catalyst activity testing	342
	3. Results and Discussion	343
	3.1. Characterization	343
	3.2. Catalytic performance	343
	3.3. Catalyst deactivation	348
	4. Conclusions	352
	Acknowledgments	353
	References	353

Abstract

Different gold nanoparticle catalysts on titania, silica, and titanasilicate supports are compared in the hydro-epoxidation of propene. All catalysts tested were active in the propene epoxidation, with Au/TiO₂ showing the highest activity at low temperature, but also a high rate of deactivation. It is shown that the deactivation of the catalysts is directly related to a side reaction of a bidentate propoxy reaction intermediate. This species can react to produce propene oxide, but as a side reaction it can also produce very strongly adsorbed species, most likely carbonates, which cause a reversible deactivation. There are no indications that the catalyst deactivation is caused by changes in the size or the state of the gold nanoparticles. Catalysts containing a lower amount of titania dispersed in or on a silica support are more stable,

* Laboratory for Chemical Reactor Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[†] Laboratory for Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

but require a higher reaction temperature for a similar activity. Ti-SBA-15 is the most promising support material, but the gold deposition inside the structure requires further optimization. A key factor, that needs to be solved for all gold catalysts, is the efficiency in which hydrogen is used as a co-reactant. The currently obtained hydrogen efficiencies of up to 10% are insufficient to run a process profitably.

Key Words: Gold, Propene oxide, Titania, SBA-15, Silica, Titanosilicate, Hydro-oxidation, Deactivation, Hydrogen efficiency, Ti-SBA-15, Gold hydrazide, Fulminating gold. © 2008 Elsevier B.V.

1. INTRODUCTION

Propene oxide is a very important chemical intermediate, produced at about six million tons per year (2006) with demand still growing by ~5% annually [1,2]. One of the important new developments for the production of propene oxide are epoxidation catalysts based on gold nanoparticles [1,3–7]. Gold–titania catalysts are capable of very selectively epoxidizing propene in one step at mild conditions using molecular oxygen in the presence of hydrogen as a sacrificial reductant. Because of the use of hydrogen as a co-reactant, this epoxidation is better called a hydro-oxidation rather than a simple oxidation reaction. The two main processes in operation for the production of propene oxide, the chlorohydrin process and the hydroperoxide processes, have disadvantages which make an alternative desirable. A recent review on all processes in use and under development for the propene epoxidation is available [1]. The chlorohydrin process produces a large salty wastewater stream as well as chlorinated side products. The hydroperoxide processes, SM-PO (styrene monomer-propene oxide) and PO-TBA (propene oxide-*tert*-butyl alcohol), produce a co-product in a fixed quantity (typically—two to four times by weight the amount of propylene oxide produced), making the process economics heavily dependent on the value of the co-product. The alternative processes that have been developed in recent years [1,8], the new Dow-BASF hydrogen peroxide combination process (together with the similar Degussa-Headwaters process) and the Sumitomo hydroperoxide process, are complex (using three different reactors) and use, similarly to gold–titania catalysts, sacrificial hydrogen. The hydrogen peroxide processes consume hydrogen in the production of the hydrogen peroxide, which is the oxidant in the epoxidation. The Sumitomo process is a hydroperoxide process, which produces cumyl alcohol out of cumene and uses the hydrogen to convert the alcohol co-product back to cumene. Therefore, the simple (single reactor process) and selective hydro-epoxidation of propene over gold–titania catalysts has good potential for being applied in a highly competitive process.

Despite this attractiveness, gold–titania-based catalyst systems have a number of weaknesses which need to be improved: the propene conversion levels remain low, often the catalyst stability is insufficient, and the hydrogen efficiency is

low [1,9,10]. The hydrogen efficiency (defined as the molar amount of propene oxide produced divided by the amount of hydrogen consumed) is dominated by the water produced by the direct hydrogen oxidation over the catalyst. The problem of low catalyst stability is mostly understood and can be solved largely by making sure of a very low level of residual chlorine [10,11] (the catalysts are commonly produced using a gold chloride precursor and residual chlorine makes the catalyst very sensitive to sintering of the gold particles) and by dispersing the titania in a silica matrix [9,10,12,13]. The low conversion levels can also be improved by using a Ti–Si support [9,10], which can produce propene oxide at a higher temperature than gold on titania, or improved even further by using a surface modified Ti–Si support [7,14]. For the activity, it should be noted that even though conversion levels remain low, the catalyst activity for a 1 wt.% gold catalyst is not exceptionally low (the more active gold/titania catalysts produce in the order of $0.1 \text{ mol}_{\text{PO}}/\text{m}^3_{\text{reactor}}/\text{s}$) compared to other chemical processes applied in industry [15]. To improve the low hydrogen efficiency (typically less than 10%), however, no solutions have been published in the literature yet. It has been claimed that mixing the catalyst with CsCl results in a significant improvement in the hydrogen efficiency [16]; however, there have been no reports confirming these results. Furthermore, the large amount of chloride contributed by the CsCl is detrimental to the catalyst stability toward sintering. Therefore, solving the problem of the low hydrogen efficiency can be seen as the main last hurdle before this type of catalyst can be applied. A hydrogen efficiency in the order of 50% is desirable for a profitable process.

In this chapter, a comparison is made between different gold-based catalysts designed for the propene epoxidation: gold supported on titania, gold supported on dispersed titania supports [Ti on amorphous silica and Ti-SBA-15 (mesoporous silica)], and gold on silica for comparative purposes. Attention will be given to the activity, selectivity, stability, and hydrogen efficiency.

2. EXPERIMENTAL

2.1. Catalyst preparation

The supports used for the preparation of the catalysts were titania (Degussa-P25, $45 \text{ m}^2/\text{g}$, primarily anatase), silica [two types: Davisil 645 (Grace Davison, $295 \text{ m}^2/\text{g}$) and OX50 (Degussa, $50 \text{ m}^2/\text{g}$)], 0.4 wt.% Ti on OX50 silica [11], and Ti-SBA-15 (Si/Ti = 40, Ti deposited by grafting, preparation according to Sacaliuc *et al.* [17]).

Catalysts were prepared by means of a deposition precipitation method using ammonia [9].¹ A quantity of 10 g of support was dispersed in 100 ml of

¹ When preparing gold catalysts using deposition precipitation using ammonia, care should be taken as the possibility exists for the formation of gold hydrazide (fulminating gold). In the preparations in this chapter the risks are very minor considering the small quantities of gold and the low loadings of the catalysts prepared. Care is advisable, however, considering a reported incident [Fisher, *Gold Bull.* 36 (2003) 155]. It is recommended that readers take the advantages (ease of making stable catalysts without chloride or sodium present) and disadvantages of this preparation method in consideration.

demineralized water with a magnetic stirrer. The pH of the slurry was 3.8 for the catalysts prepared on titania and 7 for the silica support. The pH was raised to 9.5 using 2.5% ammonia. The target loading in gold was 1 wt.%, for which 172 mg of hydrogen tetrachloroaurate(III) solution (HAuCl_4 , Aldrich—30 wt.% solution in dilute HCl) was diluted in 40 ml of demineralized water and added gradually over a 0.25-h period to the support, while keeping the pH between 9.4 and 9.6 by periodically adding ammonia. After addition of all the gold, the dispersion was stirred for 1 h after which it was filtered and washed three times with 200 ml of demineralized water. It was found that aging the dispersion had a beneficial effect on the broadness of the particle size distribution. The yellow catalyst was dried overnight in air at 333 K and then calcined. Calcination was carried out by heating to 393 K (5 K/min heating) for 2 h followed by 4 h at 673 K (5 K/min heating and cooling). The thus-obtained catalysts had an intense dark color originating from the plasmon bands of the gold nanoparticles: purple for the titania-supported catalysts, red-brown for the silica-supported catalysts, salmon pink for the Ti-OX50-supported catalysts, and red-orange for the Ti-SBA-15-supported catalyst.

2.2. Catalyst characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs were taken of the catalysts to determine the gold particle size and distribution on the catalysts, both before and after use in catalytic experiments. X-ray fluorescence (XRF) analysis was used to determine the gold loading on the catalysts and the presence of contaminants affecting the activity (e.g., chloride). X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo VG Scientific XPS system with a reaction chamber for sample pretreatment allowing the performance of quasi *in situ* measurements, which were used to determine changes in the oxidation state of the gold.

2.3. Catalyst activity testing

A flow reactor was used to determine the catalytic performance of the different catalysts. The experiments were carried out with typically 0.30 g of catalyst and a gas flow of 50 Nml/min (GHSV $10,000 \text{ h}^{-1}$). In the epoxidation experiments, a gas mixture was used similar to that in most research in the literature: 10% of oxygen, 10% of hydrogen, and 10% of propene in helium (all gas compositions given in vol.%). The pressure was 1.1 bar. In this study, the activity was determined at 323, 373, 423, and 473 K; the lowest temperature being most appropriate for the titania-supported catalyst, the higher temperatures being more optimal for the Ti-silica-supported catalysts.

The analysis of the gas leaving the reactor was carried out using an Interscience Compact-GC (gas chromatography) system, equipped with a Molsieve 5A and a Porabond Q column, each with a thermal conductivity detector (TCD). Gas samples were analyzed every 3 min. The catalysts were regenerated prior to measuring at the next reaction condition: the catalysts were heated for 1 h at 573 K (10 K/min) in a 50-ml/min gas stream consisting of 10% of oxygen in helium. Experiments

performed with the bare supports did not show any catalytic activity. The catalytic tests were performed in a fully automated system over a period of typically 5–10 days during which multiple reaction conditions were applied, including repeat conditions to verify catalyst stability.

3. RESULTS AND DISCUSSION

3.1. Characterization

The XRF analysis of the catalysts showed that for all samples the catalyst loading was close to the desired loading of 1 wt.%. No residual chloride could be detected on the catalysts. For both the Ti-OX50 and the Ti-SBA-15, SEM and TEM analysis showed a homogeneous distribution of the Ti over the supports with no amorphous titania present. The particle sizes were determined by measuring all particles on a number of TEM pictures until over 200 particles were measured. A selection of the TEM pictures is shown in Fig. 12.1. The TEM analysis showed that the gold particle size was support independent and similar (~4 nm average particle size), with the exception of the gold particles supported on the mesoporous Ti-SBA-15. For the Ti-SBA-15-supported catalysts, the gold particle size was larger. Also, the gold particles were clearly elongated, as a result of the gold particle growth being restricted by the SBA-15 mesopores. This larger gold particle size was most likely the result of mass transfer limitations during the deposition, drying, or calcination, and currently is being investigated further.

The difference in color of the catalysts, even though the gold particle size and distribution was similar, can be explained by a different interaction between the gold particles and the supports. The most relevant results of the catalyst characterization are provided in Table 12.1. The results of the catalytic tests are summarized in Table 12.2.

3.2. Catalytic performance

Figure 12.2 shows the catalytic performance for the various catalysts at two different temperatures. It can be seen that all tested gold catalysts have propene epoxidation activity, but that the support very strongly influences this activity. The titania-supported catalyst had the highest activity at low temperatures (323 K), the titania–silica-supported catalysts were most active at 423 K, while the silica-supported catalysts were most active at 473 K (not shown in the figure, see Table 12.2). The titania-supported catalyst, even though active at low temperature, lost activity very rapidly (loss of activity is 75% in 5 h). This rapid deactivation is also the reason why the conversion of the catalyst dropped as the temperature was increased from 323 to 373 K. As the temperature increased, both the rates of epoxidation and deactivation increased. At longer reaction times, this caused the propene oxide yield to be lower with increasing temperature. This is made clear in Fig. 12.3, which shows that for an increasing reaction temperature, the time at which the maximum propene oxide yield is reached

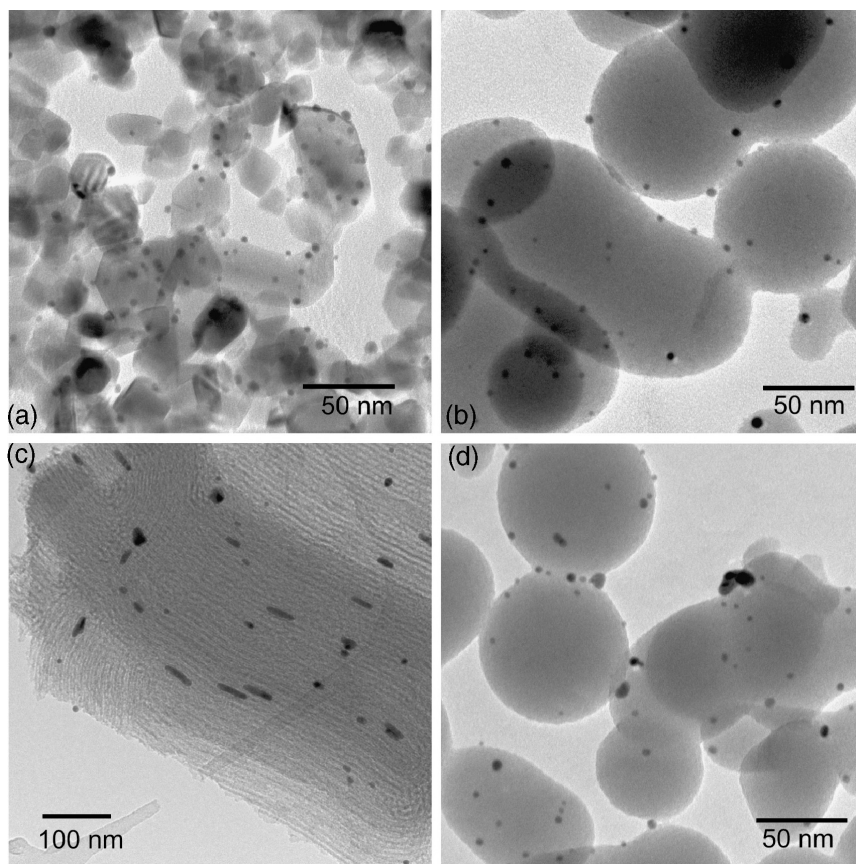


FIGURE 12.1 Selected transmission electron microscopy (TEM) pictures. (a) Au/TiO₂, (b) Au/Ti-SiO₂, (c) Au/Ti-SBA-15, and (d) Au/SiO₂ (OX50).

TABLE 12.1 Summary of catalyst characterization results

	Au/TiO ₂	Au/Ti-SiO ₂	Au/Ti-SBA-15	Au/SiO ₂ (Davisil)	Au/SiO ₂ (OX50)
BET area (m ² /g)	45	49	555	295	50
Au loading (wt.%)	0.92	0.94	1.01	1.04	1.02
Metal particle size (nm) (S.D.)	4.0 (1.1)	4.8 (1.8)	7.7 (1.8) ^a	3.5 (1.5)	4.0 (1.8)
Support Ti content (wt.% TiO ₂)	99.8	0.76	2.91	0.04	0.05

^a The gold particles size for the Au/Ti-SBA-15 sample is determined by the SBA-15 pores. The particle diameter for most particles is equal to the SBA-15 channel diameter. The channel restriction makes the particles elongated; the length of the particles is up to five times the diameter (see Fig. 12.1C). For these elongated particles, the diameter was taken.

TABLE 12.2 Summary of catalytic performance of the catalysts. [0.3 g of catalyst, 50 Nml/min gas feed rate (10% H₂, O₂, and propene), total pressure 1.1 bar(a).]

Catalyst	Propene conversion (%)				PO selectivity (%)				Hydrogen efficiency ^f (%)			
	323 K	373 K	423 K	473 K	323 K	373 K	423 K	473 K	323 K	373 K	423 K	473 K
(A) Average during 1–5 h of catalytic cycle												
Au/TiO ₂	0.18	0.10	1.36	2.78 ^b	99.9	77.6	2.2	0.0	11.3 (1.5)	1.7 (4.3)	0.1 (26.9)	0.0 (77.4)
Au/Ti-SiO ₂	0.03	0.14	0.45	0.80	100	99.9	87.6	61.2	8.6 (0.4)	5.9 (2.4)	4.2 (9.6)	1.8 (26.6)
Au/ Ti-SBA-15	0.01	0.26	0.61	1.38	100	93.9	83.8	42.2	1.6 (0.8)	8.4 (2.9)	5.3 (9.6)	2.3 (24.8)
Au/SiO ₂	0	0.06	0.48 ^b	1.78 ^b	–	40.8	61.5	59.0	0 (6.7)	0.1 (31.4)	0.2 ^a (100)	0.7 ^a (100)
(Davisil)												
Au/SiO ₂	0	0.04	0.18 ^b	1.31 ^b	–	7.2	51.3	62.9	0 (2.2)	0 (25.2)	0.1 (73.5)	0.7 ^a (100)
(OX50)												
(B) Average during 6–20 h of catalytic cycle												
Au/TiO ₂	0.05	0.08	1.45	2.53 ^b	100	74.5	1.7	0.0	7.1 (0.8)	1.5 (4.1)	0.1 (27.9)	0.0 (75.0)
Au/Ti-SiO ₂	0.02	0.10	0.42	0.73	100	100.0	85.8	62.8	7.9 (0.3)	5.2 (1.9)	4.3 (8.3)	1.8 (24.9)
Au/ Ti-SBA-15	0.04	0.17	0.46	1.28	100	94.9	84.2	43.9	7.8 (0.5)	7.6 (2.1)	4.8 (8.1)	2.4 (23.8)
Au/SiO ₂	0	0.06	0.49 ^b	1.79 ^b	–	23.2	60.4	59.2	0 (4.3)	0 (29.1)	0.2 ^a (100)	0.8 ^a (100)
(Davisil)												
Au/SiO ₂	0	0.03	0.29 ^b	1.31 ^b	–	0.0	47.2	62.0	0 (2.5)	0 (21.2)	0.3 (54.7)	0.7 ^a (100)
(OX50)												

^a Hydrogen efficiency restricted by hydrogen supply.^b For these experiments the actual catalyst temperature was significantly higher (15–20 K) than the oven temperature indicated as a result of the high conversion of hydrogen.^c Values between brackets for hydrogen efficiency denote hydrogen conversion.

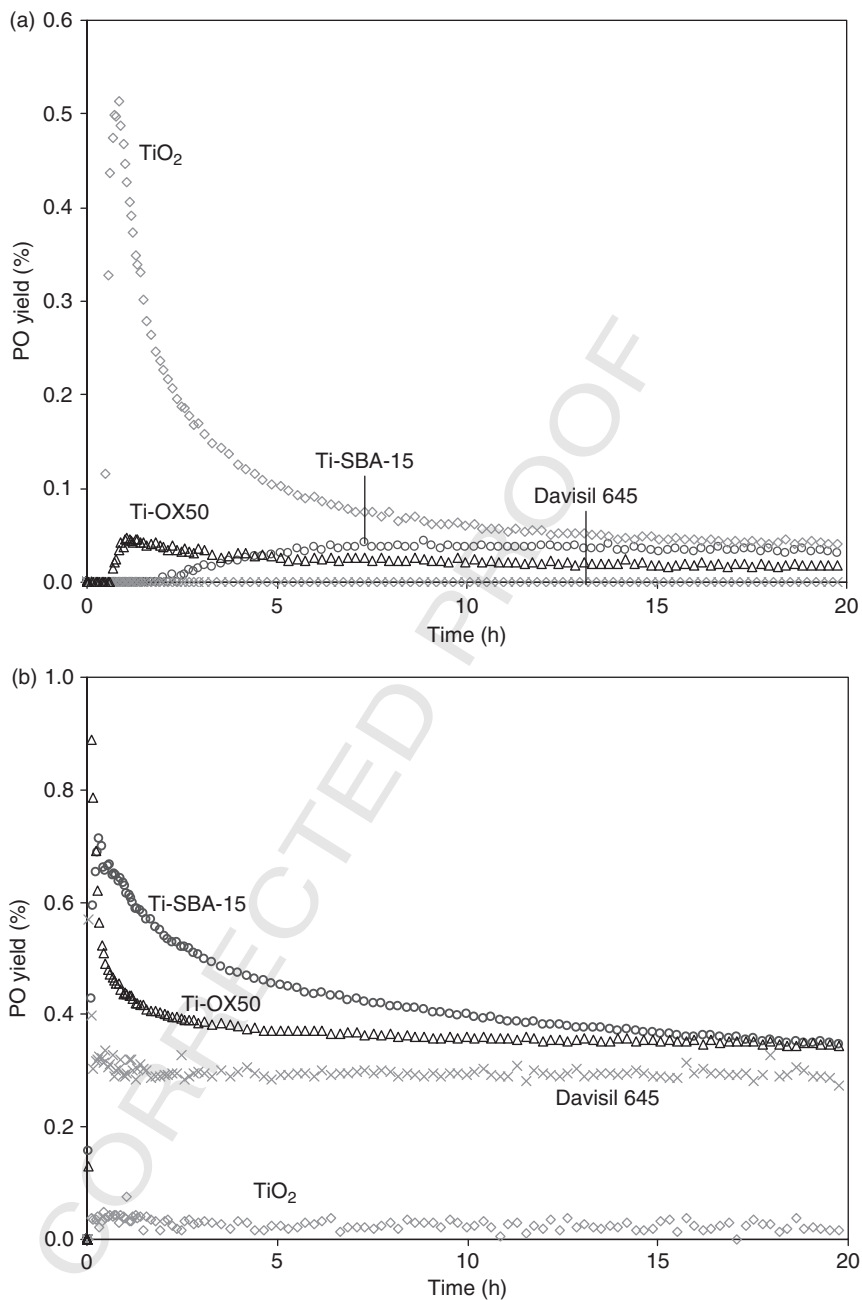


FIGURE 12.2 Catalytic performance at two selected reaction temperatures (A: 323 K, B: 423 K) for Au/TiO₂ (\diamond), Au/Ti-SBA-15 (\circ), Au/Ti-OX50 (Δ), and Au/Davisil 645 (\times). [0.3 g of catalyst, 50 Nml/min gas feedrate (10% H₂, O₂, and propene), total pressure 1.1 bar(a)].

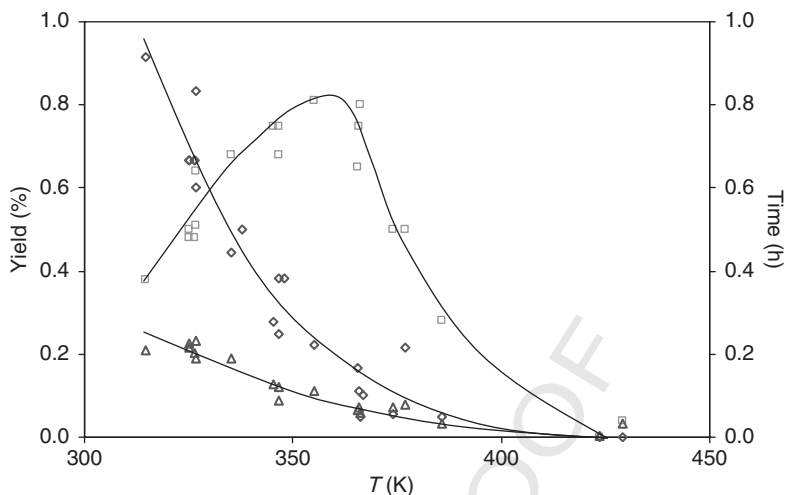


FIGURE 12.3 Average yield (Δ), maximum yield (\square), and time at which the maximum yield is obtained (\diamond) for propene epoxidation over 1 wt.% Au/TiO₂ at different reaction temperatures. [Lines are drawn as a guide to the eye; average conversion from 30 to 270 min reaction time, 0.3 g of catalyst, 50 Nml/min gas feedrate (10% H₂, O₂, and propene), total pressure 1.1 bar(a)].

decreases, and up to 373 K, the maximum obtained amount of propene oxide yield increases. The average propene oxide yield (from 0.5- to 4.5-h reaction time), however, decreased monotonously with increasing temperature. In Fig. 12.3 it can also be seen that for the gold on titania catalysts, there is a large difference between the average yield and the maximum yield. In most papers, the maximum propene oxide yield is reported, whereas in this work the emphasis is on the average yield over a few hours time, which explains why the catalyst activity is lower than other reported values.

The highest propene oxide yields were obtained with both the Ti-SBA-15- and the Ti-silica-supported catalysts, although a higher reaction temperature was needed in comparison to the titania-supported catalyst. The deactivation for these catalysts was also considerably less. At lower temperatures (up to 423 K), all catalysts had an inhibition period for both propene oxide and water formation, which is explained by product adsorption on the support. The side products produced by all catalysts were similar. Primarily, carbon dioxide and acetaldehyde were produced as side products and, in smaller quantities, also propanal, acrolein, acetic acid, and formaldehyde. Propanol (both 1- and 2- as well as propanediol), acetone, carbon monoxide, and methanol were only observed in trace amounts.

Given the fact that the gold particles were the largest for the Ti-SBA-15-supported catalysts and also for a large part inaccessible, as they are tightly restrained in the SBA-15 channels, it can be stated that this support is more promising for active propene epoxidation catalysts, once a different gold deposition method has been developed in which smaller uniform gold nanoparticles are formed in the channels. Optimally, uniform gold particles slightly larger than 2 nm

should be prepared in the SBA-15 channels, allowing for a high surface area and a good accessibility in the channels (no channel blockage). Smaller particles might be undesirable, considering the observation that on titania they started to catalyze the unwanted hydrogenation of propene to propane [18,19]. In another report for gold supported on titanosilicate, this shift in activity toward propene hydrogenation for smaller gold particles was not observed [12]. However, in our first attempts to produce smaller gold particles using an alternative preparation method, in which we produced a catalyst containing a significant amount of small (<2 nm) gold particles inside Ti-SBA-15, we also observed a strong shift toward a hydrogenation activity.

3.3. Catalyst deactivation

The deactivation for all catalysts could be reversed by a high temperature cycle at 573 K in 10% oxygen in helium, which indicates that the catalyst deactivation has to do with adsorbed species and not with sintering of the gold nanoparticles, since this would have been irreversible. This is confirmed by TEM analysis, which did not show a significant increase in the gold particle size of the “spent” catalysts. In Fig. 12.4, the particle size distributions for fresh and used (>200 h) samples of the titania- and silica (OX50)-supported catalysts are shown (>200 particles measured per sample). For the titania-supported catalyst a small increase is observed in the average particle size, for the silica-supported catalyst a small decrease is observed, both changes are considered to be within the accuracy of the method used.

Attempts to regenerate the catalyst by a high-temperature (573 K) treatment in helium, only partially restored the catalytic activity, indicating that the catalyst is cleaned primarily by combusting the adsorbed species rather than just desorbing them. Quasi *in situ* XPS measurements showed no changes in the oxidation state of gold of a calcined catalyst after it was exposed to hydrogen or oxygen at a temperature of up to 573 K. Testing the catalysts over a longer period of time (up to 10 days in multiple cycles) showed that the catalyst activity after an intermediate regeneration was stable [no loss in activity compared to the first cycle, or at worst only a minor loss in activity (the Au/Ti-SBA-15 was the least stable, this catalyst lost less than 5% of its activity)].

The link between the deactivation and the epoxidation is made clear in Fig. 12.5, in which the hydrogen oxidation reaction (no propene) is observed to be stable for 25 h. Once propene is added to the feed thereafter, the catalyst starts deactivating rapidly. Removal of the propene in the feed stops the deactivation process and the catalytic activity gradually increases. The fact that even after 25 h, the activity is not back to its original level, indicates that the deactivating species are bonded strongly to the catalyst.

Figure 12.6 shows a plot for the titania-supported catalyst of the catalytic activity versus the amount of propene oxide produced. It can be seen that initially (from the maximum activity to half of the maximum activity) the activity decreases linearly with the amount of propene oxide produced and only later on, that the rate of deactivation decreases. This behavior can be explained on the basis of the deactivation model based on spectroscopic data published

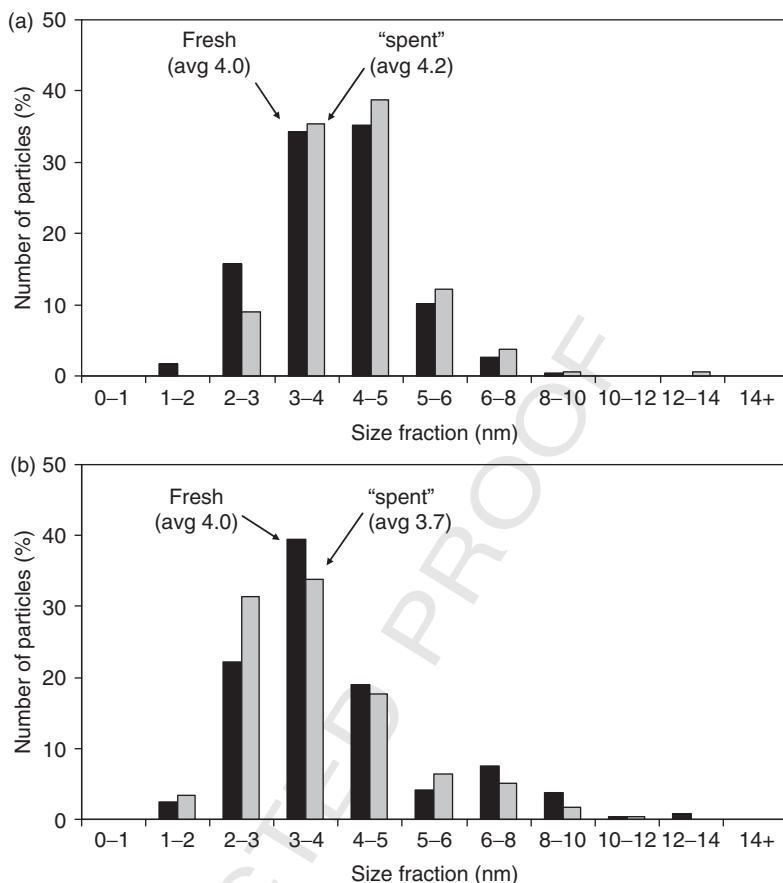


FIGURE 12.4 Particle size distributions of freshly prepared and “spent” (>200 h in operation) gold on titania (a) and gold on OX50 silica (b) catalysts as determined by transmission electron microscopy (TEM).

previously [20]. In this model, as a first step in the epoxidation, a bidentate propoxy species is formed on the titania (or titania/silica) support. The fact that the bidentate propoxy species is removed by a hydrogen/oxygen mixture from the catalyst surface indicates that it is indeed a reaction intermediate [6,11]. Both propene oxide and deactivated sites are formed in competing parallel reaction pathways from this bidentate propoxy species on the catalyst surface. Since the amount of propene oxide produced is related directly to the amount of bidentate propoxy species that were present on the surface and this same species produces the deactivating carbonate species, deactivation would be expected to be linked directly to the amount of propene oxide produced. At longer times, this direct relationship no longer applies because of a slow desorption of the deactivating carbonates. This is in agreement with the gradual increase in the activity observed for the hydrogen oxidation in Fig. 12.5, once the propene feed has been removed.

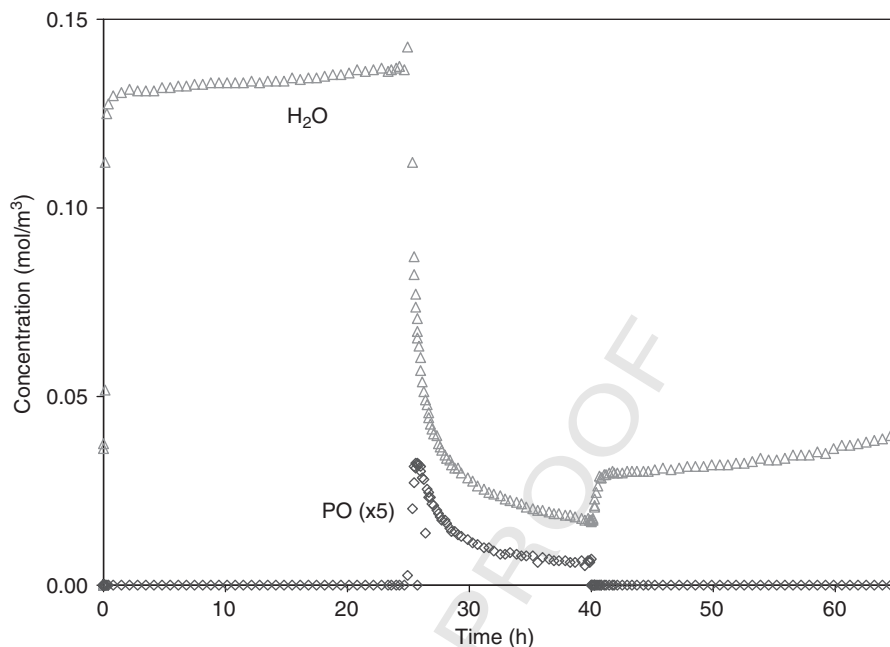


FIGURE 12.5 Deactivation during epoxidation and hydrogen oxidation over 1 wt.% Au/TiO₂. Twenty-five hours hydrogen oxidation only, followed by epoxidation for 15 h, followed by hydrogen oxidation only for 25 h. [0.3 g of catalyst, 50 Nml/min gas feedrate (6% H₂, O₂, and from $t = 25$ to 40 h propene), total pressure 1.1 bar(a).]

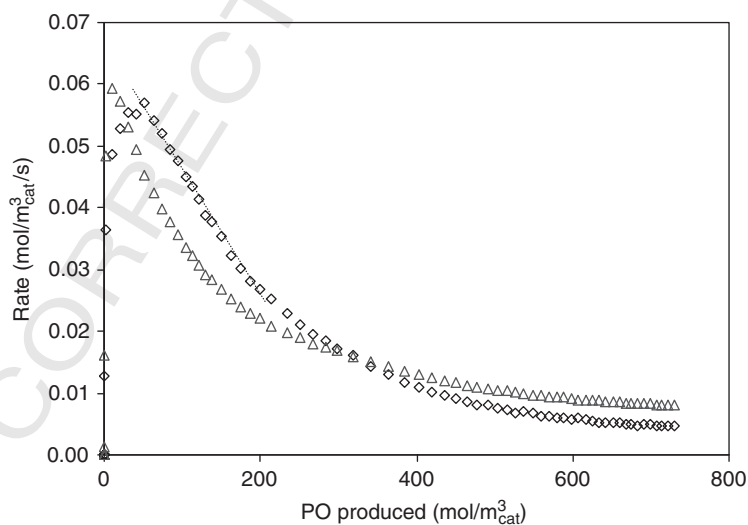


FIGURE 12.6 Deactivation versus the amount of propene oxide produced during the propene epoxidation over 1 wt.% Au/TiO₂. \diamond : propene oxide formation rate; \triangle : water formation rate/10. [0.3 g of catalyst, 50 Nml/min gas feedrate (10% H₂, O₂, and propene), total pressure 1.1 bar(a).]

In contrast to the bidentate propoxy species, *in situ* infrared experiments showed that the carbonate species could not be removed from the catalyst by exposing it to hydrogen/oxygen at reaction temperature [6,11].

To further verify the proposed deactivation model, Fig. 12.7 shows a very simple numerical model fitted to the propene epoxidation data shown in Fig. 12.6. The rate of deactivation in this model is assumed to be first order in the epoxidation rate, while the reactivation is first order in the deactivated sites. Numerically this simplified deactivation/reativation model can be expressed by Eq. (12.1):

$$\frac{\partial r_{\text{PO}}}{\partial t} = -k_{\text{deact}} \times r_{\text{PO}} + k_{\text{react}} \times (r_{\text{PO},0} - r_{\text{PO}}) \quad (12.1)$$

with t , time (s); r_{PO} , rate of propene epoxidation ($\text{mol}/\text{g}_{\text{cat}}/\text{s}$)—subscript 0 denotes the rate at $t = 0$; k_{deact} , rate constant for catalyst deactivation (formation of deactivating species) (s^{-1}); and k_{react} , rate constant for catalyst reactivation (desorption of deactivating species) (s^{-1}).

In Fig. 12.7, it can be seen that this simple model describes the observed activity pattern well. Only in the first half hour of the experiment, a discrepancy exists between the rate predicted by the model and the observed rate. This can be explained by product adsorption on the support as discussed previously [20], which was not included in this model. A more extensive version of this simplified deactivation model, which includes the occupancies of all surface species, is published elsewhere [21].

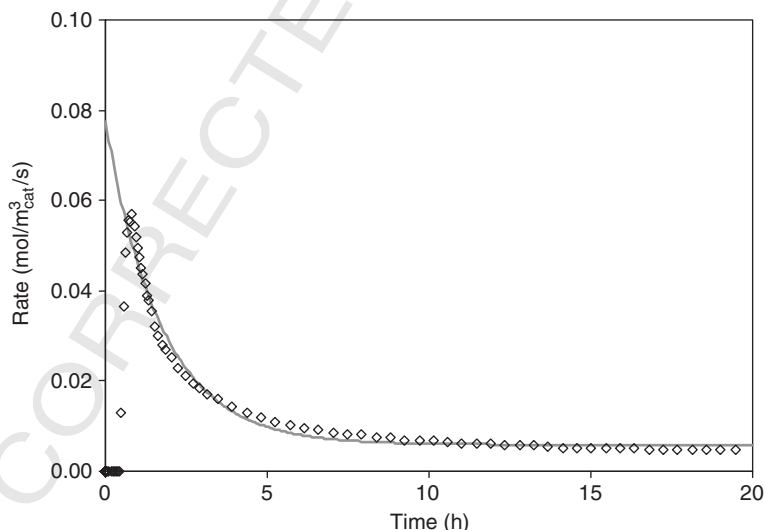


FIGURE 12.7 Deactivation modeled based on a first-order deactivation in the amount of propene oxide and a first-order reactivation of the deactivated sites [according to Eq. (1)]. Model fitted to data from $t = 0.75$ to 20 h. Propene epoxidation over 1 wt.% Au/TiO₂. \diamond : measured propene oxide formation rate; line: modeled rate. [0.3 g of catalyst, 50 Nml/min gas feedrate (10% H₂, O₂, and propene), total pressure 1.1 bar(a).]

If the rate of hydrogen oxidation (water formation) is examined versus the amount of propene oxide produced, it can be seen that the hydrogen oxidation also decreases, but not linearly with the propene oxide produced, and also more slowly than the epoxidation. This indicates that the direct hydrogen oxidation also proceeds over sites other than those involved in the epoxidation. The fact that the hydrogen oxidation rate as such does decrease, points to the support playing a role in this reaction as well, although according to other studies this reaction proceeds exclusively over the gold nanoparticles [22]. Several spectroscopic studies (using both Raman and infrared spectroscopy) carried out by us showed that no (strongly) adsorbed species on the gold particles could be detected under reaction conditions. This role of the support in the hydrogen oxidation should be seen as, for example, the formation of peroxide species on the gold, which then subsequently decompose over the support, since experiments performed over the bare support materials showed no activity.

For the catalysts supported on Ti–Si carriers or on pure silica, the lower deactivation rate can be explained in two ways. First, a bidentate propoxy intermediate on the surface is no longer bonded to two Ti sites on the catalyst (due to the low Ti loading), but to both a Ti and an Si site, or only to silica sites. This affects the relative ratio between the deactivation and propene oxide formation reactions. This reduced deactivation indicates that the energetics are relatively more favorable toward the epoxidation. The bidentate propoxy species most likely is more susceptible to C–C bond breakage, which would trigger the deactivating consecutive oxidation of this species, because of the higher acidity of the titania support compared to the Ti–silica and silica supports. Second, the silica and Ti–silica catalysts require a higher reaction temperature to produce propene oxide. At this higher temperature, the desorption of deactivating carbonate species is faster. The need for the higher reaction temperature can be explained by the weaker reactivity of the support to produce the bidentate propoxy intermediate species compared to the titania-supported catalysts. *In situ* spectroscopic infrared experiments [11] show that the largest amount of bidentate propoxy species could be observed on titania-supported catalysts, while considerably smaller amounts could be observed on Ti–silica-supported catalysts, and no measurable amount could be detected on silica-supported catalysts.

Both catalysts supported on silica produce a small amount of propene oxide at the highest temperatures; however, the selectivities remain low, proving the necessity of titania on the support to have an effective epoxidation catalyst. Furthermore, these catalysts by far have the lowest hydrogen efficiency because of the direct oxidation of hydrogen into water, making the economics of these catalysts very unattractive.

4. CONCLUSIONS

Gold nanoparticle catalysts have a good potential for a future process for the direct epoxidation of propene. In a single reactor, propene can be selectively epoxidized using a hydrogen–oxygen mixture. Catalysts containing titanium

dispersed on or in a silica support yield the highest amount of propene oxide at a high selectivity and reasonably good stability. If the maximum propene oxide yield is determined per gold surface site, the Ti-SBA-15-supported catalysts are the most active; however, the deposition of small gold particles in the mesopore structure requires further optimization. Titania-supported catalysts are intrinsically the most active; however, they severely suffer from deactivation by a sequential oxidation of the bidentate propoxy reaction intermediate. Catalyst deactivation is caused by carbonate formation on the catalyst, which can be removed easily by means of a simple regeneration in air at 573 K.

A major challenge that remains is the hydrogen efficiency of the catalyst. Since the propene epoxidation is performed in the presence of hydrogen, it is desirable that the hydrogen is used only in the epoxidation reaction and is not converted directly into water. At this time none of the catalysts have a sufficiently high hydrogen efficiency to be able to run a process profitable and, therefore, this remains one of the key challenges to be solved for this catalyst system for propene epoxidation.

ACKNOWLEDGMENTS

STW/NWO is kindly acknowledged for the VIDI grant supporting the research of T.A.N. and E.S. NWO/CW is kindly acknowledged for the VICI grant supporting the research of B.M.W.

REFERENCES

- [1] T. A. Nijhuis, M. Makkee, J. A. Moulijn, B. M. Weckhuysen, The production of propene oxide: Catalytic processes and recent developments, *Ind. Eng. Chem. Res.* 45 (2006) 3447.
- [2] D. L. Trent, Propylene Oxide, Kirk-Othmer: Encyclopedia of Chemical Technology, Wiley, New York, NY 2001.
- [3] M. Haruta, Size- and support-dependency in the catalysis of gold, *Catal. Today* 36 (1997) 153.
- [4] B. Taylor, J. Lauterbach, W. N. Delgass, Gas-phase epoxidation of propylene over small gold ensembles on TS-1, *Appl. Catal. A* 291 (2005) 188.
- [5] A. K. Sinha, S. Seelan, M. Okumura, T. Akita, S. Tsubota, M. Haruta, Three-dimensional mesoporous titanasilicates prepared by modified sol-gel method: Ideal gold catalyst supports for enhanced propene epoxidation, *J. Phys. Chem. B* 109 (2005) 3956.
- [6] T. A. Nijhuis, T. Visser, B. M. Weckhuysen, The role of gold in gold-titania epoxidation catalysts, *Angew. Chem. Int. Ed.* 44 (2005) 1115.
- [7] A. K. Sinha, S. Seelan, S. Tsubota, M. Haruta, A three-dimensional mesoporous titanasilicate support for gold nanoparticles: Vapor-phase epoxidation of propene with high conversion, *Angew. Chem. Int. Ed.* 43 (2004) 1546.
- [8] A. H. Tullo, P. L. Short, Propylene oxide routes take off, *Chem. Eng. News* 84 (2006) 22.
- [9] T. A. Nijhuis, B. J. Huizinga, M. Makkee, J. A. Moulijn, Direct epoxidation of propene using gold dispersed on TS-1 and other titanium-containing supports, *Ind. Eng. Chem. Res.* 38 (1999) 884.
- [10] A. Zwijnenburg, M. Makkee, J. A. Moulijn, Increasing the low propene epoxidation product yield of gold/titania-based catalysts, *Appl. Catal. A* 270 (2004) 49.
- [11] T. A. Nijhuis, T. Visser, B. M. Weckhuysen, A mechanistic study into the direct epoxidation of propene over gold-titania catalysts, *J. Phys. Chem. B* 109 (2005) 19309.
- [12] N. Yap, R. P. Andres, W. N. Delgass, Reactivity and stability of Au in and on TS-1 for epoxidation of propylene with H₂ and O₂, *J. Catal.* 226 (2004) 156.

- [13] A. K. Sinha, S. Seelan, T. Akita, S. Tsubota, M. Haruta, Vapor phase propylene epoxidation over Au/Ti-MCM-41 catalysts prepared by different Ti incorporation modes, *Appl. Catal. A* 240 (2003) 243.
- [14] M. Weisbeck, C. Schild, G. Wegener, G. Wiessmeier, Surface-modified mixed oxides containing precious metal and titanium for the selective oxidation of hydrocarbons, *US Patent 6734133*, 2004, Assigned to BASF.
- [15] G. Mul, A. Zwijnenburg, B. van der Linden, M. Makkee, J. A. Moulijn, Stability and selectivity of Au/TiO₂ and Au/TiO₂/SiO₂ catalysts in propene epoxidation: An *in situ* FT-IR study, *J. Catal.* 201 (2001) 128.
- [16] B. S. Uphade, M. Okumura, S. Tsubota, M. Haruta, Effect of physical mixing of CsCl with Au/Ti-MCM-41 on the gas-phase epoxidation of propene using H₂ and O₂: Drastic depression of H₂ consumption, *Appl. Catal. A* 190 (2000) 43.
- [17] E. Sacaliuc, A. Beale, B. M. Weckhuysen, T. A. Nijhuis, Propene epoxidation over Au-Ti-SBA-15 catalysts, *J. Catal.* 248 (2007) 234.
- [18] M. Haruta, M. Date, Advances in the catalysis of Au nanoparticles, *Appl. Catal. A* 222 (2001) 427.
- [19] T. Hayashi, K. Tanaka, M. Haruta, Selective vapor-phase epoxidation of propylene over Au/TiO₂ catalysts in the presence of oxygen and hydrogen, *J. Catal.* 178 (1998) 566.
- [20] T. A. Nijhuis, B. M. Weckhuysen, The direct epoxidation of propene over gold-titania catalysts—A study into the kinetic mechanism and deactivation, *Catal. Today* 117 (2006) 84.
- [21] T. A. Nijhuis, T. Q. Gardner, B. M. Weckhuysen, Modeling of kinetics and deactivation in the direct epoxidation of propene over gold-titania catalysts, *J. Catal.* 236 (2005) 153.
- [22] D. G. Barton, S. G. Podkolzin, Kinetic study of a direct water synthesis over silica-supported gold nanoparticles, *J. Phys. Chem. B* 109 (2005) 2262.