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Research Note

Switching off propene hydrogenation in the direct epoxidation of propene over gold–titania catalysts

Jiaqi Chen, Sander J.A. Halin, Dulce M. Perez Ferrandez, Jaap C. Schouten, T. Alexander Nijhuis *

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

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ABSTRACT

Low gold-loaded gold–titanium catalysts with very small gold nanoparticles for the direct epoxidation of propene have a remarkably high epoxidation activity. A disadvantage, however, is that these catalysts in certain cases also have a very high activity for the unwanted hydrogenation of propene to propane. The addition of a small amount of carbon monoxide to the feed gas can completely switch off this propene hydrogenation, while at the same time also reducing the rate of direct water formation. The co-ordination environment of titanium plays an important role in propene hydrogenation.

1. Introduction

Gold nanoparticles or clusters supported on titanium-containing supports are capable of epoxidizing propene to propene oxide (PO) by using hydrogen and oxygen at a high selectivity [1–4]. However, propene hydrogenation may occur or even prevail under certain circumstances as reported in literature: the particle size of gold supported on TiO_2 is smaller than 2 nm [1]; or Ti-based oxides are used as supports while the gold size is out of the range of 2–5 nm [5]; and recently, supported gold (+1) cyanide particles were reported to show a high selectivity toward propene hydrogenation [6]. Significant propane formation is rarely reported when titanium silicalite-1 (TS-1) is used as the support. Qi et al. [5] proposed that the contaminant of sodium on the catalysts is responsible for inhibiting propene hydrogenation on Ti-based gold catalysts.

After our recent paper [7] examining the effect of reactant concentrations on the epoxidation reaction over a Au/Ti–SiO_2 catalyst, we performed a study concerning the synergy between gold and titanium sites by simply adjusting the metal loadings. In literature, the trend for the gold–titania system is to go to low gold loadings with highly isolated Ti^{4+} sites [8–11]. These low-loaded catalysts generally have a higher PO productivity, although a higher reaction temperature is needed. The gold particle size of these catalysts is smaller. As a result, the relative amount of Au–Ti interface may be higher, which is often seen as the active site [12–15,7]. The smaller particle size, however, makes these catalysts more susceptible to propane formation [1]. Sacaliuc et al. [16] showed that the epoxidation activity of Au/Ti–SBA-15 can be related to the differences in the amount of grafted Ti. The work by Delgass's group [17] has shown that Ti-defects in TS-1 can boost the activity of Au/TS-1 in direct propene epoxidation. It is also known that Ti-defects on a silica surface can stabilize the supported gold nanoparticles/clusters [18,19]. In our study, titanium was grafted onto a commercial silica using titanium alkoxide as precursor by the surface sol–gel method. Gold was then deposited to the calcined support by the deposition–precipitation method, resulting in the Au/Ti–SiO_2 catalysts. The aim of the study on the site synergy was to obtain a catalyst with a higher epoxidation activity and higher hydrogen efficiency. Although catalysts with higher epoxidation activities were obtained, significant propane formation was observed over almost all the catalysts we prepared, which consequently reduced the hydrogen efficiency to a large extent (see Table 1). On the other hand, we found that introducing small amount of carbon monoxide in the reactant feeds suppressed propene hydrogenation over these catalysts without affecting propene epoxidation. We provide here evidence for the inhibiting effect of carbon monoxide on propene hydrogenation in the direct epoxidation of propene over Au/Ti–SiO_2 catalysts.

2. Experimental

The catalyst with 0.05 wt.% gold supported on the 1% monolayer Ti over SiO_2 (theoretical Ti/Si atom ratio on the silica surface), which has the highest PO formation rate in terms of per unit

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* Corresponding author. Fax: +31 40 2446653.
E-mail address: t.a.nijhuis@tue.nl (T.A. Nijhuis).

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Table 1
Maximum PO formation rates obtained on the Au/Ti–SiO$_2$ catalysts with different gold loadings over the 1% monolayer[a] Ti–SiO$_2$ and the corresponding selectivities.

Loading[b] (Au wt.%)	$r_{PO,\ max}$[f] (g kg$_{cat}^{-1}$ h^{-1})	T (°C)	Selectivity (%)		H_2 efficiency (%)[c]
			PO	C_3H_8	
0.05	113 (226)	210	26	69	7.8
0.09	122 (135)	192	23	73	8.1
0.20	131 (67)	184	38	53	5.4
0.48	85 (18)	164	45	40	4.0
0.63[e]	60 (10)	151	67	7	2.2

[a] 0.27 wt.% Ti as determined by induced coupled plasma (ICP) analysis.
[b] Determined by ICP analysis.
[c] Determined as $r_{PO}/(r_{H_2O} + r_{C_3H_8})$.
[e] Nominal 1 wt.% Au.
[f] Numbers in brackets are in terms of $g_{PO}\ g_{Au}^{-1}\ h^{-1}$.

weight of gold, is selected in this paper to show the catalytic performance with and without the addition of carbon monoxide. The preparation procedure for the 0.05 wt.% Au/Ti–SiO$_2$(1% ML) catalyst is described in detail in the Supplementary information. Since the preparation method used for our catalysts does not introduce sodium, an amount of 300 mg of the 0.05 wt.% Au/Ti–SiO$_2$(1% ML) catalyst was impregnated with sodium sulfate solution and was dried in vacuum at room temperature overnight. The resulting catalyst has a sodium loading of 0.5 wt.%. Catalytic tests were performed in a flow setup equipped with a fast Interscience Compact gas chromatography system (3 min analysis time) consisting a Porabond Q column and a Molsieve 5A column in two separate channels, each with a thermal conductivity detector; 300 mg of catalyst was tested under the standard reaction condition, typically with a gas feed rate of 50 mL min^{-1} in total, consisting of 10 vol.% (each) of hydrogen, oxygen, and propene (helium balance). Carbon monoxide was introduced at the concentration 1 vol.% when required. The quartz reactor is located in an oven and has an inner diameter of 6 mm.

3. Results and discussion

The general performance of the 0.05 wt.% Au/Ti–SiO$_2$(1% ML) catalyst is provided in the Supplementary information. In Fig. 1, the effect of carbon monoxide addition on the formation rates of PO, water, and propane is shown for the 0.05 wt.% Au/Ti–SiO$_2$(1% ML) catalyst. When the experiment started, the catalyst bed temperature increased sharply from *ca.* 190 °C for over 10 °C due

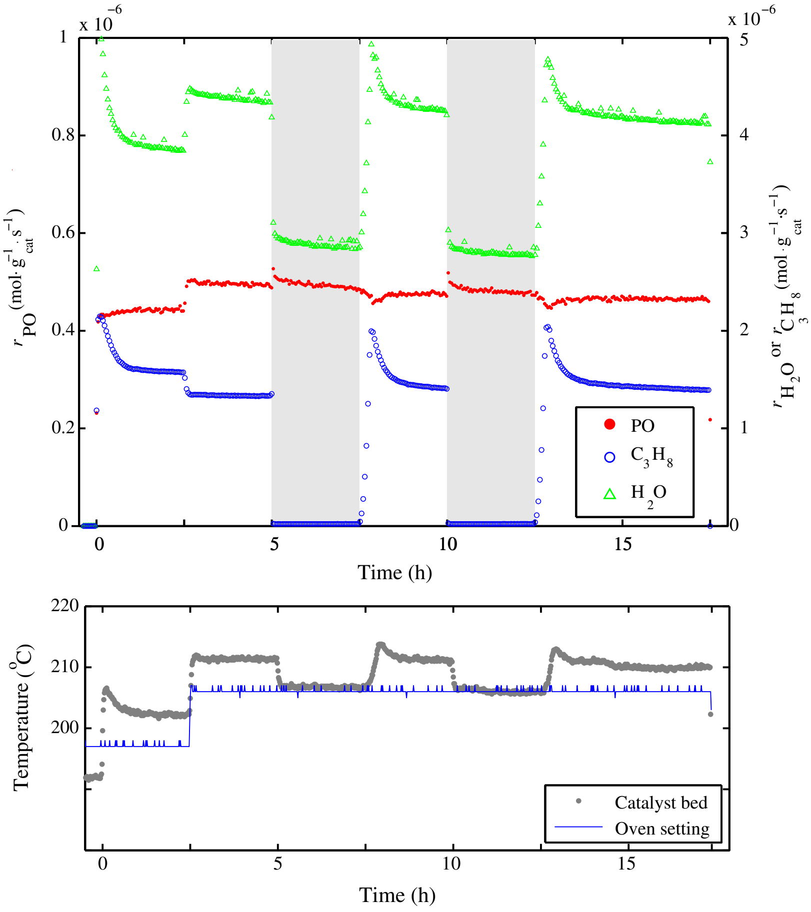

Fig. 1. Time-on-stream performance of the 0.05 wt.% Au/Ti–SiO$_2$(1% ML) catalyst (top) and the catalyst bed temperature (bottom) with and without CO addition (gas feed 10 vol.% H$_2$, 10 vol.% O$_2$ and 10 vol.% C$_3$H$_6$ in helium, GHSV 10, 000 mL g$_{cat}^{-1}$ h^{-1}, grayed area: 1 vol.% CO introduced between 5–7.5 h and 10–12.5 h).

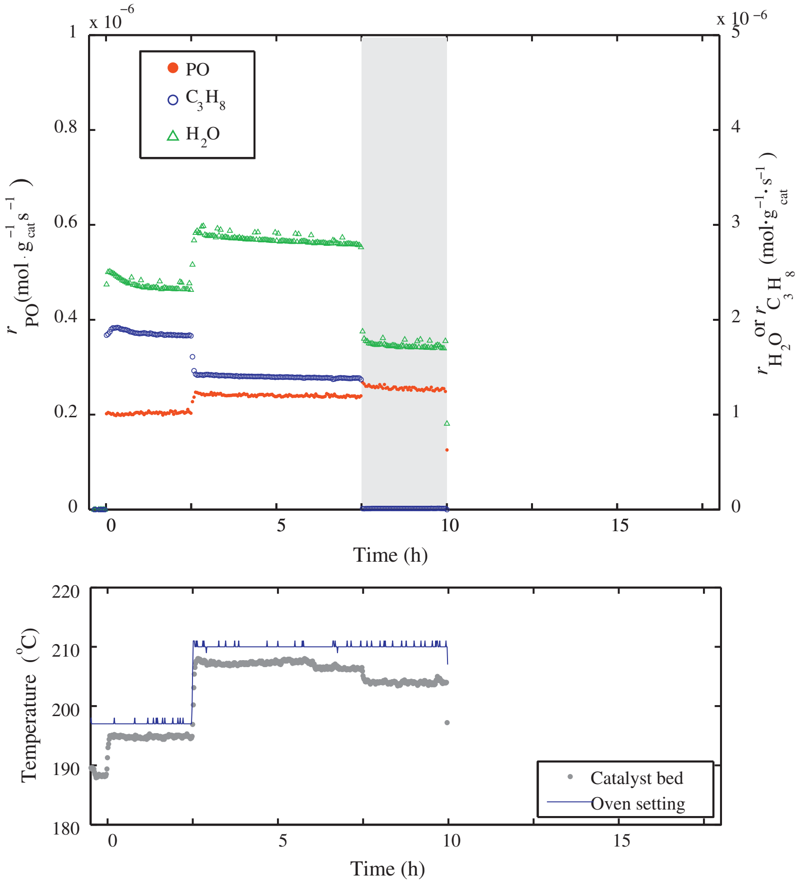

Fig. 2. Time-on-stream performance of the 0.05 wt.% Au/Ti–SiO_2(1% ML) catalyst impregnated with 0.5 wt.% sodium (top) and the catalyst bed temperature (bottom) with and without CO addition (gas feed 10 vol.% H_2, 10 vol.% O_2 and 10 vol.% C_3H_6 in helium, GHSV 10, 000 mL g_{cat}^{-1} h^{-1}, grayed area: 1 vol.% CO introduced between 7.5 and 10 h).

to the exothermic reactions. The temperature stabilized at around 200 °C after about 1 h. At $t = 2.5$ h, the catalyst bed temperature was raised to 210 °C to determine the temperature influence on the formation rate of propane. From $t = 2.5$ h till the end of the experiment, the oven temperature was kept constant. Carbon monoxide was introduced into the gas feed at a low concentration of 1 vol.% during the time intervals between 5–7.5 h and 10–12.5 h. The formation rate of propane dropped immediately by two orders of magnitude without affecting the epoxidation reaction as carbon monoxide was added. Meanwhile, water formation was also suppressed. Accordingly, the catalyst bed temperature dropped by about 5 °C. During the co-feeding of carbon monoxide, the hydrogen efficiency increased from 8% to 17%. The conversion of carbon monoxide was low at the level of 10%. An increase in the formation rate of carbon dioxide was observed when carbon monoxide was added, but this was only the result of carbon monoxide conversion while not of propene combustion. Hydrogenation of carbon monoxide to methane was not observed. Removing carbon monoxide restored the catalyst activity in propene hydrogenation (7.5–10 h, 12.5 h–17.5 h). The result in the first 5 h showed that propane formed at a higher rate when the reaction temperature was lower on this catalyst. Therefore, the suppression of propane formation between 5–7.5 h and 10–12.5 h can be completely attributed to carbon monoxide addition. While the addition of 0.05 vol.% of carbon monoxide can already reduce 80% of propane formation on our catalysts (Fig. S2), a concentration of 1 vol.% for carbon monoxide may be needed to keep the ratio of propane and PO formation rates below 0.05. The inhibition of the propane formation rate by carbon monoxide is staggeringly high: the reaction order for the inhibiting effect is minus 3.

The effect of adding sodium to the 0.05 wt.% Au/Ti–SiO_2(1% ML) catalyst was also investigated to compare the effect of the carbon monoxide addition on suppressing the hydrogenation reaction to the recently published approach of adding sodium [5]. The results are shown in Fig. 2. When the reaction started, the catalyst bed temperature increased instantly from *ca.* 190 °C to 195 °C. The catalyst bed temperature was raised to around 207 °C at $t = 2.5$ h by increasing the oven temperature. Carbon monoxide (1 vol.%) was introduced into the gas feed from $t = 7.5$ h till the end ($t = 10$ h). As seen from Fig. 2, the existence of sodium has no significant effect on propene hydrogenation over our catalyst. However, the formation of PO and water was suppressed after sodium sulfate impregnation comparing to the original activity shown in Fig. 1. It should be noted here that both sodium and sulfate might have great potential in modifying the catalyst acidity [20]. Fig. 2 clearly shows that addition of carbon monoxide inhibited propene hydrogenation without affecting propene epoxidation over the sodium-impregnated catalyst, while sodium had little effect on hydrogenation. The recent work by Haruta's group [5] proposed that propane formation could be reduced by sodium addition to the catalysts. Our results show that such a modification to the catalyst is apparently not as simple as it seems. Carbon monoxide addition, however, is a very simple and highly effective way to block propane formation (for the case where propene hydrogenation is unavoidable in the propene epoxidation under an atmosphere of hydrogen and oxygen), which we determined to be effective for all our catalysts.

We also observed that the formation rate of propane kept increasing from zero until it leveled off during the activation of our catalysts, while PO formation rate was stable at a high level from the very beginning (Fig. S3). Our results imply that propene hydrogenation and epoxidation may happen on two different sites. The size effect of gold nanoparticles is undoubtedly important in hydrogen dissociation during the direct propene epoxidation [1,21,5], since Au–Ti^{4+} interface is indispensable for the direct propene epoxidation. Carbon monoxide might be competitively adsorbed on gold where hydrogen adatoms locate and thus abate the propene hydrogenation. It could also be the situation that Ti–OH induces hydrogen dissociation (on gold or with Ti), while carbon monoxide may poison the Ti–OH group probably by forming surface formate species, or the Ti site if the stability of possible titanium species at reduced oxidation states is an issue [22]. It has been observed by Sykes et al. [23] that hydroxylated titania surface under partial reduction is capable of hydrogenating a terminal alkene. It has also been proposed that transition metals anchored on SiO_2 can hydrogenate alkene probably by forming hydride complexes [24]. The catalytic performance of our catalyst, and one step further, of the hydroxylated support only, in hydrogen and propene but without oxygen clearly shows that the surface hydroxyl, most likely Ti–OH, plays an important role in propene hydrogenation and that gold is not of necessity for propane formation (Figs. S4 and S5). The enhancement of propane formation by oxygen observed by Qi et al. [5] may be partly attributed to water formation in the presence of oxygen and accordingly the hydration/hydroxylation of catalyst surface. On the other hand, it is generally accepted that tripodal Ti^{4+} sites are favoured in liquid-phase epoxidation when concerning the co-ordination environment of titanium in silica-supported titanium catalysts [25–27]. Hydrothermal instability [28] of such tripodal Ti sites leads to the formation of bipodal and monopodal Ti sites on silica surface, which, combined with vicinal silanols, might contribute to propene hydrogenation in the complex system of propene, hydrogen, and oxygen over gold–titania catalysts. Our experimental observations suggest that on the supports where Ti–O–Si or Ti–O–Ti linkage is not that resistant to hydrolysis, the role of support in propene hydrogenation should be taken into account.

4. Conclusions

High productivity of propene oxide has been achieved in the direct epoxidation of propene over gold supported on titania–silica catalysts. Propene hydrogenation can occur on these catalysts. During the direct propene epoxidation over gold–titania catalysts when hydrogen is co-fed, propene hydrogenation can be inhibited by introducing carbon monoxide. Though we cannot explain how this inhibition occurs, it is most likely by an interaction between carbon monoxide and Ti, since propene hydrogenation is most likely proceeding over the support.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.09.022.

References

[1] T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 178 (1998) 566.
[2] E.E. Stangland, K.B. Stavens, R.P. Andres, W.N. Delgass, J. Catal. 191 (2000) 332.
[3] G. Mul, A. Zwijnenburg, B. Van der Linden, M. Makkee, J.A. Moulijn, J. Catal. 201 (2001) 128.
[4] T.A. Nijhuis, B.J. Huizinga, M. Makkee, J.A. Moulijn, Ind. Eng. Chem. Res. 38 (1999) 884.
[5] C. Qi, J. Huang, S. Bao, H. Su, T. Akita, M. Haruta, J. Catal. 281 (2011) 12.
[6] J. Gaudet, K. Bando, Z. Song, T. Fujitani, W. Zhang, D. Su, S. Oyama, J. Catal. 280 (2011) 40.
[7] J. Chen, S.J.A. Halin, J.C. Schouten, T.A. Nijhuis, Faraday Discuss. (2011), doi:10.1039/c1fd00014d.
[8] L. Cumaranatunge, W.N. Delgass, J. Catal. 232 (2005) 38.
[9] B. Taylor, J. Lauterbach, W.N. Delgass, Appl. Catal. A 291 (2005) 188.
[10] J. Lu, X. Zhang, J.J. Bravo-Suárez, T. Fujitani, S.T. Oyama, Catal. Today 147 (2009) 186.
[11] J. Huang, T. Takei, T. Akita, H. Ohashi, M. Haruta, Appl. Catal. B 95 (2010) 430.
[12] T.A. Nijhuis, T. Visser, B.M. Weckhuysen, J. Phys. Chem. B 109 (2005) 19309.
[13] B. Chowdhury, J.J. Bravo-Suárez, N. Mimura, L. Jiqing, K.K. Bando, S. Tsubota, M. Haruta, J. Phys. Chem. B 110 (2006) 22995.
[14] B. Taylor, J. Lauterbach, G.E. Blau, W.N. Delgass, J. Catal. 242 (2006) 142.
[15] J. Lu, X. Zhang, J.J. Bravo-Suárez, S. Tsubota, J. Gaudet, S.T. Oyama, Catal. Today 123 (2007) 189.
[16] E. Sacaliuc, A.M. Beale, B.M. Weckhuysen, T.A. Nijhuis, J. Catal. 248 (2007) 235.
[17] B. Taylor, J. Lauterbach, W.N. Delgass, Catal. Today 123 (2007) 50.
[18] W. Yan, B. Chen, S.M. Mahurin, E.W. Hagaman, S. Dai, S.H. Overbury, J. Phys. Chem. B 108 (2004) 2793.
[19] W.T. Wallace, B.K. Min, D.W. Goodman, J. Mol. Catal. A: Chem. 228 (2005) 3.
[20] X. Gao, I.E. Wachs, Catal. Today 51 (1999) 233.
[21] T. Fujitani, I. Nakamura, T. Akita, M. Okumura, M. Haruta, Angew. Chem. Int. Ed. 48 (2009) 9515.
[22] Y. Li, B. Xu, Y. Fan, N. Feng, A. Qiu, J. He, J. Miao, H. Yang, Y. Chen, J. Mol. Catal. A: Chem. 216 (2004) 107–114.
[23] E.C.H. Sykes, M.S. Tikhov, R.M. Lambert, Catal. Lett. 78 (2002) 7.
[24] Yu. I. Yermakov, Y.A. Ryndin, O.S. Alekseev, D.I. Kochubey, V.A. Shmachkov, N.I. Gergert, J. Mol. Catal. 49 (1989) 121.
[25] M. Crocker, R.H.M. Herold, A.G. Orpen, M.T.A. Overgaag, Dalton Trans. (1999) 3791–3804.
[26] J.K.F. Buijink, J.J.M. van Vlaanderen, M. Crocker, F.G.M. Niele, Catal. Today 93–95 (2004) 199–204.
[27] J.M. Fraile, J.I. García, J.A. Mayoral, E. Vispe, J. Catal. 233 (2005) 90–99.
[28] J. Zhou, Z. Hua, X. Cui, Z. Ye, F. Cui, J. Shi, Chem. Commun. 46 (2010) 4994–4996.