

Kinetic study of propylene epoxidation with H_2 and O_2 over $Au/Ti-SiO_2$ in the explosive regime: Supplementary information

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1 Characterization of the support

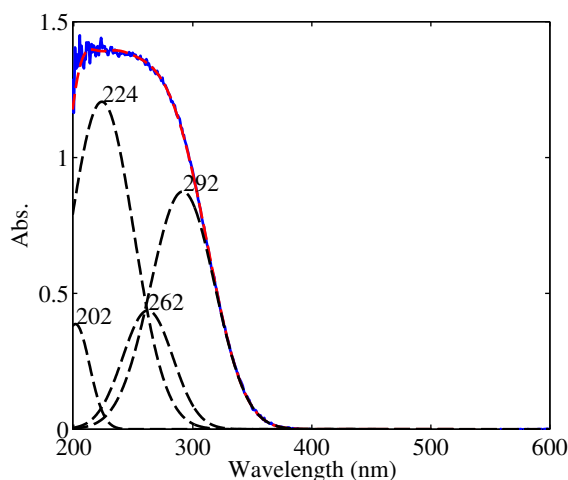


Fig. S1 Deconvoluted DRUV-visible spectrum of $Ti-SiO_2$ (5 % monolayer) with the band at 202 nm assigned to tetrahedral tetrapodal Ti, the band at 224 nm assigned to tetrahedral tripodal Ti, and the bands at 262 nm and 292 nm probably best assigned to penta- and hexacoordinated Ti structures from dinuclear Ti species.

2 Difference in activation energy

The formation rate of water due to the decomposition or hydrogenation of the active peroxy intermediate, which is also responsible for epoxidation on the active Au-Ti centers, can be given by Equation S.1,

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$$r_{\text{H}_2\text{O,d}} = k_1 \theta_{\text{OOH}}^{\text{Au}} P_{\text{H}_2} \theta_{\text{O}}^{\text{Au}} \cdot \theta_{\text{H}}^{\text{Au}} \cdot N_{\text{active}} \quad (\text{S.1})$$

where $N_{\text{active}} = N_{\text{Au-Ti}}(1 - \theta_{\text{d}})$, $N_{\text{Au-Ti}}$ is the total number of Au-Ti sites, and θ_{d} is the fraction of deactivated sites. The $r_{\text{H}_2\text{O,d}}$ here is excluded from the water formed from the epoxidation, i.e., form $\text{H}_2 + \text{O}_2 + \text{C}_3\text{H}_6 \rightarrow \text{PO} + \text{H}_2\text{O}$.

The observed formation rate of propene oxide is given by Equation S.2 with the assumption that one molecule of propene oxide may cause one deactivated Au-Ti center:

$$r_{\text{PO}} = k_2 \theta_{\text{OOH}}^{\text{Au}} P_{\text{H}_2} \theta_{\text{O}}^{\text{Au}} \cdot \theta_{\text{C}_3\text{H}_6}^{\text{Ti}} \cdot N_{\text{active}} - N_{\text{Au-Ti}} \cdot \left(\frac{d\theta_{\text{d}}}{dt} \right)_{\text{deactivating}} \quad (\text{S.2})$$

The $\theta_{\text{OOH}}^{\text{Au}}$, $\theta_{\text{O}}^{\text{Au}}$, $\theta_{\text{H}}^{\text{Au}}$, and $\theta_{\text{C}_3\text{H}_6}^{\text{Ti}}$ in Equations S.1 and S.2 are the coverage based on the sites that remain active but not on the total Au-Ti sites.

When the amount of deactivating species accumulated on the active Au-Ti sites is far less than the amount of propene oxide formed within a short period of time (Condition 1), the second term on the RHS of Equation S.2 can be omitted:

$$r_{\text{PO}} = k_2 \theta_{\text{OOH}}^{\text{Au}} P_{\text{H}_2} \theta_{\text{O}}^{\text{Au}} \theta_{\text{C}_3\text{H}_6}^{\text{Ti}} \cdot N_{\text{active}} \quad (\text{S.3})$$

Since $E_{\text{a}}^{\text{obs}} = RT^2 (\partial \ln r / \partial T)_P$, the difference between the overall activation energy of water formation and PO formation can be expressed by

$$\frac{E_{\text{a,H}_2\text{O}}^{\text{obs}} - E_{\text{a,PO}}^{\text{obs}}}{RT^2} = \left(\frac{\partial \ln \frac{r_{\text{H}_2\text{O,d}}}{r_{\text{PO}}}}{\partial T} \right)_P \quad (\text{S.4})$$

By integrating Equation S.4, Equation 7 in Section 3.4 can be obtained.

Equation 7 in Section 3.4 should satisfy the precondition that within a short period of time the amount of deactivating species accumulated on the active Au-Ti sites is far less than the amount of propene oxide formed. This should be checked by comparing the turn over frequency of deactivating species formation (TOF_{d}) and that of propene oxide formation (TOF_{PO}) based on the total number of Au-Ti sites. TOF_{d} can be easily estimated from Equation 4 in Section 3.2 by $k_{\text{deact}} r_{\text{PO}}$. At the standard condition at 403 K, $k_{\text{deact}} r_{\text{PO}}$ is estimated to be at the level of $5 \times 10^{-4} \text{ s}^{-1}$. The total amount of gold on the catalyst used in this study is $4.6 \times 10^{-5} \text{ mol} \cdot \text{g}_{\text{cat}}^{-1}$. The fraction of active gold atoms at corners and edges is roughly estimated to be 0.15 based on the mean particle size 4.5 nm.^{1,2} By assuming that each titanium alkoxide molecule forms three Ti-O-Si bonds on the silica surface, the chance that a gold atom on the edge contacts a titanium atom is therefore 0.15. The estimated TOF_{PO} is at the level of 0.3 s^{-1} , which means that the deactivation is indeed 3 orders of magnitude lower. Actually, this precondition is expected to be satisfied, otherwise a complete deactivation within few minutes should be observed. Furthermore, since in our deactivation model, the deactivation and subsequent reactivation should produce complete oxidation products, thus we could also predict that the deactivation is much slower than the epoxidation based on the product composition. Stable performance is achieved starting from the temperature 453 K and the CO_2 formation rate increases significantly above that temperature (Figure 5(a) and Table 1).

From Equations S.1 and S.3, we have

$$\frac{r_{\text{H}_2\text{O,d}}}{r_{\text{PO}}} = \frac{k_1}{k_2} \cdot \frac{\theta_{\text{H}}^{\text{Au}}}{\theta_{\text{C}_3\text{H}_6}^{\text{Ti}}} \quad (\text{S.5})$$

$$\ln \frac{r_{\text{H}_2\text{O,d}}}{r_{\text{PO}}} = \ln \frac{A_1}{A_2} - \frac{E_{\text{a,H}_2\text{O}} - E_{\text{a,PO}}}{RT} + \ln \theta_{\text{H}}^{\text{Au}} - \ln \theta_{\text{C}_3\text{H}_6}^{\text{Ti}} \quad (\text{S.6})$$

When the quasi equilibrium is reached on the active sites, $\theta_{\text{H}}^{\text{Au}}$ and $\theta_{\text{C}_3\text{H}_6}^{\text{Ti}}$ can be given by

$$\theta_{\text{H}}^{\text{Au}} = \frac{\sqrt{K_{\text{H}_2} P_{\text{H}_2}}}{1 + \sqrt{K_{\text{H}_2} P_{\text{H}_2}}} \quad (\text{S.7})$$

and

$$\theta_{\text{C}_3\text{H}_6}^{\text{Ti}} = \frac{K_{\text{C}_3\text{H}_6} P_{\text{C}_3\text{H}_6}}{1 + K_{\text{C}_3\text{H}_6} P_{\text{C}_3\text{H}_6} + K_{\text{PO}} P_{\text{PO}}} \quad (\text{S.8})$$

Thus we have

$$\begin{aligned} \left(\frac{\partial \ln \theta_{\text{H}}^{\text{Au}}}{\partial T} \right)_P &= \frac{1}{2} (1 - \theta_{\text{H}}^{\text{Au}}) \left(\frac{\partial \ln K_{\text{H}_2}}{\partial T} \right)_P \\ &= \frac{1}{2} (1 - \theta_{\text{H}}^{\text{Au}}) \frac{\Delta H_{\text{ads,H}_2}}{RT^2} \end{aligned} \quad (\text{S.9})$$

and

$$\left(\frac{\partial \ln \theta_{\text{C}_3\text{H}_6}^{\text{Ti}}}{\partial T} \right)_P = (1 - \theta_{\text{C}_3\text{H}_6}^{\text{Ti}}) \frac{\Delta H_{\text{ads,C}_3\text{H}_6}}{RT^2} - \theta_{\text{PO}}^{\text{Ti}} \frac{\Delta H_{\text{ads,PO}}}{RT^2} \quad (\text{S.10})$$

The difference in apparent activation energy can be described by

$$\begin{aligned} E_{\text{a,H}_2\text{O}}^{\text{obs}} - E_{\text{a,PO}}^{\text{obs}} &= E_{\text{a,H}_2\text{O}} - E_{\text{a,PO}} + \frac{1}{2} (1 - \theta_{\text{H}}^{\text{Au}}) \Delta H_{\text{ads,H}_2} - \\ &\quad (1 - \theta_{\text{C}_3\text{H}_6}^{\text{Ti}}) \Delta H_{\text{ads,C}_3\text{H}_6} + \theta_{\text{PO}}^{\text{Ti}} \Delta H_{\text{ads,PO}} \end{aligned} \quad (\text{S.11})$$

3 Relationship between selectivity and hydrogen efficiency

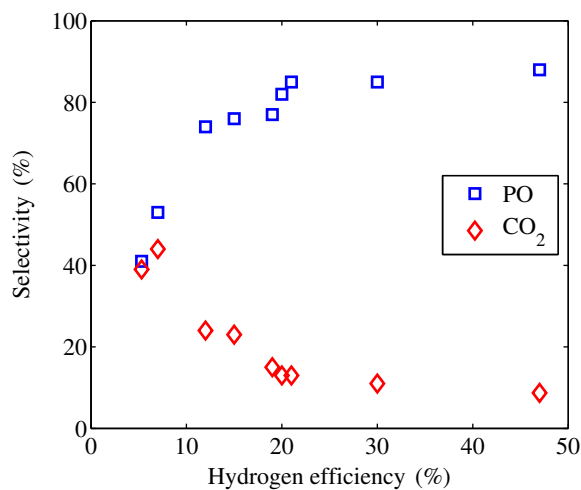


Fig. S2 Relationship between the product selectivity and the hydrogen efficiency (adapted from Table 3 in the paper by Huang et al.³).

References

- 1 A. Carlsson, A. Puig-Molina and T. V. W. Janssens, *J. Phys. Chem. B*, 2006, **110**, 5286–5293.
- 2 C. J. Weststrate, A. Resta, R. Westerström, E. Lundgren, A. Mikkelsen and J. N. Andersen, *J. Phys. Chem. C*, 2008, **112**, 6900–6906.
- 3 J. Huang, T. Takei, T. Akita, H. Ohashi and M. Haruta, *Appl. Catal., B*, 2010, **95**, 430–438.