Isotope labelling study of CO oxidation-assisted epoxidation of propene. Implications for oxygen activation on Au catalysts†

Jian Jiang,[a] Sean M. Oxford,[b] Baosong Fu,[c] Mayfair C. Kung,*[b] Harold H. Kung*[b] and Jiantai Ma[d]

Received 7th January 2010, Accepted 18th March 2010
First published as an Advance Article on the web 15th April 2010
DOI: 10.1039/c000374c

^{18}O isotope labelling studies of the CO oxidation-assisted epoxidation of propene, catalyzed by a mixture of Au/TiO_2 and TS-1, using a methanol–H_2O solvent showed the O in the epoxide was exclusively from O_2 and not H_2O or methanol.

Although the high activity of supported Au catalysts for low temperature CO oxidation has been known for some time,[1,2] the detailed mechanism of this reaction has not been resolved. Adsorbed CO has been detected by IR under conditions relevant to catalysis,[3,4] but information about the adsorbed oxygen is noticeably lacking. In particular, the manner in which molecular oxygen is activated remains unknown. Unlike other noble metals, such as Pt and Pd, that are less active but nonetheless good oxidation catalysts, there is no evidence of dissociative adsorption of oxygen on Au under catalytically relevant conditions. Conventional temperature programmed desorption experiments could not detect any oxygen desorption from a sample that had been treated in a flow of O_2, and there is no useful spectroscopic evidence of adsorbed oxygen.

Computational studies offered some insight into the oxygen activation/adsorption process. Molecular (associative) adsorption appears feasible,[5–7] and it is enhanced by coadsorption of water[8] or the presence of negative charges on the Au cluster.[8–10] However, the role of this form of adsorbed O_2 in catalysis has yet to be established.[11,12] Associative adsorption of O_2 was also proposed in the reaction mechanism without any supporting evidence.[13,14]

Recent experimental evidence offered some insight into the form of adsorbed oxygen important in CO oxidation. When CO oxidation was conducted in an aqueous medium, significant amounts of H_2O_2 were formed, even in the absence of H_2.[15] Whereas the formation of H_2O_2 from H_2 and O_2 is thermodynamically feasible and the reaction can be catalyzed by Au,[16–18] the oxidation of H_2O to form H_2O_2:

$$H_2O(l) + 1/2O_2 \rightarrow H_2O_2(l) \qquad (1)$$

is thermodynamically highly unfavourable (ΔG° = 116.8 kJ mol^{-1}). Thus, for this reaction to occur during CO oxidation, it must be mechanistically coupled to CO oxidation so as to achieve a thermodynamically favourable (ΔG° = −140.4 kJ mol^{-1}) overall reaction of:

$$CO + H_2O(l) + O_2 \rightarrow H_2O_2(l) + CO_2 \qquad (2)$$

The fact that eqn (1) is thermodynamically highly unfavourable argues that the mechanism to form H_2O_2 cannot involve dissociative adsorption of O_2 to form two identical adsorbed O atoms, which react independently with H_2O in two identical, parallel pathways. This is because each of these two pathways would be thermodynamically unfavourable. It follows that the two O atoms of the activated O_2 responsible for H_2O_2 formation during CO oxidation must react differently.

In our effort to gain insight into the CO oxidation-assisted peroxide formation process, we coupled it with epoxidation of alkene and probed the origin of the O in the epoxide with ^{18}O isotope. This Au-catalyzed, liquid phase CO oxidation was conducted by bubbling a gas mixture of CO, O_2, propene, and He through a suspension of Au/TiO_2 and TS-1 catalysts. TS-1 is a titanium substituted silicalite that is active for epoxidation of alkenes using H_2O_2.[19] The rates of CO, O_2, and propene consumption and formation of volatile products, including propene oxide (PO), acetone, propanediol, and 2-propanol, were monitored by analyzing the gas phase products at the reactor exit periodically with an on-line GC-MS. CO_2 was also analyzed, but its rate of formation could not be calculated accurately from the exit gas due to significant dissolution into the liquid. At the conclusion of the experiment, the liquid phase was analyzed for organic products by GC-MS, and for peroxides by titration. More experimental details are in Supplementary Information.†

Table 1 shows some representative results. (See Table S1† for a more complete set of results and additional experiments.) When H_2O was the solvent, propanediol was the majority organic product, most probably formed by hydrolysis of propene oxide (Exp. 1). However, when the liquid contained >80% methanol, propene oxide was formed selectively, without any detectable propanediol (Exp. 2 and 5). This could be a consequence of the hydrophobic nature of the TS-1 pores that partitions CH_3OH preferentially to H_2O. Within the uncertainties (estimated 10%) in both O_2 and propene balances over the course of the experiment, little combustion or hydration of propene had occurred under these conditions. Titration identified the presence of peroxide in the liquid (last column, Table 1),

---

[a] *On leave from the College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PRC*
[b] *Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208-3120, USA. E-mail: hkung@northwestern.edu, m-kung@northwestern.edu*
[c] *On leave from the School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PRC*
[d] *College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PRC*

† Electronic supplementary information (ESI) available: Catalyst preparation and characterization, experimental details, reaction system, product analyses, and more illustrative reaction results. See DOI: 10.1039/c000374c

Table 1 Results for liquid phase CO oxidation-assisted epoxidation of propene

			Reaction rate,[b] μmol min^{-1}			Quantity,[c] 10^{-5} moles			
Exp.[a]	Liquid composition MeOH–H_2O, mL : mL	Rxn time, min	CO	O_2	Alkene	Total PO, ±1	Other products[d]	C_3H_6 cons. ±2	–OOH[e] ±0.2
1	0 : 50	292	2.5	1.6	0.83	2.7	14.6	24	0.34
2	40 : 10	232	11	5.8	0.88	21	Trace	22	0.72
5	47.5 : 2.5	251	4.0	2.5	0.81	23	Trace	20	0.37
7	50 : 0	> 100	0	0	0	0	0	0	Nd
8	47.5(EtOH) : 2.5[f]	240	1.8	1.1	0.08	1.5	Trace	2 ± 1	Nd

[a] Reaction conditions: 100 mg Au/TiO_2 + 150 mg TS-1, 40 °C, 480 kPa total pressure; gas feed: 2.5% CO, 1.25% O_2, 1.65% propene in He, total flow rate 40 mL min^{-1}; 50 mL liquid (CH_3OH + H_2O). [b] Steady state rates, determined by analysis of composition of gas exiting the reactor. [c] Sum of products formed or propene consumed over the reaction time indicated, determined from both the gas and liquid phase compositions. [d] Only byproduct detected in any significant amount was propanediol in Exp. 1. [e] Total peroxide (H_2O_2 + ROOH) in the liquid at conclusion of experiment. [f] Ethanol was used instead of methanol.

but the technique could not distinguish H_2O_2 from other peroxides, such as CH_3OOH. When methanol was replaced by ethanol (Exp. 8), the CO oxidation rate decreased by a factor of about 2.5, and propene oxide formation by over a factor of 10. The slower epoxidation rate in ethanol than in methanol has been reported, although the decrease was less than that observed here.[20] Control experiments showed little propene oxide formation when either Au/TiO_2 (not shown) or TS-1 (Exp. 8, Table S1†) was missing from the catalyst mixture, supporting the hypothesis that a stable intermediate oxidant was formed on Au/TiO_2 that diffuses to TS-1 to effect epoxidation. CO was necessary (Exp. 9, Table S1†), confirming that this intermediate oxidant cannot be formed by oxidation of water or methanol directly, but by a mechanism that is coupled to CO oxidation. Finally, when methanol was replaced by acetonitrile in the solvent (47.5/2.5 acetonitrile–H_2O, Exp. 9), no propene oxide was formed, no peroxide was detected in the liquid by titration, and the CO oxidation activity was low.

$H_2{}^{18}O$ was used to determine whether the formation of propene oxide in experiments using a CH_3OH–H_2O mixture was from H_2O_2. We reasoned that oxidation of $H_2{}^{18}O$ would form $H^{18}O^{16}OH$, and consequently, the epoxide formed would be 50 : 50 ^{16}O : ^{18}O-labeled. Table 2 shows the results of these experiments (Exps. 12–14). Only ^{16}O-labeled PO was detected both in the exit gas and the liquid. In contrast, a distribution of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$, enriched in ^{18}O content, was detected in the gas phase product. The formation of a distribution of isotopically labelled CO_2 indicates oxygen scrambling between CO_2 and H_2O, most likely *via* a bicarbonate intermediate.

Complementary experiments were conducted using $^{18}O_2$ in the feed. The results (Exp. 15 and 16) show that only ^{18}O-labeled PO was formed until at least 1 h into the experiment, when small amounts of ^{16}O-labeled PO began to appear. Interestingly, the CO_2 was mostly labelled with ^{16}O, consistent with rapid isotope scrambling with water. A similar observation was obtained using the ethanol–H_2O solvent (Exp. 17). Only ^{18}O-labelled PO was formed when using $^{18}O_2$. In addition to the fact that the methanol results have been repeated (Table 2), other evidence also suggested that these results were not experimental artifacts due to scrambling in the detection system. Injection of a solution of unlabelled propene oxide in $H_2{}^{18}O$ into the GC-MS did not change the cracking pattern of the propene oxide (Fig. S3†), although a huge m/z = 20 peak due to the labelled water was observed. In the experiments using $H_2{}^{18}O$, trace amounts of ^{18}O-labelled (> 90% labelled) acetone could be detected, which was likely formed by hydration of propene followed by oxidative dehydrogenation of the propanol product. Thus, labelled reactive organics could be detected accurately.

These results show that H_2O, although necessary for CO oxidation, is not involved directly in the epoxidation reaction. We believe that the role of moisture is to maintain the activity of the active site on Au for CO oxidation, as suggested in the literature.[21] Alcohol is needed for epoxidation, which does not occur in the acetonitrile–water solvent. Whereas the data unequivocally show the formation of a stable intermediate oxygen carrier that is formed from O_2 on Au/TiO_2 and diffuses to TS-1 to effect epoxidation, unfortunately, there is no direct observation on the nature of this intermediate. Two logical possibilities are: H_2O_2 and CH_3OOH (or C_2H_5OOH if ethanol is used).

H_2O_2 could be formed according to Scheme 1a. O_2 is adsorbed on the active site on Au/TiO_2 as peroxy or superoxide, which reacts with CO to form CO_2 and an adsorbed O. The adsorbed O may react with another CO in a nonproductive pathway, or react with methanol to form a surface OH and a CH_2OH radical. Two surface OH combine to form H_2O_2 which carries the same isotope label as O_2. This mechanism would postulate $HOCH_2CH_2OH$ as a byproduct. Unfortunately, we searched for but could not detect its presence, although its concentration might be too low for detection.

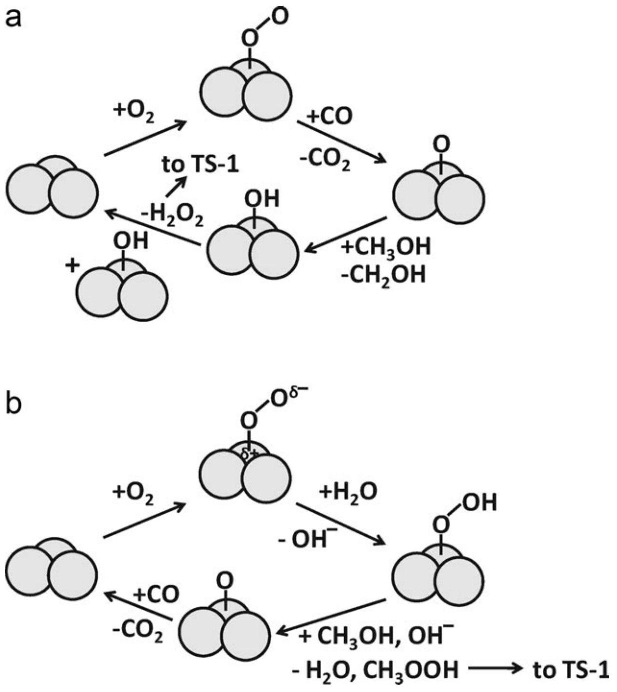
Alternatively, the Au-superoxide picks up a proton from water or methanol to form Au-peroxide (Scheme 1b), which reacts with methanol or methoxide to form CH_3OOH, in which the O of the OH would have the same isotope label as O_2. The methylhydroperoxide is responsible for propene epoxidation. In the literature, it has been reported that stable alkylperoxide can be formed by catalytic oxidation of alkane with H_2O_2 under reaction conditions similar to those used here.[22,23] Reaction of Au-superoxide with CO would lead to nonproductive consumption of CO.

We have provided isotope labelling evidence to show that the source of oxygen in propene epoxide in the liquid phase, Au-catalyzed CO oxidation-assisted epoxidation of propene is from O_2 and not H_2O. A stable intermediate, formed on Au with a mechanism that is coupled to CO oxidation, serves as

Table 2 Results of ^{18}O-labeled experiments

				Isotope distribution in products[b]	
Exp.[a]	H_2O isotope ratio, $^{18}O/^{16}O$	O_2 isotope ratio, $^{18}O/^{16}O$	Reaction time, min	$C^{18}O_2 : C^{18}O^{16}O : C^{16}O_2$	$P^{18}O : P^{16}O$
12	1/0	0/1	310	4.8 : 6.8 : 1	0 : 1
13	1/0	0/1	110	5.2 : 6.4 : 1	0 : 1
14	1/0	0/1	120	4.8 : 6.3 : 1	0 : 1
			240	4.8 : 6.3 : 1	0 : 1
15	0/1	1/0	60	0 : 0.1 : 1	1 : 0
			180	0 : 0.1 : 1	1 : 0
16	0/1	1/0	120	0 : 0.02 : 1	1 : 0
17	0/1	1/0	120	0 : 0.1 : 1	1 : 0
			180	0 : 0.1 : 1	1 : 0

[a] Reaction conditions same as Table 1; $CH_3OH–H_2O = 47.5 : 2.5$ except Exp. 16, which was 40 : 10, and Exp. 17 which used ethanol instead of methanol. [b] CO_2 in the gas product stream, and propene oxide in both gas and liquid products.



Scheme 1 Proposed mechanisms for formation of oxygen-carrying intermediate.

the oxygen carrier to TS-1 where epxoidation occurs. However, the nature of this oxygen carrier is not established, and additional experiments are needed to identify this intermediate and to establish the reaction mechanism. These results offer a novel method to perform epoxidation using green reagents, since the reactants (CO, O_2, and alcohol) and the byproduct (CO_2) are environmentally much more friendly than the typical reagents used, such as nitrous oxide, oxychlorides, and oxometal complexes.

Work was supported by the U.S. Department of Energy, Basic Energy Sciences grant DE-FG02-01ER15184. Jian Jiang was supported in part by the China Scholarship Council. The mechanism shown in Scheme 1 was suggested by a reviewer.

Notes and references

1 M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301–309.
2 M. C. Kung, R. J. Davis and H. H. Kung, *J. Phys. Chem. C*, 2007, **111**, 11767–11775.
3 F. Menegazzo, M. Manzoli, A. Chiorino, F. Boccuzzi, T. Tabakova, M. Signoretto, F. Pinna and N. Pernicone, *J. Catal.*, 2006, **237**, 431–434.
4 J. D. Henao, T. Caputo, J. H. Yang, M. C. Kung and H. H. Kung, *J. Phys. Chem. B*, 2006, **110**, 8689–8700.
5 T. Visart de Bocarme, T. D. Chau, F. Tielens, J. Andres, P. Gaspard, R. L. C. Wang, H. J. Kreuzer and N. Kruse, *J. Chem. Phys.*, 2006, **125**, 054703.
6 F. Tielens, J. Andres, M. Van Brussel, C. Buess-Hermann and P. Geerlings, *J. Phys. Chem. B*, 2005, **109**, 7624–7630.
7 X. Ding, Z. Li, J. Yang, J. G. Hou and Q. Zhu, *J. Chem. Phys.*, 2004, **120**, 9594–9600.
8 W. T. Wallace, R. B. Wyrwas, R. L. Whetten, R. Mitric and V. Bonacic-Koutecky, *J. Am. Chem. Soc.*, 2003, **125**, 8408–8414.
9 G. Mills, M. S. Gordon and H. Metiu, *J. Chem. Phys.*, 2003, **118**, 4198–4205.
10 L. M. Molina and B. Hammer, *J. Chem. Phys.*, 2005, **123**, 161104.
11 A. Roldan, S. Gonzalez, J. M. Ricart and F. Illas, *ChemPhysChem*, 2009, **10**, 348–351.
12 S. Yotsuhashi, Y. Yamada, T. Kishi, W. A. Dino, H. Nakanishi and H. Kasai, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 115413.
13 J. J. Bravo-Suarez, K. K. Bando, J. Lu, M. Haruta, T. Fujitani and S. T. Oyama, *J. Phys. Chem.*, 2008, **112**, 1115–1123.
14 J. J. Bravo-Suarez, K. K. Bando, T. Fujitani and S. T. Oyama, *J. Catal.*, 2008, **257**, 32–42.
15 W. C. Ketchie, M. Murayama and R. J. Davis, *Top. Catal.*, 2007, **44**, 307–317.
16 E. E. Stangland, K. B. Stavens, R. P. Andres and W. N. Delgass, *J. Catal.*, 2000, **191**, 332–347.
17 B. S. Uphade, M. Okumura, N. Yamada, S. Tsubota and M. Haruta, *Stud. Surf. Sci. Catal.*, 2000, **130**, 833–838.
18 E. Sacaliuc, A. M. Beale, B. M. Weckhuysen and T. A. Nijhuis, *J. Catal.*, 2007, **248**, 235–248.
19 M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71–83.
20 S. M. Danov, A. V. Sulimov and A. V. Sulimova, *Russ. J. Appl. Chem.*, 2008, **81**, 1963–1966.
21 C. K. Costello, J. H. Yang, H. Y. Law, Y. Wang, J. N. Lin, L. D. Marks, M. C. Kung and H. H. Kung, *Appl. Catal., A*, 2003, **243**, 15–24.
22 G. B. Shul'pin, M. V. Kirillova, T. Sooknoi and A. J. L. Pombeiro, *Catal. Lett.*, 2008, **123**, 135–141.
23 L. S. Shul'pina, M. V. Kirillova, A. J. L. Pombeiro and G. B. Shul'pin, *Tetrahedron*, 2009, **65**, 2424–2429.