

Low-Temperature Catalytic H₂ Oxidation over Au Nanoparticle/TiO₂ Dual Perimeter Sites**

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Dedicated to Professor Gerhard Ertl on the occasion of his 75th birthday
and to the Fritz Haber Institute, Berlin, on the occasion of its 100th anniversary

The catalytic oxidation of H₂ is of great interest due to its role in H₂O₂ synthesis, catalytic oxidation of hydrocarbons, and the selective removal of CO from hydrogen streams^[1] as well as for its simplicity which makes it ideal for fundamental bond making and breaking studies. This is especially true for supported Au nanoparticles which were found to show unusually high activity by Haruta et al.^[2] Previous explanations for this activity have invoked quantum size effects for Au particles in the 2 nm range,^[3] electronic effects in thin films of Au,^[4] and enhancement of the fraction of perimeter sites.^[5] Recent experiments on inverse TiO₂/Au catalysts have suggested that the enhanced catalytic activity may be due to active sites at the TiO₂/Au interface rather than a quantum size effect.^[5b,6]

The presence of H₂ gas in CO + O₂ reaction streams is known to produce enhanced catalytic activity for CO oxidation over Au/TiO₂ catalysts. The promotional effect originates from the addition of H₂ and has been ascribed to H₂'s ability to regenerate the catalyst by reducing the hydrocarbon accumulation^[1d,e] or by its reaction with O₂ to form hydroperoxy (OOH*) intermediates which readily oxidize CO.^[7] Previous theoretical studies have provided unique insights for this reaction, but have only focused on the role of Au.^[7c,8] To our best knowledge, there are no reported theoretical studies on the H₂ + O₂ reaction that have considered the influence or involvement of the TiO₂ perimeter sites at the Au–TiO₂ interface. Herein, we use kinetic analyses together with in situ infrared spectroscopic studies and density functional theory (DFT) calculations to examine the activity of the Au sites as well as the Au and TiO₂ perimeter sites at the Au–TiO₂ interface and elucidate a

plausible reaction mechanism. (We define a perimeter site as a Au or TiO₂ site at the external boundary between Au and TiO₂ surfaces. A dual perimeter site involves a Au perimeter site and a TiO₂ perimeter site that operate together during the catalytic reaction.)

High-vacuum transmission IR experiments were used to follow H₂O production on Au/TiO₂ powder synthesized by the deposition–precipitation method (see Supporting Information, sections I, II and Figure S1 for further details).^[9] The average Au particle size is approximately 3 nm, determined by transmission electron microscopy (Figure S2).

It has been reported that atomic H dissolved in TiO₂^[10] may be detected by the IR background upward shift, which is caused by trapped electrons from H in the conduction band

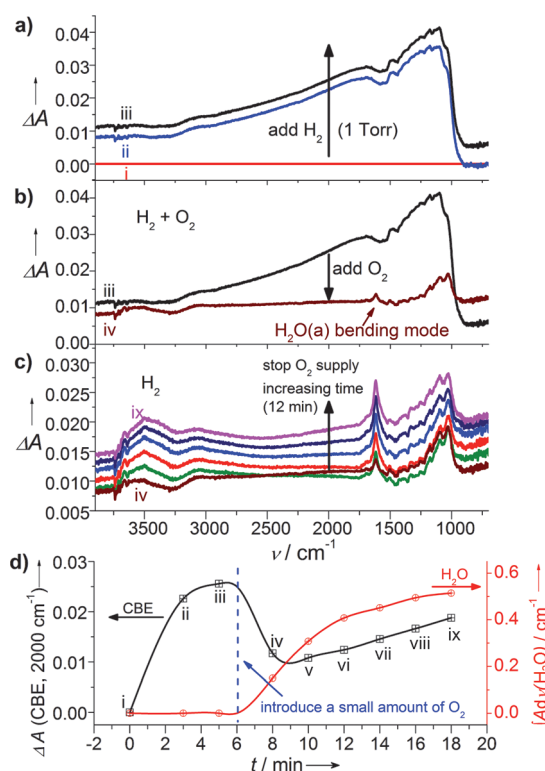


Figure 1. a) IR difference spectra of the H₂ spillover and CBE background shifting effect on the Au/TiO₂ at 295 K under 1 Torr of H₂. b) IR difference spectra of the H₂ oxidation by O₂ over the Au/TiO₂ at 295 K. c) IR difference spectra of the CBE background shifting effect on the (partially H₂O-covered) Au/TiO₂ surface when the O₂ supply is cut off. d) Plot of the CBE (left) and H₂O (right) development against time during the above processes.

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edge (CBE) states (Figure S3).^[11] Examples of this phenomenon at room temperature are shown in Figure 1a and S4, where a substantial IR background up-shift is caused by molecular H₂ dissociation on Au followed by atomic H spillover to the TiO₂ support. Figure 1b shows that when a small quantity of O₂ is introduced to the H-rich surface, it drains the CBE electrons which results in an immediate background drop. Simultaneously, the oxidation reaction of the H₂ on the Au/TiO₂ surface to form H₂O(a) is observed by the absorption band at 1620 cm⁻¹ ($\delta_{\text{H}_2\text{O}}$).^[11d,12] Removal of O₂ by reaction causes the CBE to return to an increased level in the H₂-rich environment (Figure 1c). The whole process is summarized in Figure 1d where both the CBE change and the H₂O formation are plotted with respect to time.

In an effort to observe more details of the H₂-O₂ reaction, the catalyst was cooled to 210 K and a 1:100 mixture of O₂ and H₂ was added. The reaction progress is shown in Figure 2,

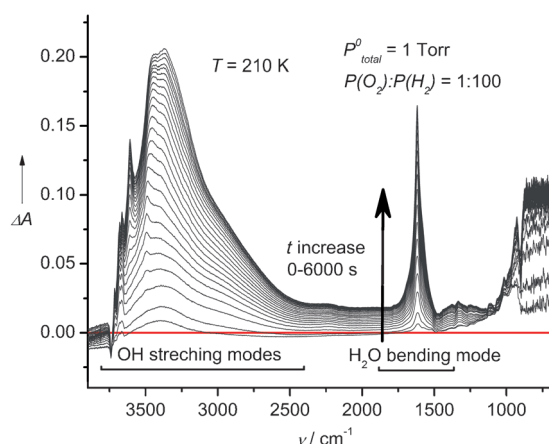


Figure 2. IR difference spectra of the Au/TiO₂ surface during H₂ oxidation by O₂ at 210 K.

indicating the production of both H₂O(a) and OH. A search for peroxide intermediate within the 1505–900 cm⁻¹ region was inconclusive.^[13] No products were observed on a pure TiO₂ sample mounted below the catalyst for the same reaction conditions (Figure S1), indicating that Au is necessary for the reaction. Similar experiments over the temperature range of 200–220 K were carried out and the kinetics studies as a function of temperature are shown in Figure 3. An Arrhenius plot of the initial rate is shown in the inset, yielding an apparent activation energy of 0.22 ± 0.02 eV. This is the first report of the kinetics of H₂ oxidation over Au/TiO₂ below room temperature. Activation energies at temperatures above 300 K have been measured as 0.38 eV for H₂ + O₂^[14] and 0.37 eV for H₂-D₂ exchange.^[5b] The rate of reaction maximizes to nearly the same limit at particular pressures of O₂ (ca. 0.08 Torr) and H₂ (ca. 1.4 Torr), as shown in Figure 4, indicating site saturation for both reactants.

DFT calculations were carried out to help elucidate the reaction mechanism and identify possible active sites for the low temperature H₂ oxidation (Supporting Information, Section III). The Au structure on the rutile TiO₂(110) surface was simulated with a Au nanorod covalently bound to the

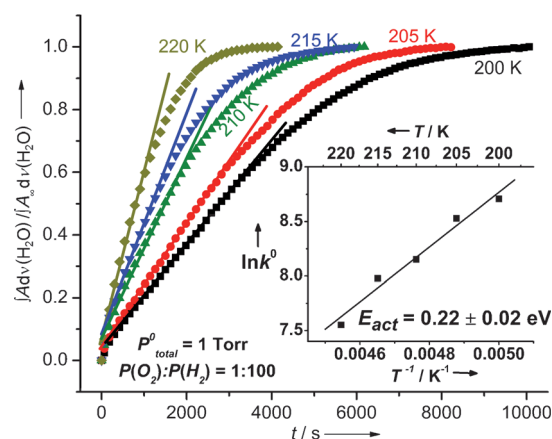


Figure 3. Kinetics for the oxidation of H₂ by O₂ over the Au/TiO₂ catalyst as measured by the change in the absorbance of H₂O as a function of time and temperature. The inset shows the Arrhenius plot.

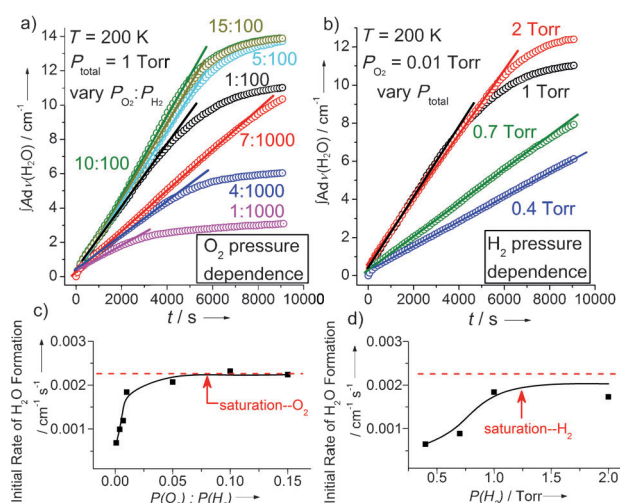


Figure 4. The effects of: a) O₂ pressure and b) H₂ pressure on the H₂ oxidation kinetics over Au/TiO₂. c) Plot of the initial rate of H₂O formation as a function of increasing O₂ partial pressure. d) Plot of the initial rate of H₂O formation as a function of the increasing H₂ pressure.

surface as shown in Figure S5. This configuration was used previously^[15] as it provides a distribution of different Au sites in contact with the support. Although not identical to the experimentally used catalyst, it is believed that the fundamental steps modeled in our simplified simulations provide viable insights. H₂ oxidation is thought to proceed by the formation of two H adatoms. Our DFT results as well as previous experiments^[11a] show that the lowest H-H dissociation barrier on Au in the absence of O₂ is approximately 0.5 eV (Figure S6). The calculations indicate that the local presence of adsorbed O₂ can promote H₂ dissociation to yield the activation energy of 0.22 eV measured experimentally.

The adsorption of O₂ at the Ti_{5c} perimeter site, the most favored of all of the sites shown in Figure S7, indeed, lowers the barrier for the dissociative adsorption of H₂(g) at the neighboring Au perimeter site down to 0.16 eV, as shown in Figure 5a,b. The dissociative adsorption of H₂ at this dual

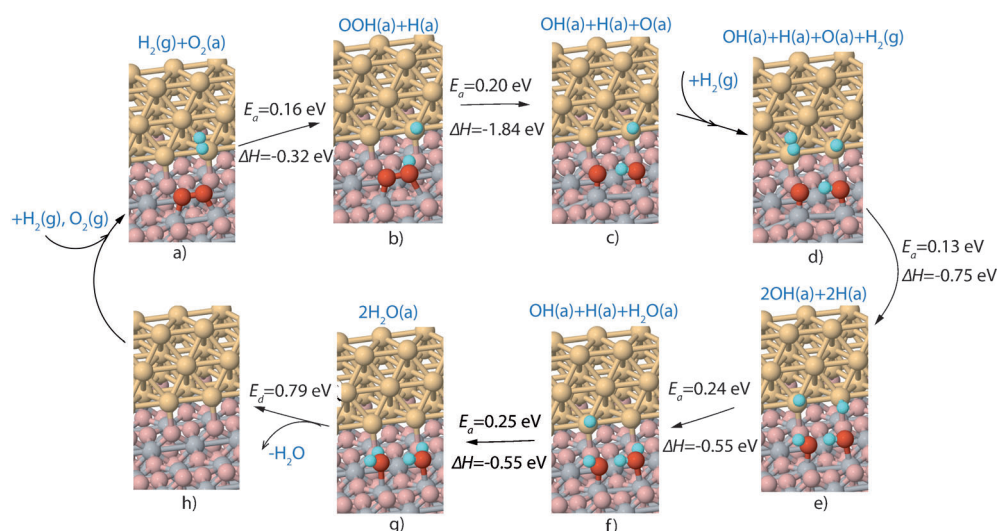


Figure 5. Catalytic reaction cycle and the corresponding activation barriers for the individual steps of the mechanism for the oxidation of H_2 to form H_2O over model Au/TiO₂ structures. The Au atoms and Ti atoms are shown in yellow and grey, respectively, whereas the O in the TiO₂ lattice, adsorbed O, and H atoms are shown in pink, red, and cyan, respectively. E_a and ΔH represent activation barriers and reaction energies separately.

perimeter site thus produces Ti–OOH intermediate and Au–H surface intermediates. Dissociation of the Ti–OOH to form Ti–OH and Ti–O was calculated to have a barrier of 0.20 eV (Figure 5c). The resulting O(a) activates and dissociates a second incident $\text{H}_2(\text{g})$ at the dual perimeter site, with a barrier of 0.13 eV, as shown in Figure 5e. The final hydrogenation of the two Ti–OH species by the two Au–H species proceeds with activation energies of 0.24 and 0.25 eV, as shown in Figure 5f,g.

The initial rate of H_2O formation involves a sequence of elementary steps (Figure 5a–g) that have rather low activation energies in the range 0.13–0.25 eV. While it is difficult to rigorously distinguish a rate-controlling step, the hydrogenation of OH(a) to form H_2O has the highest activation energy of 0.25 eV, in good agreement with the measured E_a of 0.22 eV. The low barriers of all other steps (Figure 5a–h) suggest that the Au/TiO₂ perimeter sites serve as active sites for the H_2 oxidation at low temperature, through an O_2 -assisted H–H dissociation mechanism.

Calculations of H_2O surface diffusion energies on TiO₂ (estimated to be 0.21, 0.32, and 0.43 eV at 1, 2/3, and 1/3 monolayer (ML) coverages) and desorption energy (0.79 eV in Figure 5g,h) suggest that H_2O will cluster and accumulate to block the active perimeter sites at low temperatures as the reaction proceeds. This is consistent with the results presented in Figure 3 where the reaction stops at longer times. Our measurements have therefore focused on the initial reaction rates where the effect of site blockage is minimal. This also means that the kinetic studies shown in Figure 3 are controlled by the disappearance of the active sites for H_2 oxidation.

To further elucidate the mechanism, we carried out D₂ labeling studies to measure the kinetic isotope effect (KIE). The rates of reaction of O_2 with H_2 and D_2 at 200 K, which are compared in Figure 6, show a ca. 7-fold increase in the initial

rates for H_2 over D_2 . The zero point energy (ZPE) differences for the reactant H_2 and D_2 and the corresponding transition states (TS) were considered in order to calculate the KIE to compare with the experimental results. The inset of Figure 6 shows the calculated initial state and TS and the corresponding vibrational frequencies of the H_2 dissociation reaction (steps a and b in Figure 5). If the ZPE difference is taken only for the initial state, the rate ratio, $k_{\text{H}}/k_{\text{D}}$, is calculated to be 87. Instead, using both initial and transition state frequencies, the calculated $k_{\text{H}}/k_{\text{D}} = 5$, in good agreement with the experi-

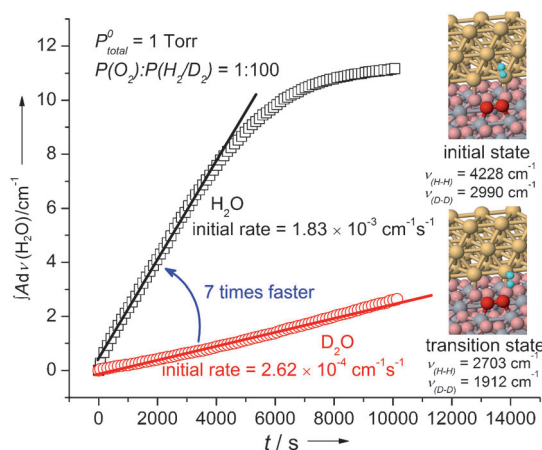


Figure 6. D₂ kinetic isotope effect for the oxidation of H_2 by O_2 over the Au/TiO₂ catalyst at 200 K. The insets show the ab initio calculated initial state and transition state frequencies for the O_2 -assisted H_2 dissociation process.

mentally measured KIE value of 7, and indicating that an early TS is involved.

In summary, the active site for the $\text{H}_2 + \text{O}_2$ reaction over a Au/TiO₂ nanoparticle catalyst at low temperature was located at dual perimeter sites at the interface between Au and TiO₂. An O_2 -assisted H_2 dissociation through a Ti–OOH intermediate was proposed involving an early transition state. The calculated activation energies for sequential steps in the range 0.13–0.25 eV agree with the measured apparent activation energy of 0.22 eV.

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- [1] a) C. Song, *Catal. Today* **2002**, 77, 17–49; b) G. C. Bond, D. T. Thompson, *Catal. Rev. Sci. Eng.* **1999**, 41, 319–388; c) J. P. Collman, L. M. Slaughter, T. A. Eberspacher, T. Strassner, J. I. Brauman, *Inorg. Chem.* **2001**, 40, 6272–6280; d) B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R. J. Behm, *J. Catal.* **2004**, 224, 449–462; e) M. Azar, V. Caps, F. Morfin, J.-L. Rousset, A. Piednoir, J.-C. Bertolini, L. Piccolo, *J. Catal.* **2006**, 239, 307–312.
- [2] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, 405–408.
- [3] M. Valden, X. Lai, D. W. Goodman, *Science* **1998**, 281, 1647–1650.
- [4] M. S. Chen, D. W. Goodman, *Science* **2004**, 306, 252–255.
- [5] a) M. Kotobuki, R. Leppelt, D. A. Hansgen, D. Widmann, R. J. Behm, *J. Catal.* **2009**, 264, 67–76; b) T. Fujitani, I. Nakamura, T. Akita, M. Okumura, M. Haruta, *Angew. Chem.* **2009**, 121, 9679–9682; *Angew. Chem. Int. Ed.* **2009**, 48, 9515–9518; c) N. Lopez, T. V. W. Janssens, B. S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J. K. Nørskov, *J. Catal.* **2004**, 223, 232–235; d) F. Cárdenas-Lizana, S. Gómez-Quero, H. Idriss, M. A. Keane, *J. Catal.* **2009**, 268, 223–234.
- [6] J. A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, M. Perez, *Science* **2007**, 318, 1757–1760.
- [7] a) L. Piccolo, H. Daly, A. Valcarcel, F. C. Meunier, *Appl. Catal. B* **2009**, 86, 190–195; b) E. Quinet, L. Piccolo, F. Morfin, P. Avenier, F. Diehl, V. Caps, J.-L. Rousset, *J. Catal.* **2009**, 268, 384–389; c) D. C. Ford, A. U. Nilekar, Y. Xu, M. Mavrikakis, *Surf. Sci.* **2010**, 604, 1565–1575.
- [8] a) D. G. Barton, S. G. Podkolzin, *J. Phys. Chem. B* **2005**, 109, 2262–2274; b) A. M. Joshi, W. N. Delgass, K. T. Thomson, *J. Phys. Chem. B* **2005**, 109, 22392–22406; c) F. Wang, D. Zhang, H. Sun, Y. Ding, *J. Phys. Chem. C* **2007**, 111, 11590–11597; d) L. Barrio, P. Liu, J. A. Rodriguez, J. M. Campos-Martin, J. L. G. Fierro, *J. Phys. Chem. C* **2007**, 111, 19001–19008.
- [9] a) I. X. Green, J. T. Yates, Jr., *J. Phys. Chem. C* **2010**, 114, 11924–11930; b) S. Kim, O. Byl, J. T. Yates, Jr., *J. Phys. Chem. B* **2005**, 109, 3499–3506; c) R. Zanella, S. Giorgio, C. R. Henry, C. Louis, *J. Phys. Chem. B* **2002**, 106, 7634–7642.
- [10] a) X. L. Yin, M. Calatayud, H. Qiu, Y. Wang, A. Birkner, C. Minot, C. Wöll, *ChemPhysChem* **2008**, 9, 253–256; b) G. H. Enevoldsen, H. P. Pinto, A. S. Foster, M. C. R. Jensen, W. A. Hofer, B. Hammer, J. V. Lauritsen, F. Besenbacher, *Phys. Rev. Lett.* **2009**, 102, 136103; c) H. Noei, H. Qiu, Y. Wang, M. Muhler, C. Wöll, *ChemPhysChem* **2010**, 11, 3604–3607.
- [11] a) D. A. Panayotov, J. T. Yates, Jr., *J. Phys. Chem. C* **2007**, 111, 2959–2964; b) D. A. Panayotov, J. T. Yates, Jr., *Chem. Phys. Lett.* **2005**, 410, 11–17; c) D. A. Panayotov, J. T. Yates, Jr., *Chem. Phys. Lett.* **2007**, 436, 204–208.
- [12] X. Wang, S. Kim, C. Buda, M. Neurock, O. B. Koper, J. T. Yates, Jr., *J. Phys. Chem. C* **2009**, 113, 2228–2234.
- [13] C. Sivadinarayana, T. V. Choudhary, L. L. Daemen, J. Eckert, D. W. Goodman, *J. Am. Chem. Soc.* **2004**, 126, 38–39.
- [14] G. Walther, D. J. Mowbray, T. Jiang, G. Johnes, S. Jensen, U. J. Quaade, S. Horch, *J. Catal.* **2008**, 260, 86–92.
- [15] a) L. M. Molina, M. D. Rasmussen, B. Hammer, *J. Chem. Phys.* **2004**, 120, 7673–7680; b) S. Laursen, S. Linic, *Phys. Chem. Chem. Phys.* **2009**, 11, 11006–11012.