

TAP study on CO oxidation on a highly active Au/Ti(OH)₄* catalyst

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The CO oxidation with O₂ on an active Au/Ti(OH)₄* catalyst has been studied using a TAP (temporal analysis of products) transient technique to gain insights into the CO oxidation mechanism. Taking advantage of the TAP system, we have tried to elucidate the controversial mechanism proposed for the CO oxidation on supported gold catalysts. Pump–probe experiments have been performed to determine the lifetime of surface reactive intermediates involved in the oxidation reaction. In a typical pump–probe experiment the catalyst is first charged with a reactant pulse from the pump valve and then interrogated with a different pulse from the probe valve. Varying the time between the pump and probe pulses gives information related to the lifetime of surface intermediates. The pump–probe experiments together with single-pulse experiments revealed that molecularly and irreversibly adsorbed oxygen contributed to the catalytic CO oxidation. When CO was a pump molecule, the CO₂ yield was not influenced by the pump–probe time interval. This means that CO reversibly adsorbs on the surface with a lifetime long enough to react with oxygen. Moreover, the nature and role of oxygen species in the reaction have been examined in the TAP reactor using ¹⁸O₂ transient experiments. The results revealed that oxygen passed over the catalyst without isotope scrambling and that the lattice oxygen atoms exchanged only with CO₂ formed by the CO oxidation reaction.

1. Introduction

The TAP (temporal analysis of products) transient technique has often been used to gain insights into the mechanism of heterogeneous catalytic reactions.^{1–16} In the TAP system an extremely narrow gas pulse is injected into the end of a cylindrical micro-reactor, while the other end is continuously evacuated. No carrier gas is used. The pulse moves across the micro-reactor as a result of the pressure gradient. The reactor is operated in a Knudsen diffusion regime in which transport is well defined. In the Knudsen regime the product pulse shape is independent of pulse-intensity.^{17,18} In this way, the TAP experiment is designed to operate in the millisecond time regime and so it provides two or more orders of magnitude better time resolution than other non-steady-state pulse reactor systems. Because of this capability the TAP system can detect short-lived active species and intermediates in a complex catalytic reaction system and give a more detailed picture of the mechanism.

That is the reason why we chose the TAP technique to attempt to elucidate the mechanism for low-temperature CO oxidation reactions on supported gold catalysts. Many conflicting and different mechanisms for the CO oxidation have been proposed to date.^{19–25}

From TPD and FTIR data obtained on gold particles supported on TiO₂, α-Fe₂O₃ and Co₃O₄ which were prepared by coprecipitation and deposition–precipitation methods, a mechanism consisting of four steps was proposed by Haruta *et al.*²⁰ The proposed mechanism involves (1) reversible adsorption of CO on the surface and perimeter of gold particles, (2) irreversible adsorption of oxygen at the perimeter

interface to produce O₂[–] as a rate-determining step, (3) fast formation of a bidentate carbonate through reaction between the adsorbed CO and the active oxygen and (4) production of CO₂ by reaction of the carbonate with adsorbed CO. This mechanism was supported by a FTIR study performed by Boccuzzi *et al.*²¹ But, the existence of another independent and slower pathway involving oxygen atoms of the support was also evidenced for TiO₂- and ZnO₂-supported gold catalysts.

In contrast to this conclusion, thermochemical data obtained by Tripathi *et al.*²³ suggest that there are not two pathways for CO oxidation on Au/Fe₂O₃ and that carbonate species may not play a significant role in the CO oxidation. Carbon monoxide oxidation on both Fe₂O₃ and Au/Fe₂O₃ occurs by a similar redox mechanism involving the removal and replenishment of lattice oxygen atoms, where the presence of gold promotes these processes.

Knell *et al.*¹⁹ studied the CO oxidation mechanism on a coprecipitated Au/ZrO₂ catalyst. They claimed that the reaction involved interaction of CO with surface hydroxy groups to form surface formates which can be oxidized by atomic oxygen on the surface of gold metallic particles. Such a route may be excluded on Au/TiO₂ and Au/ZnO catalysts pretreated in dry air,²⁰ but it might operate in the presence of moisture.

Recently, TPD, ESR and FTIR studies performed on Au/Ti(OH)₄* and Au/Fe(OH)₃* catalysts revealed that the mechanism of CO oxidation included the reversible adsorption of CO on the Au particles, the molecular adsorption of O₂ on oxygen vacancies at the oxide surfaces in the form of superoxide O₂[–], and the subsequent reaction of these adsorbed species to form carbon dioxide at the interface between the Au particles and the oxides.^{24–26} The produced CO₂ desorbs, while a part of the CO₂ readsorbs to react with lattice oxygen atoms to form carbonates. The carbonates were

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stable and not the intermediate for the low-temperature CO oxidation.^{24–26}

The mechanism may differ from one catalyst to another because the activity of gold catalysts for CO oxidation is sensitive to the nature of support, the size of gold particles and the properties of the gold–support interface.^{27,28} However, it is of importance in fundamental research to study the transient behavior of adsorbed carbon monoxide, oxygen and carbon dioxide as the key species for CO oxidation in relation to the conflicting oxidation mechanisms. The obtained data and knowledge can give insights into the origin of the unique performance of Au catalysts and may provide a new concept of catalyst design as well as a new way to regulate active species at the catalyst surface.²⁹

The aim of the present TAP study is to elucidate the nature (molecular or atomic) and lifetime of active oxygen species which contribute to the CO oxidation on a highly active Au/Ti(OH)₄* catalyst which is prepared by using a Au–phosphine complex as a precursor for gold metallic particles and an as-precipitated wet titanium hydroxide as a precursor for TiO₂, followed by calcination at 673 K.

Our single-pulse TAP experiments on the Au/Ti(OH)₄* catalyst proved the weak and reversible adsorption of CO, the irreversible and molecular adsorption of O₂ and the irreversible adsorption of CO₂, probably as a carbonate, on the catalyst.³⁰ In the present study pump–probe TAP experiments were used to determine the behavior and lifetime of active oxygen species. In the pump–probe TAP experiments a reactant is pulsed first, then another reactant is pulsed after a given time interval. The pump–probe TAP experiments were undertaken with two different CO–O₂ pulses: C¹⁶O–¹⁶O₂ and C¹⁶O–¹⁸O₂ at different time intervals between the two pulses and at different reaction temperatures. Comparison of the results of the pump–probe experiments under various conditions provided enough information on the CO oxidation mechanism involving active molecular oxygen.

2. Experimental

All experiments were conducted using the TAP reactor system which has been described in detail elsewhere.³⁰ Briefly, the apparatus (Fig. 1) consists of a catalytic micro-reactor, a gas delivery system for introduction of either high-speed gas pulses or a continuous flow of gas, a high-throughput, a high-vacuum system and a computer-controlled quadrupole mass spectrometer. The micro-reactor is made from a stainless steel tube whose diameter and length are 2 mm and 25 mm, respectively. Catalyst particles are fixed in the reactor by stainless steel mesh. The reactor can be heated up to 773 K by cartridge heaters. The two high-speed pulse valves can be operated at the interval up to 50 pulses per second. The minimum pulse width is 200 ms. The pulse intensities were varied between 10¹³ and 10²⁰ molecules per pulse. Before each experiment the catalyst was heated at 473 K for 30 min in vacuum to desorb preadsorbed species. The 150 to 250 pulses in the TAP experiments were averaged to increase the signal-to-noise ratio in the response. The pulse-to-pulse reproducibility of the system was good enough for averaging.³⁰

The preparation of supported gold catalyst has been described in detail elsewhere.^{31–34} As-precipitated wet titanium hydroxide Ti(OH)₄* was obtained by hydrolysis of Ti(OⁱC₃H₇)₄ (99.999% purity) with an aqueous NH₃ solution. The precipitate was then filtrated off and washed with deionized water until the pH became 7.0. The as-precipitated wet Ti(OH)₄* was impregnated with an acetone solution of Au(PPh₃)(NO₃) under vigorous stirring, followed by vacuum drying to remove the solvent at room temperature. The obtained sample was heated to 673 K at a ramping rate of 4 K min⁻¹ and kept at this temperature for 4 h in a flow of air (30 ml min⁻¹). The catalyst thus obtained is denoted as

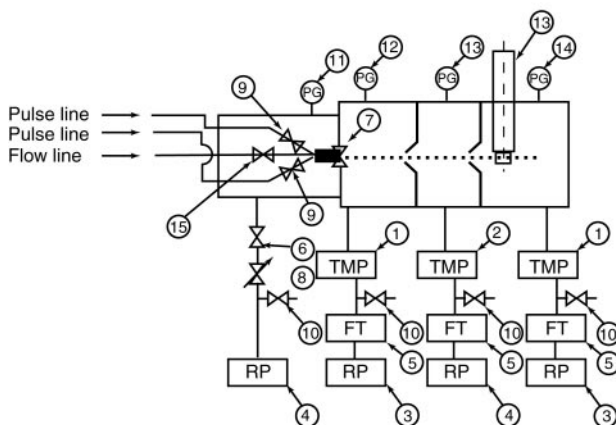
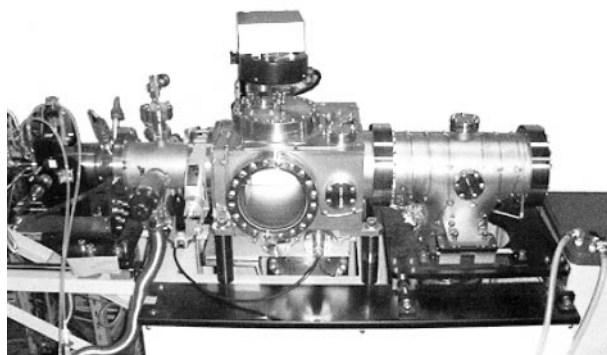


Fig. 1 Photograph and schematic drawing of the TAP system; (1,2) turbomolecular pumps; (3,4) rotary pumps; (5) flow line trap; (6,7,8,15) valves; (9) pulse valve; (10) leak valve; (11,12,13,14) pressure gauges; (16) quadrupole mass spectrometer.

Au/Ti(OH)₄*. This catalyst exhibited a high activity for CO oxidation as compared to a conventional Au/TiO₂ catalyst.²⁴

3. Results and discussion

Pump–probe TAP experiments

Pump–probe TAP experiments were performed using two pulse valves to put two reactants CO (99.99%) or O₂ (99.9%) into the micro-reactor. The typical results were obtained in an approximate 1 : 1 ratio of CO : O₂ in the inlet gas pulses, where oxygen (pump molecule) was first pulsed and after a time delay carbon monoxide (probe molecule) was pulsed second. Therefore, the pump–probe TAP experiments provide information on the life time and reactivity of adsorbed oxygen species. Seven different pump–probe intervals between the O₂ and CO pulses ranging from 50 to 10 000 ms were used and the transient output responses of the carbon dioxide product were measured at four temperatures (298, 373, 423 and 473 K). The lifetime of the surface oxygen intermediates for the CO oxidation on Au/Ti(OH)₄* was determined by measuring the product yield as a function of the pump–probe time interval.

The product profiles for seven different pump (O₂)–probe (CO) time intervals (50, 100, 500, 1000, 3000, 5000 and 10 000 ms) are plotted in Fig. 2. After an O₂ pump-pulse the subsequent CO probe-pulses were introduced to the O₂-preexposed Au/Ti(OH)₄* catalyst after the given time intervals. The CO₂ signal intensity increased with an increase in the time interval up to 500 ms and then decreased with increasing pump–probe interval. Long tails in these product curves were observed, which implies the existence of another less reactive oxygen species at the catalyst surface and/or a slow decomposition of the carbonates left on the catalyst surface.

Fig. 3 shows the effect of the pump–probe interval on the CO₂-product responses at 298, 373 and 423 K. The CO₂ pro-

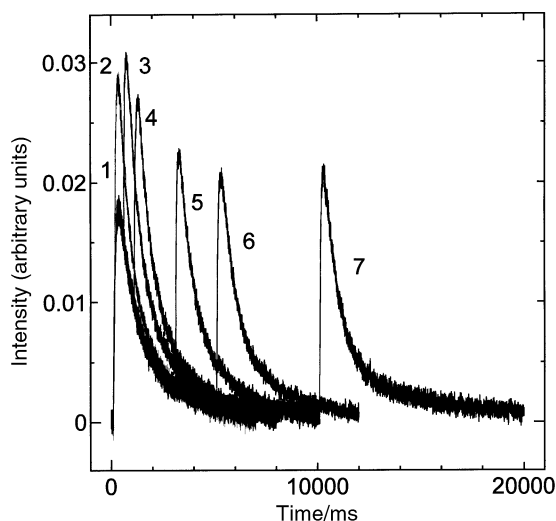


Fig. 2 Series of CO₂ product curves using O₂ as pump molecules and CO as probe molecules at 298 K at different pump-probe time intervals: (1) 50, (2) 100, (3) 500, (4) 1000, (5) 3000, (6) 5000 and (7) 10000 ms.

duction increased rapidly with increasing time intervals (50 and 100 ms) and reached a maximum at the interval of 500 ms for 298 and 423 K, and a maximum at the interval of 1000 ms for the 373 K experiments.

Our previous TAP study on the adsorption/desorption of CO, O₂ and CO₂ on the Au/Ti(OH)₄* catalyst demonstrated that the adsorption of O₂ was slower than the adsorption of CO and CO₂.³⁰ We verified whether O₂ adsorption is dissociative or associative on this catalyst by comparing the O₂ TAP response curves with the simulated O₂ molecular irreversible adsorption curve by using the eqn. (1):

$$\frac{F_A}{N_{pA}} = \frac{D_{eA}\pi}{\varepsilon_b L^2} \exp(-k'_{aA} t) \sum_{n=0}^{\infty} (-1)^n (2n+1) \times \exp\left(- (n+0.5)^2 \pi^2 \frac{t D_{eA}}{\varepsilon_b L^2}\right). \quad (1)$$

F_A , N_{pA} , D_{eA} , ε_b , L , k'_{aA} , and t represent flow of gas A at the reactor outlet (mol s⁻¹), number of molecules of A in the inlet pulse, effective Knudsen diffusivity of gas A (cm² s⁻¹), porosity of the bed, length of the reactor (cm), apparent adsorption rate constant (s⁻¹), and time (s), respectively. The result was an almost perfect fit between the two curves.³⁰ This demonstrated that O₂ molecularly adsorbed on the catalyst surface. We also verified the type of O₂ adsorption. Using the calculated value for the adsorption rate constant at 373–473 K we calculated the first moment of dimensionless exit flow, m_{1d} , and, then, we compared it with the calculated first moment,

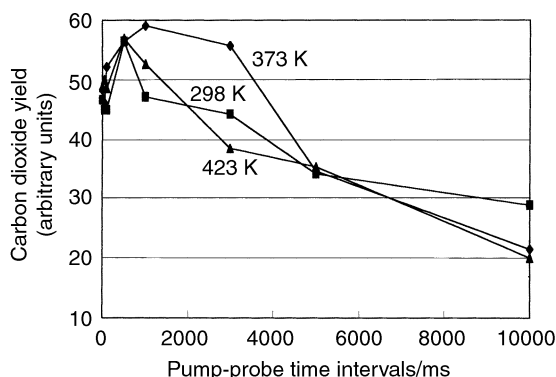


Fig. 3 Relative CO₂ product yields as a function of pump-probe time interval at 298 (■), 373 (◆) and 423 (▲) K.

m_1 , by statistical analysis:

$$m_{1d} = \pi \sum_{n=0}^{\infty} \frac{(-1)^n (2n+1)}{\left((n+0.5)^2 \pi^2 + \frac{k'_{aO_2} \varepsilon_b L^2}{D_{eO_2}} \right)} = \frac{m_1 D_{eO_2}}{\varepsilon_b L^2}. \quad (2)$$

The errors were less than 5%, which allowed us to conclude that O₂ molecularly adsorbs on the catalyst surface.³⁰

It may take time to form active oxygen species at the surface after the injection of the oxygen pulse. The quantity of adsorbed O₂ on the Au/Ti(OH)₄* catalyst showed a maximum at around 373 K.³⁰ The results in Fig. 3 are in agreement with the previous single-pulse TAP results.³⁰ As the CO₂ yields smoothly decreased with increasing pump-probe time intervals after the maximum, we can exclude the possibility that lattice oxygen atoms of the catalyst contribute to the CO oxidation. Moreover, it seems that oxygen is not strongly bound to the catalyst surface because the maximum amount of CO₂ was obtained at short pump-probe time intervals (500 ms and 1000 ms). These conclusions are also supported by the isotope experiments as discussed below. Thus it is evident that adsorbed molecular oxygen is involved in the CO oxidation. The maximum in Fig. 3 is determined as the balance of the rates of the formation and desorption of active O₂ species (probably O₂⁻).^{24–26} The pump-probe response at 373 K reflects the activation process of the active O₂⁻ formation. The maximum at the shorter interval at 423 K is due to the easier desorption of the O₂⁻ species at the higher temperature. The coincidence of time intervals for the maximum of CO₂ yields at 298 and 423 K seems to be accidental under the present pump-probe experimental conditions. The active molecular oxygen is estimated to have a lifetime of 4500–6900 ms at 373–423 K.

Using single-pulse TAP experiments, we have also studied the effect of temperature on CO₂ formation from a 1:1 mixture of CO and O₂. As shown in Fig. 4, the CO₂ product profile against the time at 373 K was broader than those at 298, 423 and 473 K, indicating that CO₂ adsorbs more strongly at 373 K. At 373 K, the shape of the CO₂ product curve was not determined by the kinetics of the surface reaction between adsorbed carbon monoxide and oxygen but by the CO₂ adsorption/desorption behavior. Indeed, the amount of CO₂ produced in Fig. 4 showed the maximum at 373 K (Table 1). In this case, the CO₂ formed by the CO oxidation reaction would further react with lattice oxygen atoms to form carbonate species.

We have compared the formation of CO₂ from the single-pulse of the 1:1 mixture of CO and O₂ with the TAP

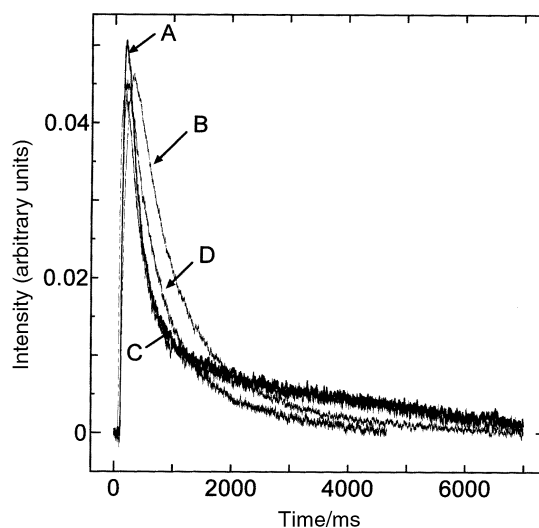


Fig. 4 Temperature effect on the the shape of CO₂ response curve in a single-pulse experiment: (A) 298, (B) 373, (C) 423 and (D) 473 K.

Table 1 Temperature effects on the CO₂ yield and the peak time (*t_p*) in the TAP experiments

Temperature/K	CO ₂ yield (arbitrary units)	<i>t_p</i> /ms
298	49.1	184
373	52.3	315
423	47.9	184
473	46.7	184

response of CO₂ pulse. The dimensionless CO₂ response curve for the CO + O₂ pulse at 373 K was similar to those for the CO₂ pulses at 298 and 373 K as shown in Fig. 5. The results indicate that the desorption of CO₂ is rate determining for the catalytic CO oxidation on Au/Ti(OH)₄* at 373 K. In contrast, the CO₂ response curve for the CO + O₂ pulse at 298 K is sharper and shows greater tailing as compared to that at 373 K, which indicates that at 298 K the surface reaction is rate determining. The value of the peak time (*t_p*) and the peak shape for the CO₂ formation varied with reaction temperature as shown in Table 1 and Fig. 4 and 5. This means that the produced CO₂ adsorbs strongly on the catalyst surface, which is consistent with our CO₂ TAP experiments on the Au/Ti(OH)₄* catalyst.³⁰

The experiments using CO as pump molecules and O₂ as probe ones were also performed. The CO pulse never produced CO₂, indicating no reactivity of lattice oxygen atoms of the catalyst. CO₂ was obtained only with the oxygen pulse after the CO pump-pulse and the CO₂ yield was not influenced by the pump-probe time interval (50–10000 ms). The product yield reflects the amount of adsorbed CO species that remains on the surface during the period of the probe pulses. The adsorbed CO molecules have a long lifetime that is long enough to allow reaction with the O₂ probe pulse.

Oxygen isotope exchange

Single-pulse and pump-probe experiments using ¹⁸O₂ and C¹⁶O were performed at 298 and 423 K. Fig. 6 shows the results of the single-pulse experiments, where C¹⁶O and ¹⁸O₂ were pulsed simultaneously on the Ti(OH)₄* catalyst. Three types of CO₂ isotopomers: C¹⁶O₂, C¹⁶O¹⁸O and C¹⁸O₂ were produced in the ratio 4 : 1.5 : 1 for both temperatures. This means that the population in the CO₂ product was about 60% C¹⁶O₂, 24% C¹⁶O¹⁸O and 16% C¹⁸O₂. If C¹⁶O reacts with ¹⁸O₂, the C¹⁶O¹⁸O isotopomer should be expected as a main product. An explanation can be the following. In the ¹⁸O₂ pulse the oxygen isotopomers ¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂

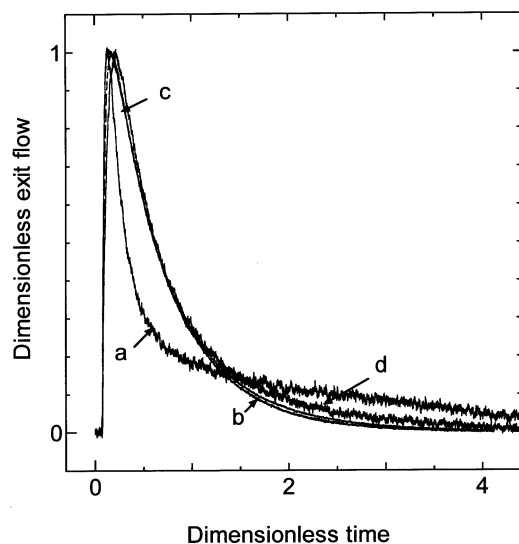
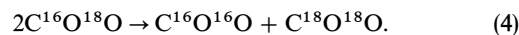
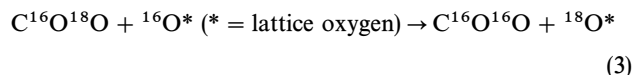
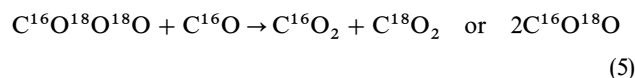


Fig. 5 CO₂ response curves in the CO + O₂ pulses (a and c) and the CO₂ pulses (b and d) at 298 K (a and b) and 373 K (c and d).

were contained in the ratio 3 : 1 : 12.6. The impurity ¹⁶O₂ should give a certain amount of C¹⁶O₂. But the amount of C¹⁶O₂ observed was far greater than that expected. Liu *et al.* reported that the CO₂ product underwent rapid secondary reactions, the oxygen exchange of CO₂ with the lattice oxygen atoms (3) and the disproportionation reaction (4) as follows.^{24,25}



As the amount of C¹⁶O₂ produced was much larger than that of C¹⁶O¹⁸O and the amount of C¹⁸O₂ produced was much lower than those of the other species, oxygen exchange by eqn. (3) is suggested to rapidly occur before desorption of the CO₂ produced by the CO oxidation reaction. This is also supported by the TAP curves in Fig. 6 where all the CO₂ isotopomers appeared at the same time. In the case of the mechanism which includes the reaction of carbonates with CO,²⁰ the ratio of the C¹⁶O₂, C¹⁸O₂ and C¹⁶O¹⁸ produced should be 1 : 1 : 2, assuming no isotope effect, as shown by eqn. (5).



In contrast to the oxygen scrambling in CO₂ product, no ¹⁸O₂/¹⁶O* (¹⁶O*, surface lattice oxygen) oxygen exchange was observed during the oxygen pulse in the TAP system.

Fig. 7 presents the dimensionless exit flows of the three oxygen isotopomers (¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂) when ¹⁸O₂ was pulsed on Au/Ti(OH)₄*. Normalization of the experimental exit curves has been made by dividing with the height of the peak. The dimensionless time was obtained by multiplying the time with *D_{eA}/ε_bL²*. As all the species have the same *t_p*, it is concluded that no oxygen exchange occurs. The ratio between the three isotopomers was 3 : 1 : 12.5, which is almost the same as the initial composition in the ¹⁸O₂ gas. If O₂ dissociated to atomic oxygen at the catalyst surface, oxygen

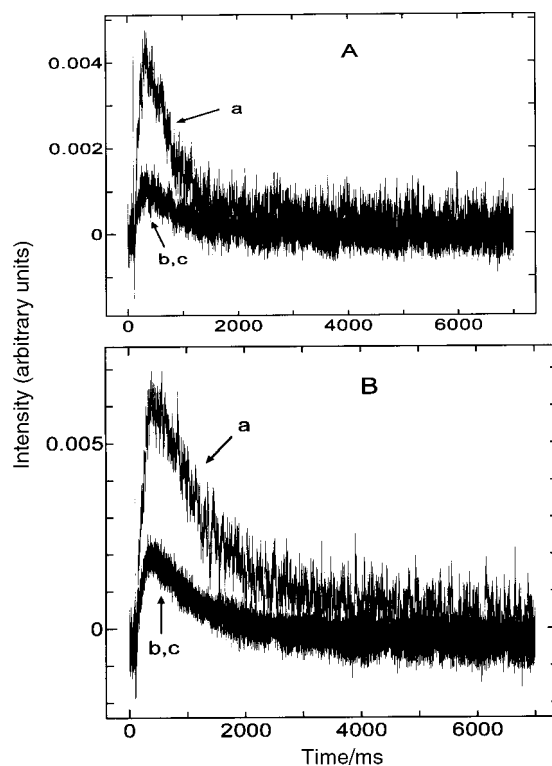


Fig. 6 TAP results of C¹⁶O oxidation with ¹⁸O₂ on Au/Ti(OH)₄* at 298 K (A) and 423 K (B). (a) C¹⁶O₂, (b) C¹⁶O¹⁸O, (c) C¹⁸O₂.

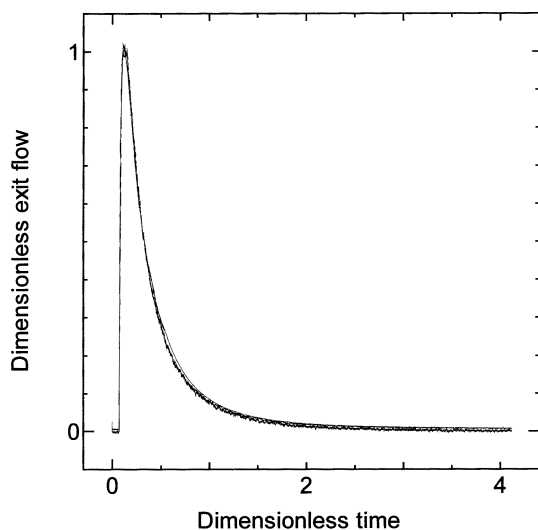


Fig. 7 Dimensionless responses of oxygen isotopes $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ when a mixture of $^{18}\text{O}_2$ (major) + $^{16}\text{O}_2$ + $^{16}\text{O}^{18}\text{O}$ was pulsed on the $\text{Au}/\text{Ti}(\text{OH})_4$ catalyst.

exchange with lattice oxygen atoms would have occurred. No oxygen exchange in $^{18}\text{O}_2$ - $^{16}\text{O}^*$ and $^{18}\text{O}_2$ - $^{16}\text{O}_2$ on $\text{Au}/\text{Ti}(\text{OH})_4$ and $\text{Au}/\text{Fe}(\text{OH})_3$ has been observed.^{24,25} Our previous TAP study has also revealed that oxygen adsorbs in a molecular form on the $\text{Au}/\text{Ti}(\text{OH})_4$ catalyst.³⁰ Moreover, the presence of CO affected neither the shape nor the intensity of the $^{18}\text{O}_2$ response significantly, as shown in Fig. 8. The ratio of the three oxygen isotopomers in the exit flow was also the same as that in the case of the $^{18}\text{O}_2$ pulse alone, i.e. 3 : 1 : 12.5, which means that $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ were equally consumed for the CO oxidation. These results demonstrate that oxygen passed through the catalyst bed without dissociative adsorption and oxygen scrambling. It has been demonstrated that O_2 adsorbs on the oxygen vacancies to form superoxide O_2^- with an angular arrangement.²⁴

4. Conclusions

To elucidate the mechanism for the CO oxidation on the active $\text{Au}/\text{Ti}(\text{OH})_4$ catalyst, the TAP single-pulse and pump-probe experiments have been performed. The discussion has been focused on active oxygen species for the CO oxidation using the oxygen isotope. The present TAP analysis indicates a reaction mechanism involving molecular oxygen, in agreement with the conclusion obtained from a conventional

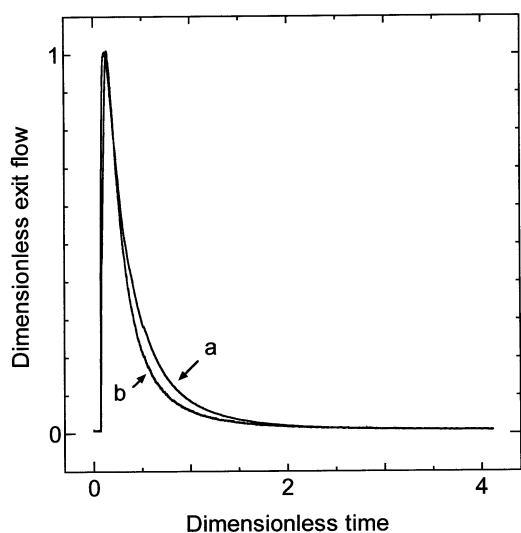


Fig. 8 Dimensionless responses of $^{18}\text{O}_2$ when (a) $^{18}\text{O}_2$ and (b) a CO + $^{18}\text{O}_2$ mixture were pulsed on $\text{Au}/\text{Ti}(\text{OH})_4$ at 298 K.

isotope technique.^{24,25} The TAP experiments also demonstrate that (1) no oxygen isotope exchange between O_2 and lattice oxygen occurs on the $\text{Au}/\text{Ti}(\text{OH})_4$ catalyst, (2) the lattice oxygen atoms are active in oxygen exchange only with CO_2 , which affects the composition in the CO_2 isotopomers in the isotope experiments, (3) oxygen molecularly adsorbs on the catalyst surface, (4) CO is reversibly adsorbed with a lifetime long enough to react with the O_2 probe molecules, and (5) the CO oxidation reaction is fast on this catalyst.

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References

- 1 G. Creten, D. S. Lafyatis and G. F. Froment, *J. Catal.*, 1995, **154**, 151.
- 2 J. T. Gleaves, A. G. Sault, R. J. Madix and J. R. Ebner, *J. Catal.*, 1990, **121**, 202.
- 3 G. D. Svoboda and J. T. Gleaves, *Ind. Eng. Chem. Res.*, 1992, **31**, 19.
- 4 G. Golinelli and T. J. Gleaves, *J. Mol. Catal.*, 1992, **73**, 353.
- 5 J. T. Gleaves and G. Centi, *Catal. Today*, 1993, **16**, 69.
- 6 B. Kartheuser, B. K. Hodnett, H. W. Zanthoff and M. Baerns, *Catal. Lett.*, 1993, **21**, 209.
- 7 O. V. Buyevskaya, M. Rothaemel, H. W. Zanthoff and M. Baerns, *J. Catal.*, 1994, **150**, 71.
- 8 Y. Schuurman and J. T. Gleaves, *Ind. Eng. Chem. Res.*, 1994, **33**, 2935.
- 9 Y. J. Mergler, J. Hoebink and B. E. Nieuwenhuys, *J. Catal.*, 1997, **167**, 305.
- 10 G. Creten, F. D. Kopinke and G. F. Froment, *Can. J. Chem. Eng.*, 1997, **75**, 882.
- 11 A. Pantazidis, S. A. Bucholz, H. W. Zanthoff, Y. Schuurman and C. Mirodatos, *Catal. Today*, 1998, **40**, 207.
- 12 K. H. Hofstad, J. H. B. J. Hoebink, A. Holmen and G. B. Marin, *Catal. Today*, 1998, **40**, 157.
- 13 T. Gerlach and M. Baerns, *Chem. Eng. Sci.*, 1999, **54**, 4379.
- 14 O. Dewaele, V. L. Geers, G. F. Froment and G. B. Marin, *Chem. Eng. Sci.*, 1999, **54**, 4385.
- 15 D. Creaser, B. Andersson, R. R. Hudgins and P. L. Silveston, *Appl. Catal. A: General*, 1999, **187**, 147.
- 16 A. Hinz and A. Andersson, *Chem. Eng. Sci.*, 1999, **54**, 4407.
- 17 J. T. Gleaves and J. R. Ebner, *U.S. Pat.* US 4, 626, 412, 1986.
- 18 J. T. Gleaves, J. R. Ebner and T. C. Kuechler, *Catal. Rev.-Sci. Eng.*, 1988, **30**(1), 49.
- 19 A. Knell, P. Barnickel, A. Baiker and A. Wokaun, *J. Catal.*, 1992, **137**, 306.
- 20 M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet and B. J. Delmon, *Catalysis*, 1993, **144**, 175.
- 21 F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, *J. Phys. Chem.*, 1996, **100**, 3625.
- 22 M. Haruta, *Catal. Today*, 1997, **36**, 153.
- 23 A. K. Tripathi, V. S. Kamble and N. M. Gupta, *J. Catal.*, 1999, **187**, 332.
- 24 H. Liu, A. I. Kozlov, A. P. Kozlova, T. Shido, K. Asakura and Y. Iwasawa, *J. Catal.*, 1999, **185**, 252.
- 25 H. Liu, A. I. Kozlov, A. P. Kozlova, T. Shido and Y. Iwasawa, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2851.
- 26 A. I. Kozlov, A. P. Kozlova, H. Liu and Y. Iwasawa, *Appl. Catal. A: General*, 1999, **182**, 9.
- 27 G. C. Bond and D. T. Thompson, *Catal. Rev.-Sci. Eng.*, 1999, **41**(3&4), 319.
- 28 G. C. Bond and D. T. Thompson, *Gold Bull.*, 2000, **33**, 41.
- 29 Y. Iwasawa, *Stud. Surf. Sci. Catal. (Proc. 11th Int. Congr. Catal., Baltimore)*, 1996, **101**, 21.
- 30 M. Olea, M. Kunitake, T. Shido, K. Asakura and Y. Iwasawa, *Bull. Chem. Soc. Jpn.*, in the press.
- 31 Y. Yuan, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, *Chem. Lett.*, 1996, 755.
- 32 Y. Yuan, A. P. Kozlova, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, *J. Catal.*, 1997, **170**, 191.
- 33 Y. Yuan, K. Asakura, A. P. Kozlova, H. Wan, K. Tsai and Y. Iwasawa, *Catal. Today*, 1998, **44**, 333.
- 34 A. P. Kozlova, A. I. Kozlov, S. Sugiyama, Y. Matsui, K. Asakura and Y. Iwasawa, *J. Catal.*, 1999, **181**, 37.