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Low temperature CO oxidation over Au/TiO_2 and Au/SiO_2 catalysts

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After a high-temperature reduction (HTR) at 773 K, TiO_2-supported Au became very active for CO oxidation at 313 K and was an order of magnitude more active than SiO_2-supported Au, whereas a low-temperature reduction (LTR) at 473 K produced a Au/TiO_2 catalyst with very low activity. A HTR step followed by calcination at 673 K and a LTR step gave the most active Au/TiO_2 catalyst of all, which was 100-fold more active at 313 K than a typical 2% Pd/Al_2O_3 catalyst and was stable above 400 K whereas a sharp decrease in activity occurred with the other Au/TiO_2 (HTR) sample. With a feed of 5% CO, 5% O_2 in He, almost 40% of the CO was converted at 313 K and essentially all the CO was oxidized at 413 K over the best Au/TiO_2 catalyst at a space velocity of 333 h^{-1} based on $CO+O_2$. Half the chloride in the Au precursor was retained in the Au/TiO_2 (LTR) sample whereas only 16% was retained in the other three catalysts; this may be one reason for the low activity of the Au/TiO_2 (LTR) sample. The reaction order on O_2 was approximately 0.4 between 310 and 360 K, while that on CO varied from 0.2 to 0.6. The chemistry associated with this high activity is not yet known but is presently attributed to a synergistic interaction between gold and titania.

Keywords: CO oxidation; Au; Au/TiO_2 catalysts; CO oxidation over Au; low-temperature CO oxidation; catalytic CO oxidation

1. Introduction

Supported gold catalysts were recently studied in this laboratory to determine whether oxygen vacancies formed at the titania surface as a consequence of Schottkey junctions, as proposed by Frost [1], could explain the enhanced catalytic activity found in certain hydrogenation reactions over TiO_2-supported noble metals [2]. Au/TiO_2 and Au/SiO_2 catalysts were found to be inactive for CO and acetone hydrogenation, even after high-temperature reduction (HTR) at 773 K; thus, these results showed that this junction model cannot explain the enhanced hydrogenation activity obtained from the metal–support interaction that is created between Pt and titania [2]. To ensure the presence of exposed gold surface atoms, CO oxidation was chosen as a test reaction over these Au/SiO_2 and Au/TiO_2 catalysts because gold had been reported to catalyze this reaction [3–6]. Furthermore, CO oxidation is an environmentally important reaction and, in addition to CO removal in homes and offices, catalysts with good low-temperature activity can also find valuable applications in orbiting CO_2 lasers [7,8] and in CO detectors [9,10]. During this study we found that certain gold catalysts were very active for CO oxidation, and this paper reports the catalytic performance of TiO_2-supported Au after different pretreatments, as well as that of a Au/SiO_2 catalyst, for CO oxidation near room temperature.

2. Experimental

The supported gold catalysts were prepared by an incipient wetness method using $AuCl_3$ (Johnson–Matthey, $99.99^{+}\%$), SiO_2 (Davison, grade 57) and TiO_2 (Degussa, P25). Details of the preparation method, together with their adsorption behavior, were reported earlier [2].

The reactor system used for these CO oxidation studies utilized a glass reactor with an internal fitted glass disc to support the catalyst powder and a heating mantle connected to a temperature controller. CO (Matheson, 99.99%) was first passed through a heated molecular sieve trap to decompose any metal carbonyls and then through an Oxytrap (Alltech Assoc.), O_2 (MG Ind., $99.99^{+}\%$) was passed through a molecular sieve trap to remove any water, while H_2 (MG Ind., $99.999^{+}\%$) and He (MG Ind., $99.999^{+}\%$) were first passed through molecular sieve traps then through Oxytraps. All gas flow rates were initially monitored with Hastings–Raydist mass flowmeters; however, the system was later upgraded by the installation of mass flow controllers (Tylan, model FC-260). The reactor effluent was analyzed with a gas chromatograph (Perkin-Elmer, Sigma 3) equipped with a TCD and a column packed with Carbosieve G. Typically a 0.6–1.0 g sample was loaded in the reactor cell, given an in situ reduction pretreatment then cooled to the reaction temperature under flowing He. CO and He flowrates were selected and given 30 min to stabilize, then O_2 was added to the stream. A total flowrate of about 50 SCCM was typically used, and after 20 min on stream a gas sample was taken for GC analysis. A bracketing technique was used during these runs in which the O_2 flow was stopped for 20 min while reaction conditions were changed, then O_2 was readmitted. The typical space velocity based on ($CO + O_2$) was 333 h^{-1} as He constituted 90% of the feed. Conversions were typically below 15% and the system was treated as a differential reactor. The Weisz criterion was also checked and found that the catalyst particles were free from mass transfer limitations [11].

The catalyst pretreatments followed the procedures mentioned earlier [2]. The Au/SiO_2 catalyst was reduced under flowing H_2 (1 atm, 2500 h^{-1}) at 723 K for 1 h. Three different pretreatments were used with the Au/TiO_2 sample: a

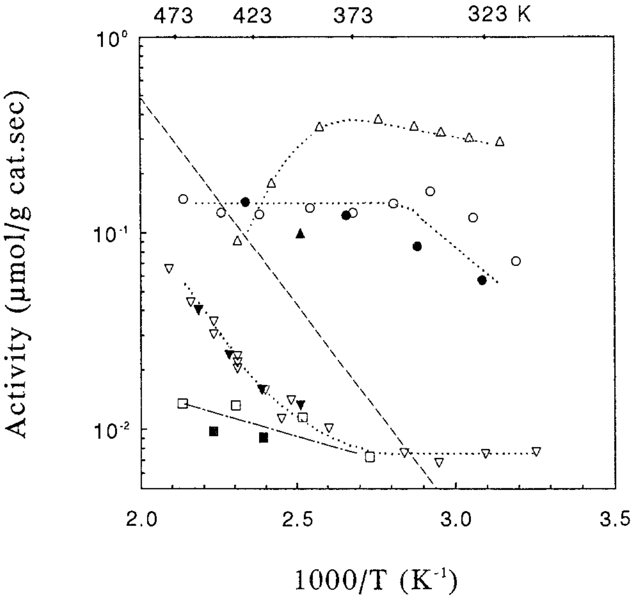

Fig. 1. Arrhenius plots of CO oxidation at $P_{CO} = P_{O_2} = 38$ Torr; open symbols represent an ascending temperature sequence and filled symbols represent a descending temperature sequence: (△) 2.3% Au/TiO_2 (HTR); (▽) 2.3% Au/TiO_2 (LTR); (○) 1.8% Au/SiO_2; (□) TiO_2 (HTR). The dashed line represents the activity of 2.2% Pd/Al_2O_3 at $P_{CO} = 26$, $P_{O_2} = 1.32$ Torr (from ref. [12]).

LTR (low-temperature reduction) step at 473 K for 2 h under flowing H_2 (1 atm, 2500 h^{-1}), a HTR (high-temperature reduction) step at 773 K for 1 h under flowing H_2, and a HTR step followed by calcination with 20% O_2 in He at 673 K for 1 h and then a LTR step (HTR/C/LTR). Residual Cl analyses were carried out on used samples using X-ray fluorescence.

Partial pressure dependence runs with the Au/TiO_2 (HTR/C/LTR) sample were carried out after upgrading the reactor system with mass flow controllers. During these tests either CO or O_2 was kept constant at 5% in the feed gas while the other gas was varied. A smaller amount of catalyst (≈ 0.35 g) and a different total flowrate (≈ 35 SCCM) were used for these tests; thus, the space velocity (CO + O_2) at standard conditions was typically 444 h^{-1} in these experiments.

3. Results

Arrhenius plots at $P_{CO} = P_{O_2} = 38$ Torr (5% CO and O_2) for the Au/SiO_2, Au/TiO_2 (LTR), Au/TiO_2 (HTR), and pure TiO_2 (HTR) samples are shown in fig. 1. Open symbols represent data collected with ascending temperatures while filled symbols represent results obtained with descending temperatures. No

Table 1
CO oxidation kinetics at temperatures below 360 K

Catalyst	Pressure (Torr)		E_A (kcal/mol)	Activity at 313 K		Au crystallite size (nm)	TOF ($s^{-1} \times 10^3$)	Ref.
	P_{CO}	P_{O_2}		(μmol/(s g cat))	(μmol/(s g Au))			
1.8% Au/SiO_2	38	37	3.6	0.069	3.85	30	20	
2.3% Au/TiO_2 (LTR)	39	37	-0.2 ± 1.8	0.007	0.33	25	1.3	
2.3% Au/TiO_2 (HTR)	38	37	1.4 ± 0.2	0.281	12.20	25	75	
	14	7	1.5 ± 1.1	0.171	7.43	25	45	
	7	3.5	3.5 ± 1.5	0.082	3.57	25	22	
2.3% Au/TiO_2								
(HTR/C/LTR)-I	38	36	3.1 ± 1.6	1.06	46.20	≈ 30	240	
(HTR/C/LTR)-II (after deactivation)	37	37	9.2 ± 2.8	0.323	14.03	≈ 30	73	
(HTR/C/LTR)-I	15	7.4	–	0.375	16.30	≈ 30	85	
(HTR/C/LTR)-I	7.4	3.6	–	0.203	8.83	≈ 30	46	
Au sponge	38	38	2.1	1.048	0.56	–	–	[4]
Au(110)	–	–	2.0 ± 1.0	–	–	–	–	[17]
5% Au/Fe_2O_3	7.6	156	7.2	0.133	2.6	16	7	[6]
12% Au/Fe_2O_3 [a] (Au/Fe = 1/19)	7.6	156	–	> 2.4	> 21.3	3.6	13	[6]
12% Au/Fe_2O_3 [a] (Au/Fe = 1/19)	7.6	3.8	7.9	0.088	0.8	–	–	[7]
12% Au/MnO_x [a] (Au/Mn = 1/19)	7.6	3.8	2.0	0.411	3.4	–	–	[7]
2.4% Au/TiO_2 (110 m^2/g)	7.6	156	–	1.23 [b]	51 [b]	≈ 10	83 [b]	[56]
2.4% Au/TiO_2 (40 m^2/g)	7.6	156	–	1.23 [c]	51 [c]	≈ 4	33 [c]	[56]
2.2% Pd/Al_2O_3	26	132	9.7	0.005	0.2 [d]	3.7	0.08	[12]

[a] Prepared by coprecipitation, washed with hot water.

[b] Measured at 308 K. [c] Measured at 273 K. [d] Per g Pd.

Table 2
CO oxidation kinetics at temperatures above 360 K

Catalyst	Pressure (Torr)		E_A (kcal/mol)	Activity at 433 K	
	P_{CO}	P_{O_2}		(μmol/ (s g cat))	(μmol/ (s g Me))
1.8% Au/SiO_2	38	37	0.5±0.6	0.136	7.54
2.3% Au/TiO_2 (LTR)	39	37	8.0±1.2	0.024	1.03
	27	136	4.8±1.0	0.035	1.50
2.3% Au/TiO_2 (HTR)	38	37	–	0.092	3.99
2.3% Au/TiO_2 (HTR/C/LTR)	37	37	2.3±4.0	2.232	97.05
SiO_2	38	37		a	
TiO_2 (LTR)	38	37		a	
TiO_2 (HTR)	38	37	1.6±2.1	0.011	–
2.2% Pd/Al_2O_3 [b]	26	132	17.3	0.788	35.98

[a] No detectable activity.
[b] From ref. [12].

measurable activity was detected with pure SiO_2 and TiO_2 (LTR). In several cases the order of introduction of the reactants was reversed, that is, CO was added to an O_2/He mixture flowing over a Au/TiO_2 (LTR) catalyst sample; no obvious effect on activity was observed between 398 and 448 K. A dashed line representing the activity of a 2% Pd/Al_2O_3 catalyst [12] is also included for comparison. It is clear that supported gold catalysts can be much more active than Pd catalysts at lower temperatures. Fig. 1 also shows an unusual characteristic of many of these Au catalysts, i.e. a break point in the slope exists around 360 K in the Arrhenius plots of these Au catalysts. The irreversible decrease in activity for Au/TiO_2 (HTR) after temperatures exceed 373 K may be associated with the oxygen sensitivity of the titania in the HTR sample, similar to that found with TiO_2-supported noble metals [13]. Consequently, for clarity, catalytic behavior is divided into a region above 360 K and a region below 360 K, and results in the respective regions are given in tables 1 and 2 along with results from previous studies. Specific activities are given per gram gold since the dispersion of Au is difficult to determine although XRD measurements indicated the presence of 25–30 nm Au crystallites on each support [2]. The Au/TiO_2 (HTR) catalyst is clearly active for low-temperature CO oxidation; its activity is almost 40 times higher than the Au/TiO_2 (LTR) sample and is 3 times higher than the Au/SiO_2 catalyst. It has a specific activity comparable to those for gold catalysts made from coprecipitation techniques which have been reported to give much smaller gold particles and, consequently, much higher dispersions [6,7]. The sample of 2.3% Au/TiO_2, (HTR/C/LTR)-II was a portion of that used in the activity maintenance runs shown in fig. 3 below, hence it had been deactivated and was not regenerated.

Fig. 2 illustrates the results of an experiment to determine the sensitivity of

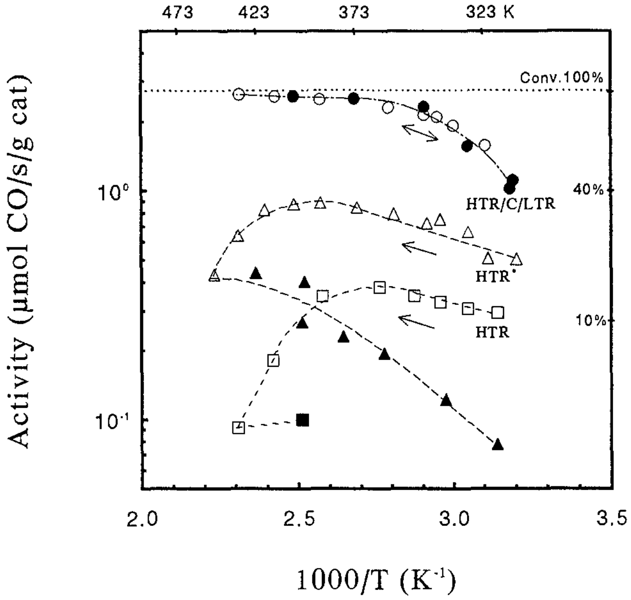

Fig. 2. Activity measurements of CO oxidation at $P_{CO} = 38$, $P_{O_2} = 38$ Torr, open and filled symbols as in fig. 1: (○) 2.3% Au/TiO_2 (HTR/C/LTR); (△) run on 2.3% Au/TiO_2 (HTR) protected from P_{O_2} surge; (□) run not protected (from fig. 1).

the Au/TiO_2 (HTR) catalyst to oxygen exposure. A test was conducted to prevent any surge of O_2 pressure in the feedstream while opening the valve to introduce O_2 into the CO/He mixture. After this precaution the activity of Au/TiO_2 (HTR) was at least a factor of 2 higher than that reported in fig. 1. Also included in fig. 2 is the activity of the Au/TiO_2 (HTR/C/LTR) sample, which not only was higher but also apparently less sensitive to O_2 than the Au/TiO_2 (HTR) sample because it did not exhibit an activity decrease above 370 K. With this catalyst a conversion of essentially 100% was obtained at 413 K at a space velocity (CO + O_2) of 333 h^{-1} and CO and O_2 pressures of 0.05 atm. The activity maintenance of the two most active catalysts at 313 K was recorded over a 24 h period and these results are shown in fig. 3, where the relative activity is normalized to that after 20 min on stream. The relative activity at 1 represents a CO conversion of about 15% for 2.3% Au/TiO_2 (HTR) and 35–40% for 2.3% Au/TiO_2 (HTR/C/LTR). The Au/TiO_2 (HTR/C/LTR) catalyst shows better stability at higher reactant pressures.

Fig. 4 illustrates the absence of any significant differences between CO adsorption on the Au/TiO_2 (HTR/C/LTR) and Au/TiO_2 (LTR) catalysts; both isotherms are essentially the same as that for the pure TiO_2 support, they represent reversible adsorption, and they fit a Langmuir isotherm well. Fig. 5 shows oxygen uptakes on Au/TiO_2 samples after either an initial LTR step or a HTR, calcination, LTR (HTR/C/LTR) pretreatment, as well as the subsequent H_2 uptakes on these O-exposed surfaces. All uptakes are very low, but the latter

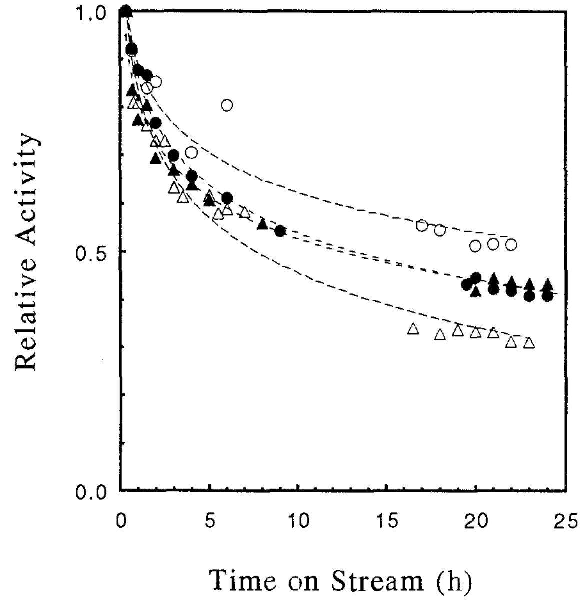

Fig. 3. Activity maintenance of CO oxidation at 313 K for 2.3% Au/TiO$_2$ (HTR) (open symbols) and 2.3% Au/TiO$_2$ (HTR/C/LTR) (filled symbols): (△, ▲) $P_{CO} = 38$, $P_{O_2} = 38$ Torr; (○, ●) $P_{CO} = 7$, $P_{O_2} = 3.5$ Torr.

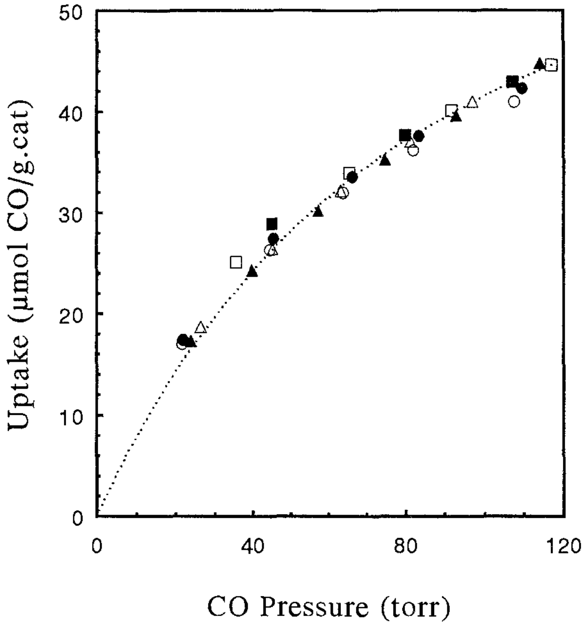

Fig. 4. CO adsorption at 300 K: (○) 2.3% Au/TiO$_2$ (LTR); (△) 2.3% Au/TiO$_2$ (HTR/C/LTR); (□) TiO$_2$ (HTR). Filled symbols represent the first isotherms and open symbols represent the second isotherms obtained after a 30 min evacuation at 300 K. The dotted line represents the fit to a Langmuir isotherm.

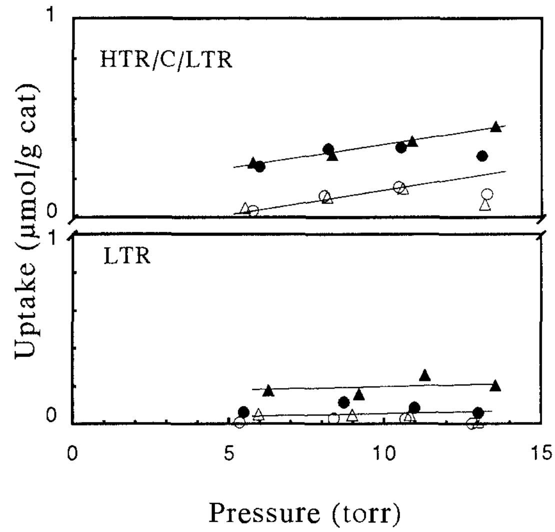

Fig. 5. O_2 adsorption (△, ▲) and H_2 titration (○, ●) at 300 K over (a) 2.3% Au/TiO_2 (LTR) and (b) 2.3% Au/TiO_2 (HTR/C/LTR). Filled symbols represent the first isotherm and open symbols represent the second isotherms obtained after a 30 min evacuation at 300 K. The lines represent the O_2 isotherms.

pretreatment gives a somewhat higher oxygen adsorption capacity as indicated by the difference between two consecutive isotherms at 10 Torr, for example.

The activity of the Au/TiO_2 (HTR/C/LTR) catalyst was determined again with a second smaller sample and a higher space velocity (444 h^{-1} based on CO + O_2). Fig. 6 shows the results of three runs which are compared to the earlier data obtained with a larger sample size and lower space velocity. It is difficult to determine a single activation energy from fig. 6 because the data are not linear; however, the average activation energy from these three runs, represented by the dashed lines, is around 9.2 kcal/mol at lower temperatures and drops to 2.3 kcal/mol above 350 K. The O_2 and CO partial pressure dependencies of the rate over the Au/TiO_2 (HTR/C/LTR) sample at 313, 333, and 353 K are shown in figs. 7 and 8. In both figures, the activity at each temperature was normalized to that at a standard set of conditions, i.e. $P_{CO} = P_{O_2} = 38$ Torr and 313 K, because a small amount of deactivation was sometimes observed. However, a catalyst usually could be regenerated by a calcination step at 673 K followed by a LTR step. When fitted to a power rate law, the results in fig. 7 gave a reaction order on oxygen that was close to 0.4, although it may be somewhat lower at lower pressures [14]. The CO reaction order appears to vary with both temperature and pressure. A power rate law gave a value of 0.24 between 17 and 187 Torr at 313 and 333 K but it increased to near 0.6 at 353 K, while at lower pressures at 313 K it was 0.5, which is close to that obtained under different pressure conditions [14]. It should be noted that the break point

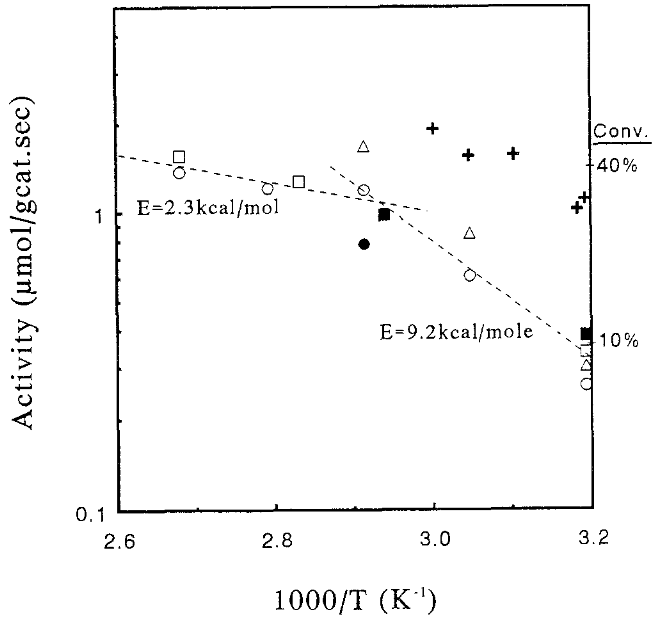

Fig. 6. Arrhenius plots of CO oxidation over 2.3% Au/TiO$_2$ (HTR/C/LTR) sample at $P_{CO} = P_{O_2} = 38$ Torr: (△, ▲, ○, ●, □, ■) three independent runs with 0.35 g sample after activity maintenance run in fig. 3 at a space velocity of 444 h^{-1} (CO + O$_2$); open symbols represent ascending temperature and filled symbols represent descending temperature. The five data points (+) from fig. 2 using 0.7 g sample and a space velocity of 333 h^{-1} are shown for comparison.

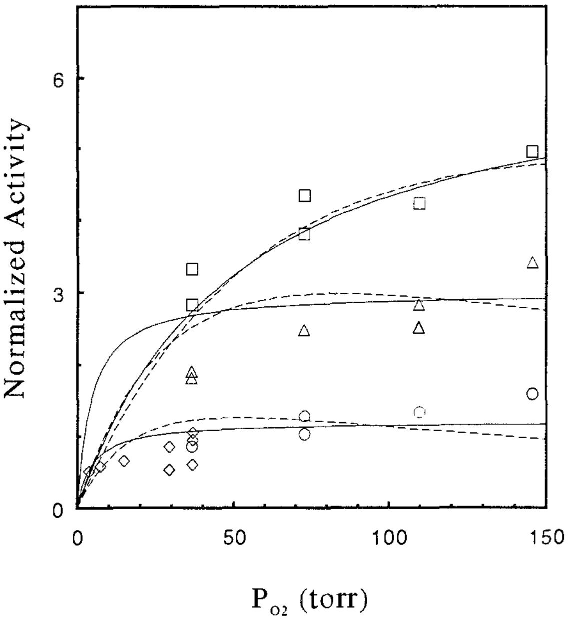

Fig. 7. Dependence of CO oxidation on O$_2$ pressure over 2.3% Au/TiO$_2$ (HTR/C/LTR) at 313 K (○, ◇), 333 K (△), and 353 K (□); $P_{CO} = 38$ Torr. Dashed lines represent the fit of the data to eq. (2) (non-competitive adsorption) while the dashed lines represent the fit to eq. (1) (competitive adsorption).

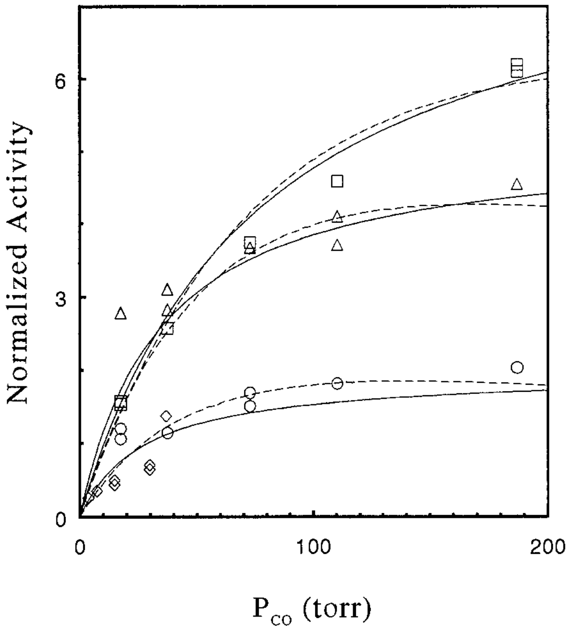

Fig. 8. Dependence of CO oxidation on CO pressure over 2.3% Au/TiO$_2$ (HTR/C/LTR) at 313 K (○, ◇), 333 K (△), and 353 K (□); P_{O_2} = 37 Torr. The solid lines represent the fit of the data to eq. (2) (non-competitive adsorption) while the dashed lines represent the fit to eq. (1) (competitive absorption).

in the Arrhenius plot of fig. 6 is around 353 K, the temperature at which the higher reaction order on CO was observed in fig. 8, and this could represent a change in reaction mechanism.

Residual Cl analyses are listed in table 3. The high Cl content of the Au/TiO$_2$ (LTR) sample may be one reason for its exceptionally low activity. After reduction, the other three catalysts had residual Cl contents equivalent to 16% of the Cl in the catalyst precursor, thus giving a final Cl/Au ratio of 0.5. The calcination step did not reduce the Cl content.

Table 3
Residual chloride analysis on supported gold catalysts

Catalyst	XFS (cps)	Cl (wt%)	% Cl retained	Cl/Au
2.3% Au/TiO$_2$ (fresh)	830.2	1.244	100	3.0
1.8% Au/SiO$_2$ (723 K red.)	107.0	0.160	16.4	0.49
2.3% Au/TiO$_2$ (LTR)	384.7	0.576	46.3	1.39
2.3% Au/TiO$_2$ (HTR/C/LTR)	130.2	0.195	15.7	0.47
2.0% Au/TiO$_2$ (HTR)	119.6	0.179	16.5	0.50

4. Discussion

Gold is typically a very poor catalyst for most reactions, which is most likely due to the limited chemisorption of most molecules on Au surfaces. Deposited gold films have been found to adsorb CO only at temperatures below 110 K [15], and an Au(110)-(1 × 2) single crystal was found to adsorb O atoms, but not O_2 molecules [16]. The conversion of gas-phase CO to CO_2 occurred on this latter surface at 300 K when the surface was precovered with oxygen atoms [17], and the reaction between CO and molecular O_2 has been reported to proceed on gold wires and gold sponge [3,4]. A very low apparent activation energy of about 2 kcal/mol was observed in all three studies [3,4,17]. Recently, gold dispersed on certain oxide supports has been found to be very active for CO oxidation and these catalysts have been proposed for use in long-life orbiting CO_2 lasers and in CO sensors and converters [5–10].

This study has found that TiO_2-supported gold catalysts can be very active for CO oxidation and can also be considered for potential use in low-temperature applications. Supported Group VIII metals, such as Pd, at comparable loadings are much less active near room temperature [12], and Cu, a Group IB metal as is Au, also has a much lower activity [18]. Among the Au/TiO_2 samples studied, the HTR and HTR/C/LTR pretreatments gave the most active catalysts, and both samples retained about half their initial activity over a 24 hour period and appeared to be reaching a stable activity. Because the HTR/C/LTR catalyst appeared to be less sensitive to the O_2 pressure and temperature conditions, this pretreatment is preferred; however, we do not yet know if it is optimum. The origin and the nature of the active sites in these supported gold catalysts are not known at this time. Due to the fact that Au/SiO_2 is active while SiO_2 and TiO_2 alone are inactive at 313 K, at least a portion of the activity must be associated with the gold, although it may be influenced by residual chloride or some form of metal–support interaction. Unfortunately, one cannot express the specific activity as a turnover frequency with great accuracy because it is very difficult to measure the surface area of gold [2], so activities are compared per gram gold in tables 1 and 2. Furthermore, it is difficult to compare specific activities because reaction conditions have been noticeably different in the different studies and no kinetic parameters were previously reported to allow adjustment to a standard set of temperature and pressures. However, a very approximate estimate of turnover frequency (TOF) can be obtained from the crystallite sizes obtained from XRD [2] or TEM [6,56] and the relationship between crystallite size (d (nm)) and dispersion (D) for Au, i.e. $D = 1.2/d$. When possible these TOF values are listed in table 1. The estimated TOFs also show that the Au/TiO_2 (HTR) catalysts are the most active, especially when given the (HTR/C/LTR) pretreatment, and our TOF values are close to those obtained from a recent paper called to our attention even though the O_2 pressure used was over 40 times higher than that in the present study.

As shown in table 2, pure SiO_2 and TiO_2 after a LTR step were not active for CO oxidation; however, a low level of activity developed at higher temperatures with TiO_2 after a HTR step. This could be a consequence of a transformation from the anatase to the rutile phase or it could be due to the presence of defect sites caused by oxygen vacancies in the lattice. Golodets et al. reported that rutile was more active than anatase for CO oxidation at 800 K or higher [19]; although the reaction temperature was much higher, this may still imply that the structure of the TiO_2 can affect its catalytic activity. Titania and other oxides have been reported to catalyze this reaction at these much higher temperatures [19–22], and the participation of lattice oxygen is generally proposed as part of the reaction mechanism [21–26]. However, in addition to the possibility that defect sites on the titania at the Au–titania interface could serve as the source of activated oxygen for CO oxidation, it is equally plausible that these sites on the titania adsorb CO and increase the surface concentration of CO, as implied by fig. 4, and the role of the Au is primarily to adsorb and activate O_2 molecules which react with adsorbed CO in the interfacial region.

The 100-fold difference between activities after an initial LTR step and a HTR/C/LTR treatment cannot be correlated with the small difference in O_2 adsorption exhibited in fig. 5. The irreversible oxygen adsorption, as well as that which interacts with adsorbed hydrogen, on the HTR/C/LTR sample is only about twice that on the LTR sample based on the difference between the two isotherms; furthermore, the actual difference is only about 0.1 μmol/g cat, which is very small. Considering the nearly identical CO uptakes on the pure TiO_2, Au/TiO_2 (LTR), and Au/TiO_2 (HTR/C/LTR) samples shown in fig. 4, these adsorption results for CO probably reflect contributions primarily from the TiO_2 surface rather than the exposed gold surface. This conclusion is different from that reached by Shastri et al. who attributed the CO uptake at 323 K on a 0.64% Au/TiO_2 catalyst to adsorption on the gold; however, their pure titania showed essentially no adsorption [27].

As suggested, two explanations of the activity difference between the LTR and the HTR/C/LTR samples are the change in TiO_2 phase structure and the level of residual chloride. It is anticipated that during the HTR treatment some transformation to the rutile structure will occur [27,28], and a reversal back to the anatase phase during calcination is not expected because rutile is the thermodynamically favored phase [27]. Although the rutile structure is more easily depleted of oxygen than anatase [19,21], which could facilitate the formation of oxygen vacancies, it is unlikely that this phase transition alone could cause the 100-fold variation in activity. Consequently, at this time we believe that chloride on the catalyst surface can affect catalytic behavior, presumably in a negative way [6]. Table 3 shows that neither the HTR step nor the calcination step was severe enough to remove all the chloride, and the three samples reduced at 723 K or higher – Au/SiO_2, Au/TiO_2 (HTR) and Au/TiO_2 (HTR/C/LTR) – retained a Au/Cl ratio of 2. This implies the possibility of a strong residual Au–Cl interaction with small Au particles even though Spencer and Lambert found that Cl on an Au(111) surface reacted readily with H_2 near 800 K [29]. The amounts of Cl retained in these catalysts are lower than the monolayer coverages of Cl on TiO_2 and SiO_2 surfaces [30–32], and chloride bound in the sublayer structure in Au/MnO_x catalysts has been proposed [33]. Although the reason why these three catalysts retain the same Cl/Au ratio remains unanswered at this time, it must be pointed out that a Cl effect alone cannot account for the higher activities of Au/TiO_2 (HTR) and Au/TiO_2 (HTR/C/LTR) compared to Au/SiO_2. To help clarify the role of chloride, future studies will involve the preparation of Cl-free Au catalysts.

Consequently, some form of metal–support interaction is proposed and, in fact, the support has been previously proposed to affect the activity of supported gold particles for CO oxidation [6,7], isotopic O_2 exchange [34] and oxygen exchange between CO and CO_2 [35,36]. Previous studies on clean, unsupported gold surfaces have clearly shown that gold does not adsorb CO [15], H_2 [15,16] or O_2 [16] at room temperature, whereas small gold particles dispersed on a support have been found not only to adsorb CO [38,39] and O_2 [27,40] but also to catalyze reactions involving these gases, especially those involving O_2 [6,7,41,42]. Also, the addition to the feed of molecular oxygen at low levels (2–3%) has been reported to markedly increase the reaction rate of the H_2–D_2 exchange reaction and propene hydrogenation over 0.05% Au/SiO_2 at 423 K [43]. Our recent study using an O_2 adsorption/H_2 titration technique at 473 K showed that oxygen does adsorb on small dispersed gold crystallites and that impurities could not account for the amount of uptake [2]. The presence of the titania complicated interpretation of the behavior of the Au/TiO_2 catalysts; however, oxygen adsorption on SiO_2-supported Au was clearly established, which implies that small Au particles have different surface properties than bulk Au. This conclusion is supported by spectroscopic studies which have characterized dispersed Au systems. Based on EXAFS studies, Parravano and co-workers proposed that Au crystallites, if they were small enough, could interact with certain oxides like MgO, but no interaction was found with SiO_2 [44,45]. Kageyama et al. also proposed an interaction between Au and Fe_2O_3 based on their EXAFS results [46], and positively charged Au on Al_2O_3 was found in the Mössbauer study of Delgass et al. [47]. Furthermore, noticeable shifts in the Au_{4f} binding energy have been observed in XPS data, and an oxidized state of Au has been proposed by a number of investigators [33,48,49]; however, an alternative interpretation has been proposed by Kim and Winograd which attributes this binding energy shift to a matrix effect which occurs only in very small Au particles [50]. Despite the difference in interpretation, these spectroscopic studies imply that small dispersed Au particles might be expected to have properties different from bulk gold surfaces; consequently, under appropriate conditions this form of Au could become an active catalyst.

No previous CO oxidation study has examined the kinetics of this reaction;

therefore, partial pressure dependencies were determined at three temperatures and various sequences of elementary steps were examined to determine which, if any, were consistent with the results shown in figs. 7 and 8. Six different possibilities were considered: (a) a Rideal–Eley mechanism, (b) adsorption as the rate determining step (RDS), (c) Langmuir–Hinshelwood (LH) models with either competitive (one type of site) or noncompetitive (two types of sites) adsorption between CO and O_2 and the reaction between adsorbed CO and O atoms as the RDS and, finally, (d) Langmuir–Hinshelwood models with either competitive or noncompetitive adsorption and the reaction between adsorbed CO and O_2 molecules as the RDS [14]. The models represented by (a) and (b) can be rejected because both derived rate expressions require a first-order dependence on one of the reactants, and this was not observed in the data. The rate expressions derived from the last four models were fitted to the data in figs. 7 and 8 using a nonlinear regression technique employing the Gauss–Newton method and a convergence criterion requiring a change in the residual to decrease below 10^{-8}. This procedure allowed values to be obtained for the rate constant of the RDS, k, and the equilibrium adsorption constants for CO and O_2, K_{CO} and K_{O_2}. From these values at different temperatures, the activation energy of the RDS and the enthalpy and entropy of adsorption were determined, and the latter two parameters were evaluated for physical consistency [14]. The two models in (c) invoking adsorbed O atoms were rejected because the calculated entropy losses for dissociative oxygen adsorption were greater than the entropy of the gas-phase O_2 molecule; this is not possible [51,52]. However, both the enthalpy and entropy values derived from either of the models proposed in (d) were reasonable, and they are listed in table 4. In either

Table 4
Kinetic parameters obtained from fitting of rate expressions along with calculated activation energy, entropy of adsorption and enthalpy of adsorption

Model		Estimate ± standard error				E_A [c] (kcal/mol)	$-\Delta S^0_{ad}$ (cal/mol K)	$-\Delta H^0_{ad}$ (kcal/mol)
		313 K [a]	313 K	333 K	353 K			
d1	k' [b]	5.3 ± 4.3	22 ± 7	46 ± 13	130 ± 20	−14	–	–
	K_{CO} [d]	35 ± 72	7.1 ± 2.7	7.1 ± 2.6	3.6 ± 0.5	–	−21	−8.1
	K_{O_2} [d]	65 ± 102	11 ± 5	12 ± 5	5 ± 1	–	−23	−9.3
d2	k' [b]	1.7 ± 1.0	2.5 ± 0.7	5.8 ± 1.7	20.0 ± 3.6	−12	–	–
	K_{CO} [d]	24 ± 27	27 ± 11	22 ± 9	10 ± 2	–	−8.9	−4.8
	K_{O_2} [d]	170 ± 150	170 ± 320	170 ± 360	15 ± 4	–	−27	−12

[a] Data measured in partial pressure range of 5–37 Torr, other data obtained between 30 and 180 Torr.

[b] Dimensionless rate constant after normalization to that at standard conditions of 313 K, $P_{CO} = P_{O_2} = 38$ Torr.

[c] Activation energy of RDS.

[d] In atm^{-1}.

case, chemisorption of both CO and O_2 is weak and reversible at reaction temperatures, which is consistent with the isotherms in figs. 4 and 5.

Consequently, this initial analysis of the rate data indicates that the most consistent model invokes a surface reaction between an adsorbed CO molecule and an adsorbed O_2 molecule. If competitive adsorption on one type of site is assumed, the standard LH expression is obtained,

$$r = \frac{kK_{CO}K_{O_2}P_{CO}P_{O_2}}{\left(1 + K_{CO}P_{CO} + K_{O_2}P_{O_2}\right)^2}, \tag{1}$$

whereas if noncompetitive adsorption is assumed, the following LH expression is derived:

$$r = \frac{kK_{CO}K_{O_2}P_{CO}P_{O_2}}{(1 + K_{CO}P_{CO})(1 + K_{O_2}P_{O_2})}. \tag{2}$$

The capabilities of these two models to fit the data are shown in figs. 7 and 8. The latter model does a somewhat better job of correlating the data, but at this time we cannot choose between these two models because of the variations between the predicted and observed rate behavior with either model. Therefore, we propose that the data suggest an activated O_2 molecule reacts with an adsorbed CO molecule in a RDS, and further studies are underway to test this hypothesis. The possibility that O_2 molecules are involved, rather than O atoms, is consistent with the known adsorption behavior of oxygen on gold, and it is further supported by the recent study of Zhao and Gomer, who found that CO adsorbed on a Pd monolayer pseudomorphically formed on a W(110) surface can be oxidized by adsorbed dioxygen at low temperatures [53]. If the model represented by eq. (2) should prove to be correct, one interpretation is that CO adsorbs on sites on the titania surface near the gold, consistent with the results in fig. 4 which imply Au has no significant influence on CO adsorption, while dioxygen adsorbs on the gold and is activated by defect sites at the Au–titania interface. Another similar possibility is that dioxygen is adsorbed and activated at the Au–titania interface and CO is supplied to these sites via a reverse spillover process on the titania surface, as proposed by Kieken and Boudart for Al_2O_3-supported Pd [54]. However, two other situations can be proposed: the first is that the principal role of the Au is to create O vacancies at the titania surface and these are the primary active sites, and the second is that the gold is modified by the titania so that CO adsorption is enhanced on the gold itself. Work is underway to ascertain which of these possibilities is the most appropriate.

5. Summary

CO oxidation over Au/SiO_2 and Au/TiO_2 has been studied. The Au/TiO_2 catalyst was given given three different pretreatments: low-temperature reduction (LTR), high-temperature reduction (HTR), and HTR followed by calcination and then LTR (HTR/C/LTR). The LTR sample had very low activity, while the latter two samples had high CO oxidation activity near room temperature. The activity of the Au/SiO_2 catalyst was ten-fold higher than the Au/TiO_2 (LTR) sample but ten-fold lower than the Au/TiO_2 (HTR/C/LTR) catalyst. The LTR and HTR/C/LTR Au/TiO_2 samples had very similar CO and O_2 uptakes; consequently these two parameters cannot explain the 100-fold difference in the activity. Residual Cl analyses showed that the Au/TiO_2 (LTR) sample retained approximately 50% of the Cl from the Au precursor, while the other three catalysts retained only 16%, which gave a final Cl/Au ratio of 0.5; consequently, the low activity of the Au/TiO_2 (LTR) sample may be due to its high chloride content. However, the role of Cl, which is presumably inhibitive, has not yet been established and future studies will involve the preparation of Cl-free Au catalysts. The activation energies were typically low and varied from 2 to 9 kcal/mol, with the Au/TiO_2 (HTR/C/LTR) catalyst giving a value of 9 kcal/mol below 360 K and a value near 2 above this temperature. Partial pressure dependency runs showed that the overall reaction order on the Au/TiO_2 (HTR) and Au/TiO_2 (HTR/C/LTR) catalysts was near unity, the reaction order on O_2 was around 0.2–0.4 and that on CO was about 0.5, with the last value depending on temperature and pressure. Initial kinetic results allowed a number of reaction models to be rejected, and only Langmuir–Hinshelwood models involving a reaction between adsorbed CO and O_2 molecules gave a consistent fit with the data; however, a choice between competitive and noncompetitive adsorption could not be made. The role of the titania is not yet clear; however it may be not only to increase the surface concentration of adsorbed CO, but also to provide interfacial sites capable of activating O_2 molecules adsorbed on gold. It is well established that titania can increase specific activities in certain hydrogenation reactions, including CO [28,55]; however, to the best of our knowledge, this represents the first evidence that titania can enhance the activity of a metal in an *oxidation* reaction.

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