

Cobalt promotion of Au/TiO₂ catalysts for the reaction of carbon monoxide with oxygen and nitrogen oxides

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Abstract

A range of 3d transition metal-promoted 2% Au/TiO₂ catalysts has been prepared and tested for low-temperature CO oxidation. It has been demonstrated that only cobalt acts as a promoter, with maximum effect at the same weight loading as Au, while the other additives have either no effect or severely suppress the Au/TiO₂ system. Pretreatment conditions play a critical role in establishing highest activity for the reaction. Comparative studies of the catalytic activity of Au/TiO₂ and Co-promoted Au/TiO₂ have been carried out for the reactions of CO with N₂O and NO, and cobalt acts as a promoter in these reactions also. Kinetic analysis of the reactions of CO with O₂ and N₂O indicate a slight positive order in each reactant in both cases. Measurements of CO and CO₂ adsorption under transient pulse conditions has shown that CO uptake occurs primarily on the support and is strongly dependent on the conditions of pretreatment. The uptake on samples reduced at 773 K is substantially lower than that observed after subsequent re-oxidation at the same temperature. CO₂ uptakes are substantially greater and subject to the same effect but to a lesser extent.

Keywords: Carbon monoxide; Oxidation; Gold catalysts; Nitrogen oxides; Cobalt promotion

1. Introduction

Catalysts capable of oxidising carbon monoxide at ambient temperature are of interest for use in regenerative CO₂ lasers [1,2], rescue equipment, and air purification [3]. The moisture sensitivity of traditional hopcalite (MnO₂/CuO) catalysts has generated increasing interest in noble metal based systems. Platinum on tin oxide catalysts, first described by Stark et al. [4] are now available commercially [5]. It has recently been reported that addition of an iron promoter improves its activity and decay profile [6]. Haruta et al. [7] have demonstrated that

some gold-transition metal oxides are active to 200 K and there are claims that Au/MnO_x has the optimum long-term reaction characteristics [8]. Some of the gold-based systems are also quite effective for other reactions, including carbon dioxide and carbon monoxide hydrogenation [9,10], hydrocarbon combustion [11] and hydrogen oxidation [7].

The mechanism by which the transition metal oxide is able to induce activity in the otherwise catalytically inactive gold is yet to be established with certainty although there is agreement activity resides at the narrow metal-metal oxide junction which can be maximised by dispersion of the gold as finely as possible. In this respect the phenomenon resembles the strong

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metal support interaction (SMSI) effect which inhibits carbon monoxide adsorption, and changes catalytic properties, for strongly reduced Pt/TiO₂ and other platinum metal/reducible oxide combinations [12,13]. Indeed recent work by Haruta et al. [7] and Lin et al. [14] has established that Au/TiO₂ can be substantially active for carbon monoxide oxidation. In the present work we have investigated whether this system is amenable to further promotion by transition metals and whether the activity extends to nitrogen containing oxidants. We have also assessed the amounts of carbon monoxide, oxygen and carbon dioxide adsorbed on such catalysts by transient pulse methods.

2. Experimental

The catalysts were prepared by an incipient wetness technique. ACS or higher grade HAuCl₄ and nitrate salts of the selected 3d transition metals were dissolved in Milli-Q water and deposited on the support in the ratio of 0.4 ml g (TiO₂)⁻¹. The resulting pastes were dried at 313 K for 24 h, followed by 12 h at 383 K. The TiO₂ (Cab-O-Ti; BET surface area 54 m² g⁻¹) was dried for 24 h at 393 K and calcined in air for 3 h at 773 K before impregnation. BET surface areas of the prepared catalysts were in the range 52 ± 5 m² g⁻¹. Catalyst samples were pretreated in either 100% H₂, 10% H₂/He (for transient analysis) or 5% O₂/He by staged heating to the maximum temperature and held there for one hour. The catalysts were cooled to reaction temperature in the pretreatment atmosphere.

Catalyst activity was determined using a standard continuous flow system. Gas mixtures were supplied to the reactor (Pyrex 6 mm ID) by a set of mass flow controllers and the exit gases from the reactor analysed by a two column gas chromatograph (Shimadzu GC8A) which was programmed to switch between a 13X molecular sieve column at 313 K (for O₂ or N₂ and CO) and one of Porapak Q at 273 K

(for CO₂ and N₂O). In experiments using CO and NO the 13X column was replaced by one of Porapak Q cooled to 195 K. The system allowed the determination of conversion with reproducibility of ±3% using product analyses at low conversions and residual reactant analyses at high conversion. The reactor fitted closely in a 15 mm OD aluminium block grooved to take a stainless coil through which cold nitrogen gas could be passed. The reactor and block were located vertically in a tube furnace and driven by a programmable temperature controller. The system provided temperature control to ±0.5 K from 173 K to 873 K as measured by a 1.5 mm sheathed iron-constantan thermocouple with its tip touching the bottom (outlet) side of the catalyst bed.

All catalyst screening was carried out using 200 ± 2 mg samples and standard test mixtures comprising 1% CO and 0.6% O₂, 1.0% CO and 1.0% N₂O, 0.7% CO and 0.7% NO all diluted in helium with a total flowrate of 100 cm³ (STP) min⁻¹ (GHSV = 2 × 10⁴ h⁻¹ at room temperature). The adsorption measurements were carried out using a basically similar system with a leak to a quadrupole mass spectrometer (VG SX300), via 0.6 mm ID stainless steel tubing arranged to draw gas from a point a few mm downstream of the catalyst sample. A small volume 4-port valve upstream of the reactor was used to switch the flow to the reactor from helium to test gas with one or other of the streams containing a known concentration of Ar (up to 0.7% depending upon the experiment). A multiple ion monitoring system allowed 2 to 6 scans of 4 masses each second. The measured rise time for the tracer Ar signal was 1–1.5 s when using a standard flow rate of 50 cm³ (STP) min⁻¹ and 200 mg of catalyst.

3. Results and discussion

3.1. Oxidation of CO by O₂

Only preparations initially pretreated in hydrogen showed low temperature catalytic activ-

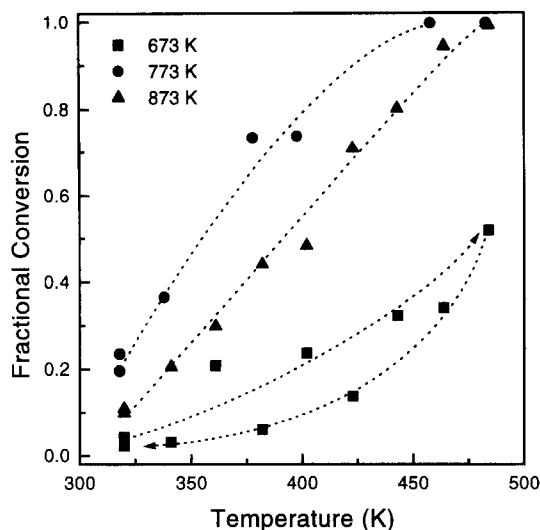


Fig. 1. Effect of pretreatment on the activity of Au/TiO₂ for the CO/O₂ reaction under standard conditions.

ity. Samples initially pretreated in O₂ showed no activity even after subsequent H₂ reduction. Active catalysts usually showed a sharp fall in activity during the first hour of exposure to the test gases and a subsequent slow decline to a pseudo-steady state over a period of several hours thereafter. The usual procedure was to allow the catalyst to line out for a minimum of 12 h at 320 K by which time the activity decline was 2% per hour or less and then to determine conversion as a function of temperature first with increasing temperatures and then decreasing ones.

Fig. 1 shows the effect of reduction temperature on the activity of a 2% Au/TiO₂ catalyst for the CO/O₂ reaction when tested in this way under standard conditions. Activity is induced on reduction at 673 K but the conversion-temperature curve exhibits some hysteresis with lower activity when cooling. Best activity is achieved on reduction at 773 K with a temperature giving 50% conversion, T_{50} , of 360 K. Reduction at 873 K results in lower activity (T_{50} of 390 K). A catalyst which had been reduced at 773 K retained moderate activity after reoxidation at 773 K even though samples initially pretreated in O₂ and then reduced showed no

activity. All the following work was carried out with catalysts reduced at 773 K.

The corresponding conversion-temperature curves for 2% Au/TiO₂ catalysts doped with 2% 3d transition metals (based on metal content) are shown in Fig. 2. Cobalt alone has a promoting effect. Nickel is without effect while iron, chromium and especially manganese are detrimental. Co-promoted Au/TiO₂ behaves similarly to Au/TiO₂ in displaying maximum activity after reduction at 773 K, moderate activity on reoxidation and having zero activity at 320 K after calcination at 773 K as the initial pretreatment. It is possible that a different reduction temperature, perhaps lower with manganese and higher with iron and chromium would be preferable as observed for the development of the SMSI effect with platinum group metals/3d oxides [12,13].

Fig. 3 illustrates the effect of cobalt loading on light-off performance. Reduced 2% Co/TiO₂ itself exhibits some activity and hysteresis in this case with higher activity when the temperature is being reduced. The same effect is evident to some extent with 2% Au/0.5% Co/TiO₂. Highest activity is observed when the cobalt loading is 2%. This gives 50% conversion at

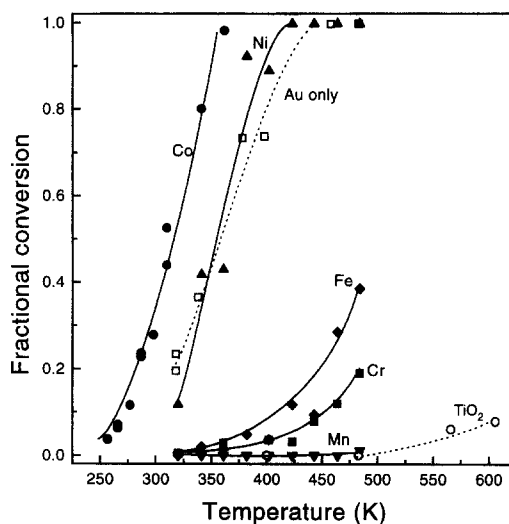


Fig. 2. Effect of 3d transition metals on the activity of Au/TiO₂ for the CO/O₂ reaction under standard conditions.

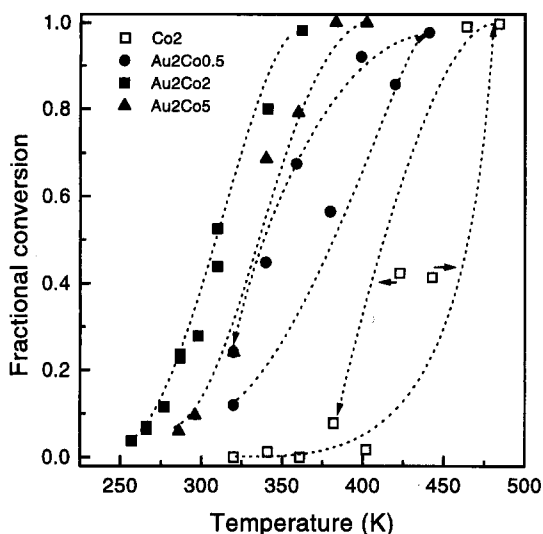


Fig. 3. Effect of cobalt loading on light-off performance for the CO/O₂ reaction under standard conditions.

320 K and close to complete conversion at 360 K. The activity of samples containing 0.5 and 5% Co is lower but both are significantly more active than Au/TiO₂ alone.

The dependence of reaction rate on concentration was determined using catalysts which had been used for long periods and under conditions giving conversions of < 20% so that the differential reactor approximation could be used to calculate reaction rates. As may be seen from Fig. 4 and Fig. 5 the rate of CO oxidation reaction increases with both CO and O₂ concentration but the dependence is somewhat less for O₂. These kinetic behaviours are consistent with Langmuir–Hinshelwood models describing either competitive adsorption at one type of site:

$$\text{Rate} = kK_{\text{CO}}K_{\text{O}_2}P_{\text{CO}}P_{\text{O}_2} / (1 + K_{\text{CO}}P_{\text{CO}} + K_{\text{O}_2}P_{\text{O}_2})^2,$$

or non-competitive adsorption at different sites:

$$\text{Rate} = kK_{\text{CO}}K_{\text{O}_2}P_{\text{CO}}P_{\text{O}_2} / (1 + K_{\text{CO}}P_{\text{CO}})(1 + K_{\text{O}_2}P_{\text{O}_2}).$$

Kinetic orders, obtained from log–log plots, and activation energies, from Arrhenius plots, are summarised in Table 1. The apparent order

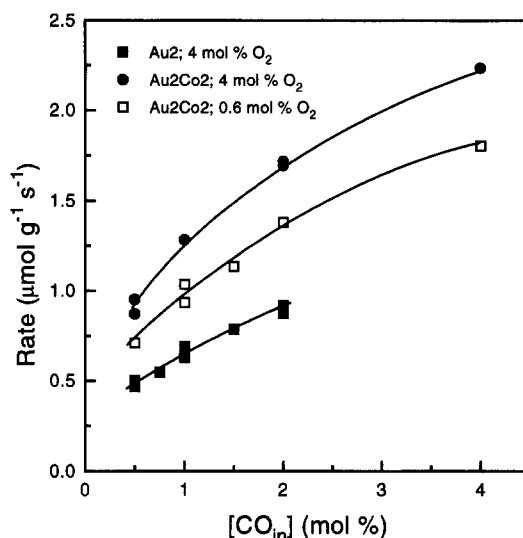


Fig. 4. Dependence of reaction rate on carbon monoxide concentration for CO + O₂ at 320 K.

is 0.45 in CO and about 0.2 in O₂ for both Au/TiO₂ and Au/Co/TiO₂. Kinetic orders are almost identical whether measured under standard conditions or with the fixed reactant in excess. The activation energies are also similar: 35 ± 3 kJ/mol. Table 1 also gives the measured activity at 300–320 K in comparison with other values reported in the literature. The catalysts

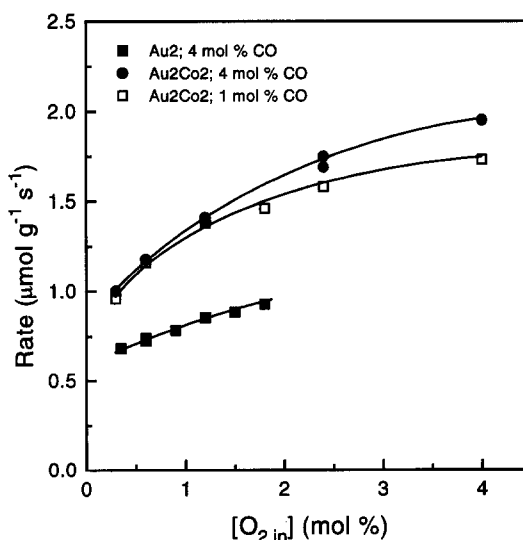


Fig. 5. Dependence of reaction rate on oxygen concentration for CO + O₂ at 320 K.

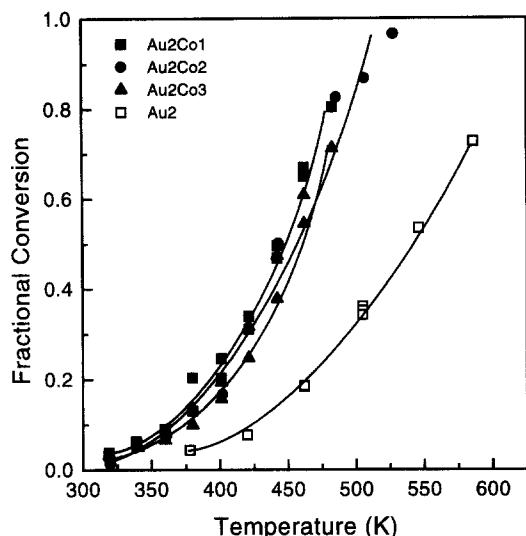


Fig. 6. Effect of cobalt loading on light-off performance for the CO/N₂O reaction under standard conditions.

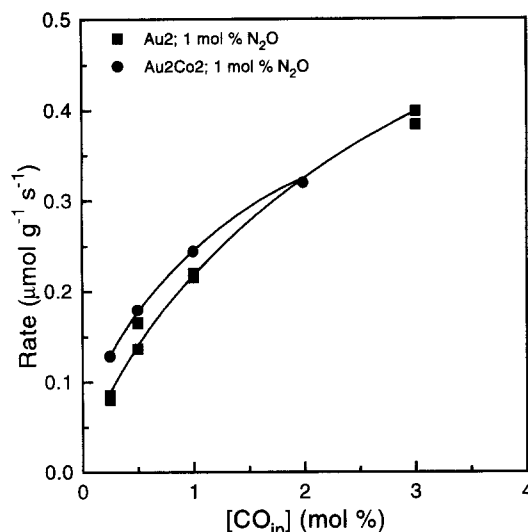


Fig. 7. Dependence of reaction rate on CO concentration for CO + N₂O at 400–420 K.

tested here are of comparable or higher activity than most. They are notably less active than those of Haruta et al. [7] but those measurements were made with a 5-fold higher oxygen pressure than used here. This would result in higher activity given the positive order in O₂. Also, in that case deposition–precipitation was used as the preparation technique which generally gives much smaller gold crystallites than those produced by incipient wetness preparations. Average particle sizes have not yet been determined for our catalysts, but these are expected to be about 30 nm as reported for similarly-prepared Au/TiO₂ [14].

3.2. Oxidation of CO by N₂O and NO

Fig. 6 shows the activity of another set of cobalt-promoted Au/TiO₂ catalysts, all reduced at 773 K, for the oxidation of CO by N₂O rather than O₂. Again the inclusion of cobalt leads to a large increase in activity with T_{50} lowered by 80 K from that for Au/TiO₂. The extent of promotion shows little dependence on the cobalt concentration over the range 1 to 3% but the presence of both Au and Co is clearly required, since Co/TiO₂ did not catalyse the reaction at temperatures below 600 K. N₂O decomposition was not observed on Au/TiO₂ or any Co-pro-

Table 1

Rate data and kinetic parameters for CO oxidation on Au/TiO₂ and Au/Co/TiO₂ at 320 K and comparison with other low temperature Au catalysts in the literature

Catalyst	P_{CO} (Torr)	P_{O_2} (Torr)	E_a (kJ mol ⁻¹)	Rate (mmol g ⁻¹ s ⁻¹)	GHSV	CO order	O ₂ order	Ref.
2% Au/TiO ₂	7.6	30.4	32	0.80 (320 K)	2×10^4	0.45	0.19	^a
2% Au/2% Co/TiO ₂	7.6	30.4	38	1.16 (320 K)	2×10^4	0.44	0.22	^a
2.3% Au/TiO ₂	7.4	3.6	13	0.20 (313 K)	$(3-5) \times 10^3$	0.24	0.4	[14]
3.3% Au/TiO ₂	7.6	156	34	~ 2.9 (310 K)	2×10^4	0.05	0.24	[7]
11.3% Au/Fe ₂ O ₃	7.6	156	35	> 2.4 (310 K)	2×10^4	0	0.05	[7]
12% Au/MnO _x	7.6	3.8	n/a	1.15 (328 K)	8×10^3	< 0	> 0	[8,15]
19.5% Pt/SnO _x	7.6	3.8	n/a	0.2 (328 K)	2.7×10^3	n/a	n/a	[8]
2.2% Pd/Al ₂ O ₃	26	132	40	0.005 (313 K)	1.4×10^4	-0.10	1.3	[16]

^a = this work; n/a = not available.

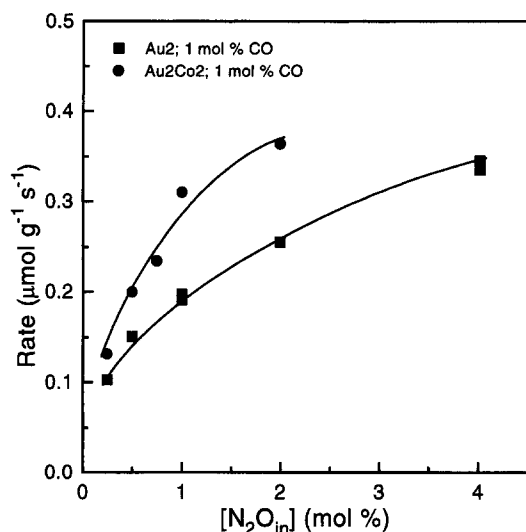


Fig. 8. Dependence of reaction rate on N_2O concentration for $\text{CO} + \text{N}_2\text{O}$ at 400–420 K.

moted catalysts at the highest temperatures examined. Slow deactivation of both Au/TiO_2 and Co -promoted Au/TiO_2 was observed at 440 K and 400 K, respectively. On the Co -promoted catalyst, this lining-out continued for up to 60 h before a pseudo-steady state was attained.

Increased reaction rates are observed with both CO and N_2O pressures in a similar manner to that observed for CO oxidation (Fig. 7 and Fig. 8). The kinetic orders and activation energies for both 2% Au/TiO_2 and 2% $\text{Au}/2\%$

Co/TiO_2 are shown in Table 2. The table also contains a summary of results obtained for this reaction using other types of catalysts since there is no previous work with Au -based systems. Allowing for the temperature and concentration differences it would appear that the present catalysts are substantially more active than any reported previously. However, the conditions vary so much that exact comparisons are impossible.

Au/TiO_2 also promotes to some extent the reaction between CO and NO at low temperatures. Approximately 10% conversion of a feed of 0.7 mol% in both CO and NO was found initially at 320 K, decreasing to about 2% after 15 h. The product of the reaction was almost exclusively N_2O . However, the catalyst was rapidly poisoned at higher temperatures and activity was virtually zero at 440 K. These results are generally similar to those of Cant and Fredrickson [22] who observed similar loss of activity for the reaction on unsupported gold sponge and attributed the effect to a reaction between NO and Au . Au/TiO_2 has not been examined for activity in this reaction above 440 K but the Co -promoted catalyst showed a stable conversion of 12% at 480 K. The products were N_2 and N_2O in approximately equal amounts. The formation of N_2 is not surprising given the high activity of the catalyst for the $\text{CO} + \text{N}_2\text{O}$ reaction at the same temperature (Fig. 6). Formation

Table 2

Rate data and kinetic parameters for $\text{CO} + \text{N}_2\text{O}$ on Au/TiO_2 and $\text{Au}/\text{Co}/\text{TiO}_2$ catalysts at 400–420 K and comparison with other values from the literature

Catalyst	P_{CO} (Torr)	$P_{\text{N}_2\text{O}}$ (Torr)	E_a (kJ mol ⁻¹)	Rate (mmol g ⁻¹ s ⁻¹)	GHSV	CO order (T (K))	N_2O order	Ref.
2% Au/TiO_2	7.6	7.6	45.00	0.29 (420 K)	2×10^4	0.58 (478)	0.42	^a
2% $\text{Au}/2\% \text{Co}/\text{TiO}_2$	7.6	7.6	37.00	0.67 (400 K)	2×10^4	0.44 (478)	0.52	^a
0.5% $\text{Rh}/\text{Al}_2\text{O}_3$	4.3	4.3	170	1.26 (630 K)	6×10^4	-0.86 (583)	0.68	[17]
0.6% $\text{Cr(II)}/\text{SiO}_2$ gel	360	360	n/a	0.016 (353 K)	67	n/a	n/a	[18]
0.6% $\text{Co(II)}/\text{SiO}_2$ gel	360.00	360	n/a	0.016 (433 K)	67	n/a	n/a	[18]
2.1% $\text{MoO}_3/\text{SiO}_2$ gel	60	60	n/a	0.018 (333 K)	Constant volume 200 cc	0 (333)	1	[19]
$\text{Cr}/\text{Fe}_2\text{O}_3$	65	65	n/a	~ 1.5 (533 K)	6400	n/a	n/a	[20]
MnO	40	40	130	8.6 (573 K)	1.4×10^4	0 (573)	1	[21]
Co_3O_4	40	40	105	0.96 (493 K)	1.4×10^4	0 (493)	0.7	[21]

^a = this work; n/a = not available.

of both products is characteristic of standard Rh/Al₂O₃ catalysts which develop activity for the CO + NO reaction at ~ 470 K and become more selective to N₂ at higher temperature [23].

The activity losses observed in the reactions between CO and N₂O and NO did not translate into corresponding deleterious effects on the CO/O₂ reaction. Instead, Au/TiO₂ exposed to CO + O₂ following either of the other reactions immediately produced > 50% conversion at 440 K, further recovering to a stable 75% within 60 min. This indicates that adsorbed intermediates from the other reactions, perhaps N₂O itself and adsorbed nitrosyl (NO₂), respectively, bind very weakly at the Au/oxide interface and can be quickly flushed off. Recovery was somewhat more complete following the CO + NO reaction.

3.3. Adsorption of CO, O₂ and CO₂ by transient pulse method

Adsorption of CO, O₂ and CO₂ were measured under plug flow conditions by mass spectrometry at 300 K. Concentrations of 4000 ppm in each gas were used with a flow rate of 50 cm³ (STP) min⁻¹. Pulses were of 2 min length

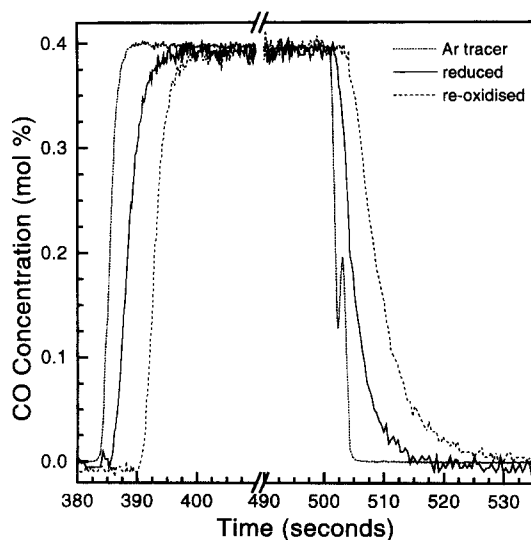


Fig. 9. CO uptake on Au/TiO₂ at 300 K following reduction in 10% H₂ and re-oxidation in 5% O₂ at 773 K.

Table 3
CO uptakes on TiO₂, Au/TiO₂ and Au/Co/TiO₂ at 300 K

Catalyst	Pretreatment	CO _{ads} (total)	CO _{ads} (rev)	CO _{ads} ^{av} (irrev)
TiO ₂	reduction	4.2	3.6	0.6
TiO ₂	re-oxidation	8.0	7.7	0.3
TiO ₂	re-reduction	5.0	4.5	0.5
Au/TiO ₂	reduction	1.5	1.3	0.2
Au/TiO ₂	re-oxidation	6.0	5.4	0.5
Au/TiO ₂	re-reduction	1.4	0.9	0.4
Au/Co/TiO ₂	reduction	2.4	2.2	0.2
Au/Co/TiO ₂	re-oxidation	7.9	6.3	1.8
Au/Co/TiO ₂	re-reduction	0.9	0.8	0.2

Values are in mmol g⁻¹ and accurate to ± 10%.

and 90% or greater of adsorption was complete within the first 15 s for CO. CO uptakes were strongly dependent on the method of pretreatment. Fig. 9 shows that the amount of CO taken up after reoxidation is greater than that following reduction as evidenced by the longer breakthrough time. Switching the stream back to He alone leads to rapid and near complete desorption (within 25 s for reoxidised Au/TiO₂ and 15 s for reduced Au/TiO₂). This might be first considered to be a type of SMSI behaviour with partial coverage of Au by reduced TiO_x species and consequent suppression of CO adsorption. However this is not the case since TiO₂ exhibits similar behaviour. As indicated in Table 3 the oxidised forms of TiO₂, Au/TiO₂ and Au/Co/TiO₂ have reasonably similar capacities of 6–8 mmol g⁻¹ ((7–9) × 10¹⁶ CO molecules m⁻²). Thus, the observed CO uptake is occurring on the TiO₂ component. The result may be interpreted in terms of the removal of oxide sites for CO adsorption following reduction which are then restored upon reoxidation. Reduced TiO₂ adsorbs half the above amount while both Au-containing samples adsorb significantly less again. The lower capacity of the latter two samples may reflect more extensive reduction of the TiO₂ by hydrogen spillover at the Au/TiO₂ interface. With one exception the amount of irreversibly adsorbed CO is small and not very much greater than experimental error in integrating the tails of the desorption

Table 4

CO₂ uptakes on TiO₂, Au/TiO₂ and Au/Co/TiO₂ at 300 K

Catalyst	Pretreatment	CO ₂ ads (total)	CO ₂ ads (rev)	CO ₂ ads (irrev)
TiO ₂	reduction	23.10	22.20	0.9
Au/TiO ₂	reduction	15.8	14.80	1.0
Au/Co/TiO ₂	reduction	18.4	12.70	5.7
Au/Co/TiO ₂	re-oxidation	19.6	18.8	0.8

Values are in mmol g⁻¹ and accurate to $\pm 10\%$.

curves. Reoxidised Au/Co/TiO₂ exhibits more significant irreversible adsorption which may reflect some oxidation of CO by labile oxygen in the CoO_x component. It should be noted that the data in Table 3 was acquired after one or two pulses to equilibrate the sample. Some CO₂ evolution was usually observed during initial pulse(s) and CO uptakes were correspondingly higher.

Similar pulse experiments were conducted to determine if O₂ and CO₂ were adsorbed. Within the accuracy of the measurements, no O₂ adsorption occurred. Lin et al. [14] have reported small uptakes of O₂ (< 1 mmol g⁻¹) at 300 K on Au/TiO₂ reduced in 100% H₂ at 773 K in a constant volume apparatus over exposure times of up to one hour. Uptake rates this small are below the detection limit of our pulse method.

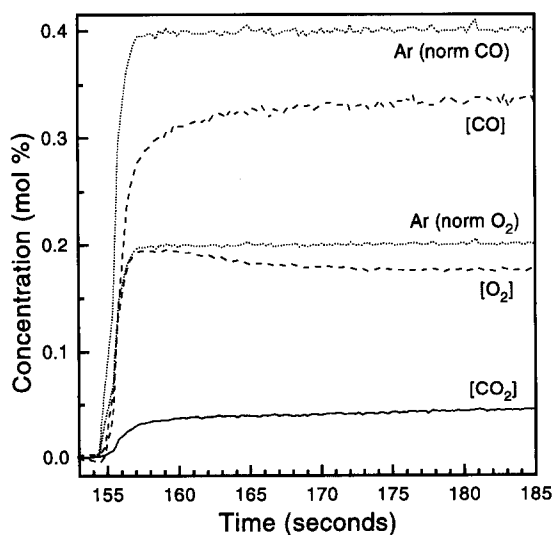


Fig. 10. Transient response of reduced Au/TiO₂ at 300 K to a reaction feed of 4000 ppm CO + 2000 ppm O₂ at 50 cm³ (STP) min⁻¹.

The amount of CO₂ adsorbed was 3–5 times that of CO as may be seen from Table 4 and appears to be taking place on the TiO_x as was the case with CO. The difference between reduced and reoxidised samples is less than with CO and this time the reduced form of Au/Co/TiO₂ shows the greatest irreversible adsorption (with the same cautions as outlined in the case of CO desorption).

The absence of immediate O₂ uptake on reduced Au/TiO₂ carries over to reaction mixtures as may be seen from Fig. 10. The CO curve is delayed relative to the normalised Ar one as expected for CO adsorption on TiO₂. After 5 s exposure the CO curve is approaching the plateau value of ~ 3300 ppm ($\sim 18\%$ conversion). By contrast, the O₂ curve closely matches its normalised Ar curve for the initial 5 s and takes approximately 15 s to approach its steady state value. It is perhaps significant that CO₂ evolution commences before there is detectable O₂ consumption. This would suggest that the initial step is removal of very small amounts of a surface oxygen species which is then continuously replaced from the gas phase as the catalytic process ensues. The apparent shortfall in mass balance also resolves within 90 s (not shown) and measurement of CO₂ desorption following the switch back to carrier alone corresponds to the CO initially taken up by the TiO₂.

The foregoing experiments were somewhat disappointing in that they failed to reveal any specific adsorptive capacity by active catalysts. Indeed, reduced catalysts adsorb less CO than reoxidised ones. However, it should be noted that the method used would be insufficiently

sensitive to detect adsorption which was confined to the Au/oxide interface (calculated to be $\sim 0.04 \text{ mmol g}^{-1}$ assuming circumferential contact at Au particles of $d = 30 \text{ nm}$ and $\sim 0.35 \text{ mmol g}^{-1}$ for $d = 10 \text{ nm}$). The technique is of value in following fast adsorption and initial reaction profiles and further experiments are in progress to determine more precisely the transient behaviour of both Au/TiO₂ and Au/Co/TiO₂ in response to different pretreatment conditions and reactant pressures.

4. Conclusions

Au/TiO₂ is highly active for CO oxidation at 320 K and exhibits significant activity for the reaction between CO and N₂O below 420 K. Initial examination has indicated that it may have some further promise in the CO + NO reaction. Cobalt acts as promoter for all three reactions and is unique among the tested 3d transition metals in this regard. Both CO + O₂ and CO + N₂O exhibit positive order kinetics and low activation energies. Transient pulse analysis indicates that CO and CO₂ are adsorbed reversibly on the TiO₂ component at room temperature and that adsorptive capacity is a function of the pretreatment conditions.

Acknowledgements

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