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CO oxidation over Au/TiO_2 prepared from metal-organic gold complexes

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A series of Au/TiO_2 catalysts has been prepared from precursors of various metal-organic gold complexes (Au_n, $n = 2$–4) and their catalytic activity for CO oxidation studied. The Au/TiO_2 catalyst synthesized from a tetranuclear gold complex shows the best performance for CO oxidation with transmission electron microscopy of this catalyst indicating an average gold particle size of 3.1 nm.

KEY WORDS: CO oxidation; Au/TiO_2; gold catalysts; gold complexes; PROX reaction.

1. Introduction

Although the early publications by Bond et al. [1,2] and Parravano et al. [3,4] reported that small gold particles exhibited catalytic activity for some reactions, such as hydrogenation of olefins and oxygen transfer reactions, gold was generally considered to be catalytically inactive [5]. Over the past 20 years, the volume of literature on the application of gold catalysts has been steadily increasing since Haruta reported that highly dispersed gold particles supported on metal oxides are extremely active for CO oxidation [6,7]. Studies on high-surface-area catalysts have shown that the catalytic performance of gold catalysts depends strongly on the size of the Au particles, with a maximum activity found for particles with an average diameter ~3 nm [8]. Valden *et al.* [9] found that the size dependence of CO oxidation on model catalysts is similar to that on high-surface-area catalysts, and explained this size dependence as arising from quantum size effects.

For the preparation of highly dispersed gold catalysts, specific methods have been used, such as co-precipitation, deposition-precipitation, and chemical vapor deposition [10]. Conventional impregnation methods, which are widely used to prepare supported metal catalysts, were thought to be ineffective in producing active gold catalysts. Haruta reported that gold catalysts prepared by the impregnation method using $HAuCl_4$ as a precursor, had a particle size larger than 30 nm, and were catalytically inactive for CO oxidation [10].

Metal-organic and organometallic complexes have been widely used in the synthesis of catalysts, however, the use of metal-organic or organometallic gold complexes has been limited. Gates and coworkers reported that a supported mononuclear gold complex was active for ethylene hydrogenation at 353 K [11]. Recently, Iwasawa and coworkers [12–16] prepared highly active CO oxidation catalysts by grafting Au-phosphine complexes onto as-precipitated $Ti(OH)_4$. They found that the as-precipitated $Ti(OH)_4$ was essential for obtaining highly dispersed gold catalysts and the use of a conventional TiO_2 support resulted in a much less active catalyst with a particle size greater than 15 nm. Previous work from our laboratories used a $[Au_6(PPh_3)_6](BF_4)_2$ complex to prepare Au catalysts by the impregnation method on a conventional TiO_2 support; the resulting catalyst was highly dispersed (<5 nm) and active for CO oxidation [17]. Here we report a series of Au/TiO_2 catalysts prepared from Au_n ($n = 2$–4, number of gold atoms in the complex) metal-organic complexes together with their catalytic activity for CO oxidation.

2. Experimental

The Au/TiO_2 catalysts were prepared from metal-organic gold complexes using conventional impregnation methods. Gold complexes with a varying number of gold atoms were used, including $[Au_2(dppm)_2](PF_6)_2$, $Au_3(Ph_2pz)_3$, $[Au_4(dppm)_2(3,5\text{-}Ph_2pz)_2](NO_2)_2$, and $Au_4(form)_4$, dppm = bis(diphenylphosphino)methane, form = (*p*-tolyl)NCN(*p*-tolyl). The synthesis and structures of these complexes are reported elsewhere [18,19]. The amount of the particular gold complex was dissolved in CH_2Cl_2 and mixed with TiO_2 (Degussa P-25) to obtain a nominal gold loading of 1 wt% with respect to the TiO_2 support. The mixture was stirred at room temperature for

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ca. 1 h, heated on a hot plate to evaporate the solvent, and then vacuum dried overnight at 343 K. The as-synthesized catalyst was reduced in hydrogen and helium mixture at 773 K for 3 h, followed by calcination in oxygen and helium at 673 K for 0.5 h. After pretreatment, the sample was cooled to the desired reaction temperature for activity measurements. The catalysts prepared from $[Au_2(dppm)_2](PF_6)_2$, $Au_3(Ph_2pz)_3$, $[Au_4(dppm)_2(3,5\text{-}Ph_2pz)_2](NO_2)_2$, and $Au_4(form)_4$ are designated as Au_2, Au_3, Au_4 #1, and Au_4 #2, respectively.

The TEM data were acquired on a high-resolution JEOL 2010 microscope at the University of New Mexico. The catalytic activity tests were carried out in a conventional flow reactor system. The products were analyzed by a Varian 3400 gas chromatograph equipped with a thermal conductivity detector and a carbosphere column. Fifty milligrams of Au/TiO_2 were used in each activity test, and the gas compositions were $CO/O_2/He = 1:2:25$ with a GHSV of 54,000 $cm^3/g/h$ for the oxidation of CO, and $CO/O_2/H_2 = 1:2:50$ with a GHSV of 100,000 $cm^3/g/h$ for the preferential oxidation (PROX) of CO.

3. Results and discussion

Figure 1 shows the CO conversion as a function of temperature over 1 wt% Au/TiO_2 catalysts prepared from various gold complexes. The two samples prepared from tetranuclear gold complexes were found to be more active than those prepared from di- and tri- nuclear complexes. The Au_4 #1 and Au_4 #2 catalysts showed apparent CO oxidation activities at temperatures below 273 K, with the lowest temperature of CO oxidation observed at about 220 K over the Au_4/TiO_2 #1 sample. The room-temperature CO conversion over the Au_4 #1 sample was over 90%, while no reaction was observed over the Au_2 sample at the same temperature. The catalyst lifetime tests showed that the catalytic activities of the two Au_4/TiO_2 samples decreased slowly with time, with approximately 20% of their activities being lost in the first 4 h at room temperature. Figure 2 shows the Arrhenius plots for CO oxidation over the Au/TiO_2 catalysts. The activation energies for these catalysts were between 18 kJ/mol and 37 kJ/mol, consistent with the literature values for CO oxidation over supported Au catalysts [20].

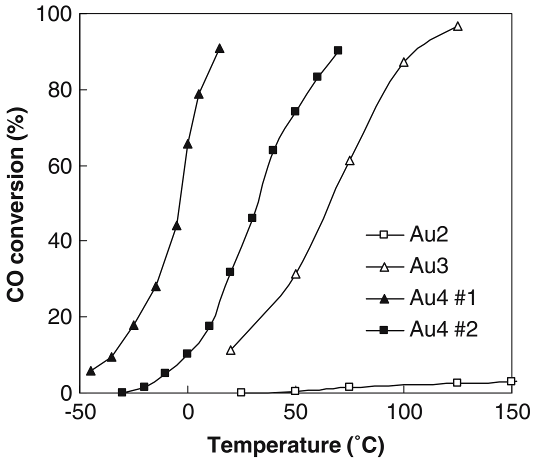

Figure 1. CO conversion as a function of temperature over 1 wt% Au/TiO_2 catalysts. The data were measured in a mixture of $CO/O_2/He$ (1:2:25) with a GHSV of 54,000 $cm^3/g/h$.

The TEM image and the particle size distribution of Au_4/TiO_2 #1 are shown in Figure 3. Most of the gold particles are in the range of 2–6 nm; the average Au particle diameter is 3.1 nm with a percent deviation of 40%. The average gold particle sizes of the Au_2, Au_3 and Au_4 #2 samples are 7.7 nm, 4.8 nm and 3.0 nm, respectively.

The preferential oxidation (PROX) of CO in excess hydrogen was measured over the Au_4/TiO_2 #1 catalyst. Figure 4 shows the CO conversion and CO_2 selectivity as a function of reaction temperature. At room temperature, CO conversion was approximately 54% and the selectivity for CO_2 was over 60%. As the reaction temperature increased, both CO conversion and CO_2 selectivity decreased, however, the CO_2 selectivity dropped more quickly. From room temperature to 325 K, CO conversion was almost constant, whereas CO_2 selectivity decreased from 62% to 23%.

These data show that Au/TiO_2 catalysts prepared from certain metal-organic gold complexes are highly active for CO oxidation. Using a particular precursor complex is critical to obtaining a highly active gold catalyst. Contrary to the assumptions by Haruta [10] and Iwasawa [12–16], these results indicate that a highly-dispersed gold catalyst can be prepared utilizing the impregnation method and a conventional TiO_2 support.

Specific CO oxidation activities of Au/TiO_2 prepared by various methods are compared in Table 1. The Au/TiO_2 catalysts prepared from Au_4 complexes in this work show similar activities as the gold catalysts prepared using the deposition–precipitation method, and are superior to those prepared by other methods.

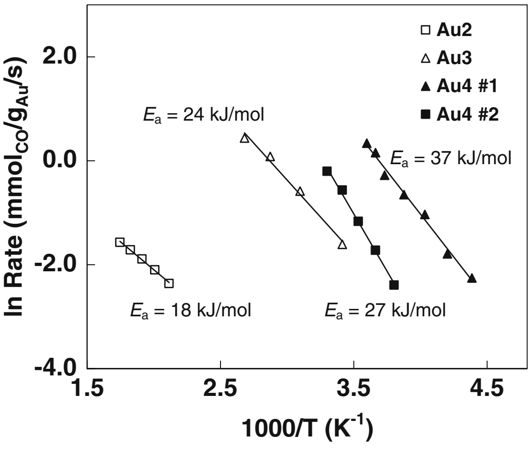

Figure 2. Arrhenius plots for CO oxidation over Au/TiO_2 catalysts.

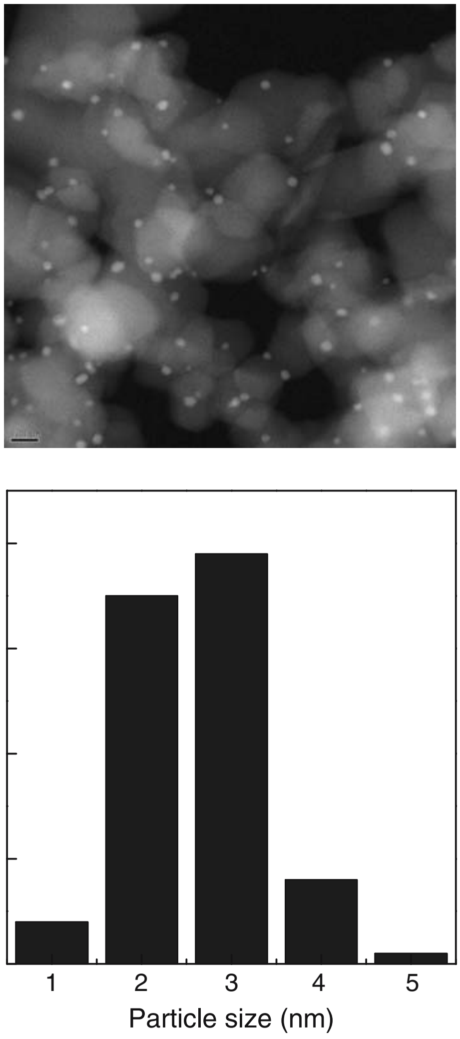

Figure 3. TEM image and gold particle size distribution of Au_4 #1/TiO_2 catalyst.

Several factors may contribute to the high activity of our Au/TiO_2 catalysts. First, the use of metal-organic complexes as precursors avoids chloride. $HAuCl_4$ is widely used as a gold precursor in catalytic studies, invariably leaving a certain amount of chloride residue in the catalysts after preparation. Recently, both experimental and theoretical studies have shown that chloride can poison the catalytic performance of gold catalysts for CO oxidation. Oh *et al.* [24] have shown that chloride residue on a catalyst can promote agglomeration of Au particles during heat treatment, and can inhibit the catalytic activity by poisoning the active site. Density functional calculations show that chloride can act as a poison by weakening the adsorption of O_2 and lowering the stability of the $CO{\cdot}O_2$ intermediate complex [25]. Clearly metal-organic or organometallic precursors provide an attractive route for the preparation of chloride-free gold catalysts.

Another explanation for the high activity of our Au/TiO_2 catalysts also relates to the use of metal-organic precursor complexes. Upon deposition onto the oxide support, these complexes interact with the surface OH groups and become less mobile compared to gold atoms deposited using $HAuCl_4$. Several studies have shown that metal-organic and organometallic complexes are capable of reacting directly with surface OH groups on inorganic oxide surfaces, such as SiO_2, Al_2O_3, and TiO_2, to form well-defined covalent bonds [26,27]. The organic groups in metal complexes could be retained partially or completely following deposition onto oxide supports. For example, Iwasawa *et al.* showed that the cluster framework of $[Au_9(PPh_3)_8](NO_3)_3$ was virtually the same after attachment to TiO_2 [28]. The framework can inhibit agglomeration of gold particles during calcination. Altogether these factors prevent the sintering of gold, and the well-defined structures of the gold complexes lead to a narrow particle size distribution compared to the deposition-precipitation method.

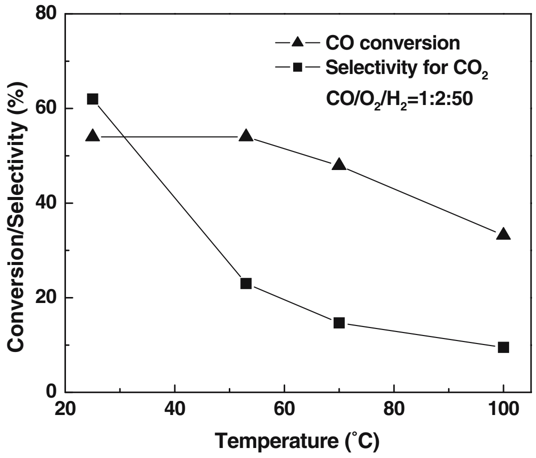

Figure 4. Preferential oxidation of CO on Au_4 #1/TiO_2. The data were measured in a mixture of $CO/O_2/H_2$ (1:2:50) with a GHSV of 100,000 cm^3/g/h.

Our results show that the use of a specific gold precursor complex correlates directly with the gold particle size and the catalytic activity of the resulting catalysts. Gold complexes with varying charges and numbers of gold atoms yield Au/TiO_2 catalysts with varying particle size distributions. The detailed relation between the gold atom number in the precursor and the charges on the complexes to the resulting catalyst is a subject of ongoing investigation.

The Au/TiO_2 catalysts show a potential application for the PROX reaction, which is used to remove trace amounts of CO from hydrogen for fuel cell applications. The most widely used PROX catalyst in industry is alumina-supported platinum, which operates at 423–473 K [29,30]. Recently, Behm and co-workers studied the PROX reaction over Au/Fe_2O_3 and found that the gold catalyst had comparable activity and selectivity to that of Pt/Al_2O_3 at considerable lower temperature [30]. Recent theoretical studies showed that gold is more selective than Pt for the PROX reaction at low

Table 1
Comparison of CO oxidation rates on Au/TiO$_2$ catalysts prepared by different methods

Gold precursor	Catalyst	Prep.[a]	T (K)	Rate (mmol/g$_{Au}$/s)	Ref.
$HAuCl_4$	1% Au/TiO$_2$	IMP	300	2×10^{-5}	[8]
$HAuCl_4$	1% Au/TiO$_2$	FD	300	2×10^{-5}	[8]
$AuPPh_3NO_3$	3% Au/TiO$_2$	IMP	313	6×10^{-3}	[15]
$HAuCl_4$	1.7% Au/TiO$_2$	AuC	300	0.01	[21]
$HAuCl_4$	2.3% Au/TiO$_2$	IMP	313	0.05	[22]
$Me_2Au(acac)$	4.6% Au/TiO$_2$	CVD	262	0.05	[23]
$AuPPh_3NO_3$	3% Au/Ti(OH)$_4$	IOH	300	0.05	[15]
$Me_2Au(acac)$	2.4% Au/TiO$_2$	CVD	293	0.06	[23]
$HAuCl_4$	2.3% Au/TiO$_2$	DP	300	0.2	[8]
$Au_6(PPh_3)_6(BF_4)_2$	1% Au/TiO$_2$	IMP	293	0.3	[17]
$HAuCl_4$	3.1% Au/TiO$_2$	DP	300	0.6	[8]
$Au_4(form)_4$	1% Au/TiO$_2$	IMP	300	0.7	[b]
$[Au_4(dppm)_2(3,5\text{-}Ph_2pz)_2]_2(NO_3)_2$	1% Au/TiO$_2$	IMP	300	3	[b]

[a] IMP, impregnation of oxides; FD, photodecomposition; DP, deposition–precipitation; CVD, chemical vapor deposition.
[b] Present work.

temperature [31]. Our Au/TiO$_2$ catalysts exhibited comparable reaction rates and selectivities to those found for Au/Fe$_2$O$_3$ prepared by the co-precipitation method. Although the CO conversion is insufficient for application to fuel cells, the low-temperature activity of gold catalysts has distinct advantages over Pt-based catalysts.

4. Conclusions

The present work shows that highly active Au/TiO$_2$ catalysts can be prepared from specific metal-organic gold complexes and a conventional TiO$_2$ support utilizing the impregnation method. The catalytic activity and the particle size of the gold catalysts strongly depend on the gold complexes, and the Au/TiO$_2$ with the maximum CO oxidation activity was prepared from a Au$_4$ complex. The catalysts also showed promising results for the PROX reaction.

Acknowledgments

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References

[1] G.C. Bond, P.A. Sermon, G. Webb, D.A. Buchanan and P.B. Wells, J. Chem. Soc., Chem. Commun 444 (1973) .

[2] P.A. Sermon, G.C. Bond and P.B. Wells, J. Chem. Soc., Faraday Trans. I 75 (1979) 385.

[3] D.Y. Cha and G. Parravano, J Catal 18 (1970) 200.

[4] G. Cocco, S. Enzo, G. Fagherazzi, L. Schiffini, I.W. Bassi, G. Vlaic, S. Galvagno and G. Parravano, J Phys Chem 83 (1979) 2527.

[5] J. Schwank, Gold Bull. 16 (1983) 103.

[6] M. Haruta, N. Yamada, T Kobayashi and S. Iijima, J. Catal. 115 (1989) 301.

[7] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J Genet and B. Delmon, J. Catal. 144 (1993) 175.

[8] G.R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, Catal. Lett. 44 (1997) 83.

[9] M. Valden, X. Lai and D.W. Goodman, Science 281 (1998) 1647.

[10] M. Haruta, Catal. Today 36 (1997) 153.

[11] J. Guzman and B.C. Gates, Angew. Chem. Int. Ed. 42 (2003) 690.

[12] Y. Yuan, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, Chem. Lett. (1996) 755.

[13] Y. Yuan, A.P. Kozlova, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, J. Catal. 170 (1997) 191.

[14] A.P. Kozlova, S. Sugiyama, A.I. Kozlov, K. Asakura and Y. Iwasawa, J. Catal. 176 (1998) 426.

[15] Y. Yuan, K. Asakura, A.P. Kozlova, H. Wan, K. Tsai and Y. Iwasawa, Catal. Today 44 (1998) 333.

[16] A.P. Kozlova, K. Asakura, A.I. Kozlov, S. Sugiyama, Y. Matsui and Y. Iwasawa, J. Catal. 181 (1999) 37.

[17] T.V. Choudhary, C. Sivadinarayana, C.C. Chusuei, A.K. Datye, J.P. Fackler and D.W. Goodman Jr., J. Catal. 207 (2002) 247.

[18] A.A. Mohamed, H.E. Abdou, M.D. J.M. Irwin López-de-Luzuriaga, J.P. Fackler and Jr., J. Cluster Sci. 14 (2003) 253.

[19] A.A. Mohamed, J.M. López-de-Luzuriaga, J.P. Fackler and Jr., J. Cluster Sci. 14 (2003) 61.

[20] (a) M. Haruta, CATTECH 6 (2002) 102. (b) M. Okumura, S. Tsubota and M. Haruta, J. Mol. Catal. A Chem. 199 (2003) 73.

[21] J.-D. Grunwaldt, C. Kiener, C. Wogerbauer and A. Baiker, J. Catal. 181 (1999) 223.

[22] S.D. Lin, M. Bollinger and M.A. Vannice, Catal. Lett. 17 (1993) 245.

[23] M. Okumura, K. Tanaka, A. Ueda and M. Haruta, Solid State Ionics 95 (1997) 143.

[24] H.-S. Oh, J.H. Yang, C.K. Costello, Y.M. Wang, S.R. Bare, H.H. Kung and M.C. Kung, J. Catal. 210 (2002) 375.

[25] P. Broqvist, L.M. Molina, H. Grönbecka and B. Hammer, J. Catal. 227 (2004) 217.

[26] Iwasawa Y., in: *Tailored Metal Catalysts*, ed. Y. Iwasawa (Reidel, Dordrecht, Holland, 1986) ch. 1.

[27] Y. Iwasawa, Adv. Catal. 35 (1987) 187.

[28] Y. Yuan, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, Catal. Lett. 42 (1996) 15.

[29] Y. Choi and H.G. Stenger, J. Power Source 129 (2004) 246.

[30] M.J. Kahlich, H.A. Gasteiger and R.J. Behm, J. Catal. 182 (1999) 430.

[31] S. Kandoi, A.A. Gokhale, L.C. Grabow, J.A. Dumesic and M. Mavrikakis, Catal. Lett. 93 (2004) 93.

[32] N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard and J.K. Norskov, J. Catal. 223 (2004) 232.