

Kinetics of CO Oxidation Catalyzed by Supported Gold: A Tabular Summary of the Literature

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Abstract The literature of CO oxidation catalyzed by supported gold is extensive, but reports of the kinetics of the reaction are incomplete and fragmented. This paper is a summary of such information presented in tables that state (1) how the catalysts were made, treated, and tested; (2) their physical properties, such as the average gold particle size; and (3) kinetics data, including turnover frequencies, reaction orders, and apparent activation energies.

Keywords Gold catalyst · Supported gold · CO oxidation · Kinetics of CO oxidation

1 Introduction

Extensive research on catalysis by supported gold has been reported since the pioneering discoveries by Hutchings [1] and Haruta [2] demonstrating high catalytic activities of highly dispersed gold. CO oxidation and the water gas shift are among the best investigated of the reactions catalyzed by supported gold; most of the work has focused on the former [3], as it apparently offers the advantages of taking place at low temperatures combined with the simplicity of small reactant molecules and the value of CO as a sensitive probe of surface structure [4].

Notwithstanding the extensive research on supported gold catalysts for CO oxidation, the mechanism(s) of the reaction and the catalytically active species remain matters of debate, and the reports of quantitative kinetics of the reaction, although numerous, are largely incomplete.

The lack of thorough kinetics data reflects the complexities of the catalyst performance, influenced by catalyst activation and deactivation, which are often rapid; it is sometimes difficult to determine from published reports whether the reaction rates or conversions characterize fresh or deactivated catalysts.

Our goal was to provide a summary facilitating access to the literature of the kinetics of CO oxidation catalyzed by supported gold. The literature is summarized here in tabular form; earlier, much less complete summaries were reported by Bond et al. [5], Deng et al. [6], and Kung et al. [7]. Some issues regarding the challenges of comparing supported gold catalysts on the basis of performance were addressed by Long et al. [8]. We have limited the content here by excluding catalysts with doped supports (except when they were part of a set including undoped supports) and results characterizing “preferential oxidation” of CO in the presence of excess H₂. Otherwise, the compilation contains most of the literature that includes kinetics data for CO oxidation catalyzed by supported gold, although it is not exhaustive, with a number of examples of only partially documented kinetics data being omitted.

2 Tables of Data

The data are presented in three tables, with the entries linked by the entry number shown in the left-hand column of each table. Table 1 is a list of supported gold catalysts used for CO oxidation, how they were made and treated, their gold contents and surface areas, and the average gold particle sizes and methods used to determine them. Table 2 is a summary of the conditions under which the kinetics data were determined, with information about the degree of deactivation of the catalyst. Table 3 is a summary of the kinetics data,

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Table 1 Characteristics of the supported gold CO oxidation catalysts

Entry number	Catalyst	Catalyst surface area (m ² /g)	Catalyst precursor	Preparation method ^a	Catalyst treatment	Gold content (wt %)	Average gold particle size (nm)	Method of determining gold particle size	References
1	Au/SiO ₂	Not stated	AuCl ₃	IW	1 h in H ₂ (1 bar, 2,500 h ⁻¹) at 723 K	1.8	30	XRD	[9]
2	Au/TiO ₂				2 h in H ₂ at 473 K, 1 bar, 2,500 h ⁻¹	2.3	25		
3	Au/TiO ₂				1 h in H ₂ at 773 K, 1 bar, 2,500 h ⁻¹	2.3	25		
4	Au/TiO ₂				1 h in H ₂ at 773 K 1 bar, 2,500 h ⁻¹	2.3	25		
5	Au/TiO ₂				1 h in H ₂ at 773 K, 1 bar, 2,500 h ⁻¹	2.3	25		
6	Au/TiO ₂				1 h in H ₂ at 773 K, 1 bar, 2,500 h ⁻¹ followed by a calcination with 20% O ₂ in He at 673 K for 1 h, then 2 h under H ₂ at 473 K 1 bar, 2,500 h ⁻¹	2.3	~30	XRD	
7	Au/TiO ₂ (after deactivation)				1 h in H ₂ at 773 K 1 bar, 2,500 h ⁻¹ followed by a calcination with 20% O ₂ in He at 673 K for 1 h, then 2 h under H ₂ at 473 K 1 bar, 2,500 h ⁻¹ after deactivation				
8	Au/TiO ₂ (HTRC/LTR)-I				1 h in H ₂ at 773 K 1 bar, 2,500 h ⁻¹ followed by a calcination with 20% O ₂ in He at 673 K for 1 h, then 2 h under H ₂ at 473 K 1 bar, 2,500 h ⁻¹				
9	Au/TiO ₂ (HTRC/LTR)-I				1 h in H ₂ at 773 K 1 bar, 2,500 h ⁻¹ followed by a calcination with 20% O ₂ in He at 673 K for 1 h, then 2 h under H ₂ at 473 K 1 bar, 2,500 h ⁻¹				
10	Au/Fe ₂ O ₃	Not stated	HAuCl ₄	CP	Calcination at 673 K in air for 4 h	10	3.6	XRD	[10]
11	Au/Co ₃ O ₄	73					6.0		
12	Au/NiO	69					8.0		
13	Au/CuO	116					Not stated		
14	Au/Fe ₂ O ₃	20	HAuCl ₄	CP	Calcination in air at 673 K for 4 h	5 ^b	Not stated	Not stated	[11]
15	Au/MnO _x	Not stated				5 ^b			
16	Au/CeO _x	74 ^c				5 ^b			
17	Au/CeO ₂	Not stated	Au(CH ₃) ₂ (C ₃ H ₇ O ₂)	GR	48 h under CO oxidation conditions at 353 K	1	Mononuclear Au species	EXAFS	[12, 13]
18	Au/CeO ₂	173.3 ^c	Au(CH ₃) ₂ (C ₃ H ₇ O ₂)	GR	48 h under CO oxidation conditions at 353 K followed by 48 h under CO oxidation conditions at 303 K	1	0.8	EXAFS	[12, 13]
19	Au/TiO ₂	173.3 ^c	HAuCl ₄	DP	Calcined in air at 673 K for 4 h	0.7	3.1 ± 0.7	TEM	[14]
20	Au/TiO ₂					1.8	2.7 ± 0.6		
21	Au/TiO ₂					1.0	10 <		
22	Au/TiO ₂					1.0	4.6 ± 1.5		
23	Au/TiO ₂	50 ^c	HAuCl ₄	DP	Calcined in air at 673 K for 4 h	0.7–1.8	2.7 ± 0.6	TEM	[15]
24	Au/TiO ₂					0.5	3.5 ± 1.1		
25	Au/TiO ₂					0.7	3.1 ± 0.7		

Table 1 continued

Entry number	Catalyst	Catalyst surface area (m ² /g)	Catalyst precursor	Preparation method ^a	Catalyst treatment	Gold content (wt %)	Average gold particle size (nm)	Method of determining gold particle size	References
26	Au/TiO ₂			DP		1.8	2.7 ± 0.6		
27	Au/TiO ₂			DP		2.3	2.5 ± 0.6		
28	Au/TiO ₂			DP		3.1	2.9 ± 0.5		
29	Au/TiO ₂			PD		1.0	4.6 ± 1.5		
30	Au/TiO ₂			PD		3.6	6.0 ± 2.5		
31	Au/TiO ₂			IMP	No treatment	1.0	Not stated	TEM	[16]
32	Au/TiO ₂	Not stated	HAuCl ₄	DP (supplied by the World Gold Council)	Calcined at 573 K	1.5	3.7		
33	Au/MgO	Not stated	Not stated	Gold clusters prepared on single crystal surfaces of TiO ₂	Not stated	Not stated	2.5–6	STM/STS/STM	[17]
34	Unsupported nanoporous gold	Not stated	Silver/gold alloy	Dealloying of silver from silver/gold alloy	Not stated	Not stated	5–20	SEM	[18]
35	Nanoporous gold foams	Not stated	Silver/gold alloy	Selective leaching of silver from a silver/gold alloy	Untreated	Not stated	~Tens	SEM	[19]
36	Au/MgO	Not stated	Au ₄ (<i>p</i> -tolyl) ₄	GR	Treated in O ₂ at 773 K for 3 h. Annealing at 972	Not stated	Not stated	TEM	[20]
37	Au/MgO		NCN (<i>p</i> -tolyl) ₄		Treated in O ₂ at 773 K for 3 h. Annealing at 1,073		4.3		
38	Au/MgO				Treated in O ₂ at 773 K for 3 h. Annealing at 1,121		Not stated		
39	Au/MgO				Treated in O ₂ at 773 K for 3 h. Annealing at 1,173		3.8		
40	Au/TiO ₂	Not stated	Not stated	Gold clusters prepared on single crystal surfaces of TiO ₂	Treated in O ₂ at 773 K for 3 h. Annealing at 1,273	Not stated	Not stated	STM	[21]
41	Au/TiO ₂	Not stated	HAuCl ₄	DP (supplied by the World Gold Council)	Not stated	1.47	3.7	TEM	[22]
42	Au/TiO ₂	Not stated	High purity gold foils	VD	None	Not stated	2.6	XPS, LEIS (low energy ion spectroscopy)	[23]
43	Au/TiO ₂	50 ^c	HAuCl ₄	CP	Calcined in air at 673 K for 5 h	3.3	3.6 ± 1.3	EXAFS, TEM, XRD	[24]
44	Au/Fe ₂ O ₃	37 ^c				0.66	4.0		
45	Au/Co ₃ O ₄	59 ^c				1.1	6–7		

Table 1 continued

Entry number	Catalyst	Catalyst surface area (m ² /g)	Catalyst precursor	Preparation method ^a	Catalyst treatment	Gold content (wt %)	Average gold particle size (nm)	Method of determining gold particle size	References
46	Au/Fe ₂ O ₃	Not stated	HAuCl ₄	DP	Calcined in O ₂ at 673 K for 30 min (20 mL/min, 100 mbar)	Not stated	2.3–7	TEM, XRD	[25]
47	Au/Fe ₂ O ₃			Not stated			Not stated		
48	Au/Fe ₂ O ₃			CP			5.5–7		
49	Au/NiO _x			CP			3.2 ± 1.0		
50	Au/CoO _x			IMP			3.4 ± 1.4		
51	Au/TiO _x			IMP			2.4 ± 0.7		
52	Au/Mg(OH) ₂			CP			<4		
53	Au/MgO			CP			6		
54	Au/Al ₂ O ₃			IMP			4.4		
55	Au/Al ₂ O ₃	Not stated	HAuCl ₄	DP	Calcined in He at 673 K for 4 h (100 mL/min)	1.08	2.5 ± 1.1	STEM, EXAFS	[26]
56	Au/TiO ₂					1.22	3.3 ± 0.5		
57	Au/TiO ₂	Not stated	HAuCl ₄	DP	Calcined at 353 K in air for 8 h	3.1	2.0 ± 1.0	TEM	[27]
58	Au/TiO ₂	58	HAuCl ₄	DP	Initial sample	3.1	21–30	XRD	[28]
59	Au/TiO ₂	63			6 h, air, 673 K ^d	2.8	12		
60	Au/TiO ₂	99			20 h, vacuum, 573 K ^d 4 h, air, 673 K	3.5	9		
61	Au/TiO ₂	76			4 h, air, 673 K ^d	2.9	11		
62	Au/TiO ₂	110			4 h, air, 673 K ^d	3.5	9		
63	Au/TiO ₂	Not stated	HAuCl ₄	DP	Heating from room temperature to 573 K in N ₂ followed by 30 min in H ₂ O ₂ /N ₂ 25/25/50	Not stated	3.0 ± 0.6	TEM	[8]
64	Au/Al ₂ O ₃	Not stated	HAuCl ₄	DP	In helium at 623 K for 4 h	1.16	1.2	EXAFS	[29]
65	Au/ <i>z</i> -Fe ₂ O ₃	44.2	HAuCl ₄	DP	None	2.0	5.0	XRD	[6]
66	Au/ <i>z</i> -Fe ₂ O ₃	41.1	HAuCl ₄	DP	Leached	0.7	Not stated	Not stated	
67	Au/ <i>z</i> -Fe ₂ O ₃	Not stated			Leached then reduced in H ₂ at 673 K for 2 h	0.7	Not stated	Not stated	
68	Au/CeO ₂	146.3			None	4.7	5.0	XRD	
69	Au/CeO ₂	161.6			Leached	0.5	Not stated	Not stated	
70	Au/CeO ₂	Not stated			Leached then reduced in H ₂ at 673 K for 2 h	0.5	Not stated	Not stated	
71	Au/Al ₂ O ₃	Not stated	HAuCl ₄	DP	In air at 473 K for 1 h	1	2–7	TEM	[30]
72	Au/Al ₂ O ₃	210 ^c					3–9		
73	Au/Al ₂ O ₃	Not stated	HAuCl ₄	DP	0.5 h in air at 523 K	0.4	3.9	TEM	[31]
74	Au/SiO ₂			GR		10	8.2		
75	Au/TiO ₂			DP		0.9	3.0		
76	Au/TiO ₂	Not stated	HAuCl ₄	DP	4 h in helium at 623 K	1.22	3.3 ± 0.5	TEM	[32]
77	Au/Al ₂ O ₃					1.08	2.5 ± 1.1		
78	Au/TiO ₂	150 ^c	HAuCl ₄	DP	1 h in H ₂ flow (50 mL/min) at room temperature	4	2	Not stated	[33]
79	Au/MgO	60 ^c	Au(CH ₃) ₂ (C ₅ H ₇ O ₂)	GR	No treatment	1.0	3.0	EXAFS	[34]

^a The abbreviations regarding the preparation methods are as follows: DP deposition precipitation, IW incipient wetness, CP co-precipitation, IMP impregnation, PD photochemical deposition, GR grafting, VD vapor deposition

^b Atom %

^c This value corresponds to the surface area of the support

^d Treatment of the support

Table 2 Reaction conditions under which the supported gold CO oxidation catalysts were tested

Entry number	Catalyst	Degree of deactivation	Catalyst mass (mg)	Reactor type	Total feed flow rate (mL)/min	Feed flow conditions	Space velocity (mL/min g _{cat})	Feed partial Pressures (mbar)		Reaction temperature (K)	References
								P _{CO}	P _{O₂}		
1	Au/SiO ₂	Not stated	600–1,000	Plug flow	50	Normal	50–83.3	50.7	49.3	313	[9]
2	Au/TiO ₂					temperature and pressure		52	49.3		
3	Au/TiO ₂							50.7	49.3		
4	Au/TiO ₂							18.7	9.3		
5	Au/TiO ₂							9.3	4.7		
6	Au/TiO ₂	Not stated	350	Plug flow	35	Normal	100	50.7	48	313	
7	Au/TiO ₂ (after deactivation)					temperature and pressure		49.3	49.3		
8	Au/TiO ₂							20	9.9		
9	Au/TiO ₂							9.9	4.8		
10	Au/Fe ₂ O ₃	Not stated	200	Fixed bed	66	Normal	330	10.1	208	203	[10]
11	Au/Co ₃ O ₄					temperature and pressure				203	
12	Au/NiO									203	
13	Au/CuO									Not stated	
14	Au/Fe ₂ O ₃	Initial activities are above 90% decreasing 10% after 167 h	150	Fixed bed (integral mode, high X)	10	1 bar	66.6	10.1	5.1	303,323,348	[11]
15	Au/MnO _x									303,323,348	
16	Au/CeO _x									303,323,348	
17	Au/CeO ₂	Activates during CO oxidation at 353 K increasing activity during CO oxidation at room temperature	25	Plug flow	200	298 K, 1 bar	800	20.3	10.1	298	[12, 13]
18	Au/CeO ₂	Catalyst activated during CO oxidation at 353 K then stabilized at 303 K after 48 h of reaction	25	Plug flow	200	298 K, 1 bar	800	20.3	20.3	303	[12, 13]
19	Au/TiO ₂	Not stated	200	Fixed bed	67	Normal	1,340	10.1	208	300	[14]
20	Au/TiO ₂					temperature and pressure					
21	Au/TiO ₂										
22	Au/TiO ₂										
23	Au/TiO ₂	Not stated	50	Fixed bed	17	Normal	340	10.1	208	313	[15]
24	Au/TiO ₂					temperature and pressure					
25	Au/TiO ₂										
26	Au/TiO ₂										
27	Au/TiO ₂										
28	Au/TiO ₂										
29	Au/TiO ₂										
30	Au/TiO ₂										
31	Au/TiO ₂										
32	Au/TiO ₂	Not stated	55	Fixed bed	25	Not stated	454.5	10.1	10.1	243–363	[16]
33	Au/MgO	Not stated	Not stated	Fixed bed UHV	Not stated	Total pressure: 53.3 mbar	Not stated	8.6	43.3	300	[17]

Table 2 continued

Entry number	Catalyst	Degree of deactivation	Catalyst mass (mg)	Reactor type	Total feed flow rate (mL/min)	Feed flow conditions	Space velocity (mL/min g _{cat})	Feed partial Pressures		Reaction temperature (K)	References
								P _{CO}	P _{O₂}		
34	Unsupported nanoporous gold	Not stated	50	Fixed bed	66.7	Not stated	222.3	10.1	101.3	243, 273, 303	[18]
35	Nanoporous gold foams	Not stated	80	Fixed bed	15	1 bar	187.5	10.1–81	18.4–19.8	253–323	[19]
36	Au/MgO	Not stated	Not stated	Not stated	45	Not stated	Not stated	36.2	72.4	373	[20]
37	Au/MgO							36.2	72.4	373	
38	Au/MgO							36.2	72.4	373	
39	Au/MgO							36.2	72.4	373	
40	Au/TiO ₂	Not stated	Not stated	Fixed bed	Not stated	Total pressure: 6.7 mbar	Not stated	8.6	43.3	300	[21]
41	Au/TiO ₂	Not stated	45	Fixed bed	25	Not stated	555.6	10.1	10.1	248	[22]
42	Au/TiO ₂	Not stated	Not stated	Plug flow	Not stated	UHV	Not stated	4×10^{-7}	2×10^{-5}	Room temperature	[23]
43	Au/TiO ₂	Not stated	200	Fixed bed	67	Not stated	5.6	10.1	211	273	[24]
44	Au/Fe ₂ O ₃										
45	Au/Co ₃ O ₄										
46	Au/Fe ₂ O ₃	Not stated	100	Plug flow	Not stated	273 K, 1 bar	Not stated	10	10	353	[25]
47	Au/Fe ₂ O ₃										
48	Au/Fe ₂ O ₃										
49	Au/NiO _x										
50	Au/CoO _x										
51	Au/TiO _x										
52	Au/Mg(OH) ₂										
53	Au/MgO										
54	Au/Al ₂ O ₃										
55	Au/Al ₂ O ₃										
56	Au/TiO ₂										
57	Au/TiO ₂	Not stated	90	Plug flow	100–239	1.22 bar, room temperature	111–2,655	20.2 ^a	20.2 ^b	296	[26]
58	Au/TiO ₂	Catalyst shows high initial activity which decreases during operation in flow reactor	65–70	Plug flow	60	1 bar, room temperature	857–923.1	10.1	10.1, 202	303, 353	[27]
59	Au/TiO ₂	Activity decreased 25% after 16.7 h of operation	65–70	Plug flow	60	1 bar, room temperature	857–923.1	10.1	10.1	353	[28]
60	Au/TiO ₂	Activity decreased 17% after 16.7 h of operation	65–70	Plug flow	60	1 bar, room temperature	857–923.1	10.1	10.1	353	
61	Au/TiO ₂	Activity decreased 18% after 16.7 h of operation	65–70	Plug flow	60	1 bar, room temperature	857–923.1	10.1	10.1	353	
62	Au/TiO ₂	Activity decreased 14% after 16.7 h of operation	65–70	Plug flow	60	1 bar, room temperature	857–923.1	10.1	10.1	353	
63	Au/TiO ₂	Activity decreased 15% after 16.7 h of operation	65–70	Plug flow	60	1 bar, room temperature	857–923.1	10.1	10.1	353	

Table 2 continued

Entry number	Catalyst	Degree of deactivation	Catalyst mass (mg)	Reactor type	Total feed flow rate (mL)/min	Feed flow conditions	Space velocity (mL/min) g_{cat}^{-1}	Feed partial Pressures (mbar)		Reaction temperature (K)	References
								P_{CO}	P_{O_2}		
63	Au/TiO ₂	Catalyst activity showed a slight decrease in activity in the first hour on stream	0.2	Plug flow	27	1 bar, room temperature	135,000	10.1	208	293	[8]
64	Au/Al ₂ O ₃	Not stated	5–100	Plug flow	75–250	1 bar, room temperature	1,000–15,000	3–70	3–70	298	[29]
65	Au/ α -Fe ₂ O ₃	Not stated	10–50	Plug flow	150	1 bar, room temperature	3,000–15,000	20.3	10.1	303	[6]
66	Au/ α -Fe ₂ O ₃										
67	Au/ α -Fe ₂ O ₃										
68	Au/CeO ₂										
69	Au/CeO ₂										
70	Au/CeO ₂										
71	Au/Al ₂ O ₃	Not stated	Not stated	Plug flow	Not stated	1 bar, room temperature	15,000 ^c	10.1	208	298	[30]
72	Au/Al ₂ O ₃	Not stated	Not stated	Plug flow	Not stated	1 bar, room temperature	333–1,333	10.1	208	200–500	[31]
73	Au/Al ₂ O ₃	Not stated	Not stated	Plug flow	Not stated	1 bar, room temperature					
74	Au/SiO ₂										
75	Au/TiO ₂										
76	Au/TiO ₂	Not stated	45–160	Plug flow	250–382	1.22 bar, room temperature	1,500–8,500	20.2	20.2	273	[32]
77	Au/Al ₂ O ₃										
78	Au/TiO ₂	Not stated	20	Plug flow	70	273 K, 1 bar	3,500	10.1	25.2	213	[33]
79	Au/MgO	Not stated	Not stated	Plug flow	Not stated	273 K, 1 bar	83.3–333.3	15–293	15–293	373	[34]

^a CO in feed, was C¹⁶O; total pressure was greater than atmospheric (1,216 mbar)

^b Oxygen in feed was ¹⁶O₂

^c Values are for gas hour space velocity

Table 3 Kinetics data reported for the supported gold CO oxidation catalysts considered in this work

Entry number	Catalyst	Conversion (%)	Temperature range (K) for activation energy	Apparent activation energy (kJ/mol)	TOF (s ⁻¹)	Details about TOF calculations	Reaction order			Comments	References
							CO	O ₂	CO ₂		
1	Au/SiO ₂	<15	312–454	15.1 ^a	2.0×10^{-2}	Lower limit based on total number of Au atoms	Not stated	Not stated	Not stated	Catalyst from entry number 2 showed the lowest activity. Catalysts from entries 3–9 showed catalytic activity near room temperature. Activity of Au/SiO ₂ was tenfold higher than that of the catalyst in Entry Number 2, but tenfold lower than that of catalysts in Entry Numbers 3–9.	[9]
2	Au/TiO ₂			-0.2 ± 1.8^a	1.3×10^{-3}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	$0.4^{b,c}$		
3	Au/TiO ₂			1.4 ± 0.2^a	7.5×10^{-2}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	$0.4^{b,c}$		
4	Au/TiO ₂			1.5 ± 1.1^a	4.5×10^{-2}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	$0.4^{b,c}$		
5	Au/TiO ₂			3.5 ± 1.5^a	2.2×10^{-2}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	$0.4^{b,c}$		
6	Au/TiO ₂	<15	312–454	3.1 ± 1.6^a	2.4×10^{-1}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	Not stated	Catalyst in Entry Number 1 retained 50% of Cl from precursor, other catalysts only 16%. Low catalytic activity.	
7	Au/TiO ₂ (after deactivation)			9.2 ± 2.8^a	7.3×10^{-2}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	$0.4^{b,c}$		
8	Au/TiO ₂			Not stated	8.5×10^{-2}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	$0.4^{b,c}$	Langmuir–Hinshelwood equation used to fit data, but not able to distinguish between competitive or noncompetitive adsorption	[10]
9	Au/TiO ₂			Not stated	4.6×10^{-2}		$0.2-0.6^{b,c}$	$0.4^{b,c}$	$0.4^{b,c}$	Enhanced catalytic activity attributed to a combined effect of gold and transition metal oxides. These catalysts were active for CO oxidation at temperatures as low as 203 K	[11]
10	Au/Fe ₂ O ₃	50	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated		
11	Au/Co ₃ O ₄			Not stated	Not stated	Not stated	Not stated	Not stated	Not stated		
12	Au/NiO			Not stated	Not stated	Not stated	Not stated	Not stated	Not stated		
13	Au/CuO			Not stated	Not stated	Not stated	Not stated	Not stated	Not stated		
14	Au/Fe ₂ O ₃	~100	313	33 ^d	Not stated	Not stated	Not stated	Not stated	Not stated	Au/MnO _x stated to be most active catalyst that these authors tested. The catalyst sustained 100% conversion for >300 h	[11]
15	Au/MnO _x	~100	313	8.4 ^d	Not stated	Not stated	Not stated	Not stated	Not stated		
16	Au/CeO _x	>80	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated		
17	Au/CeO ₂	<5	333–348	138 ± 2^a	$(6.5 \pm 0.6) \times 10^{-3}$	Lower limit based on total number of Au atoms	Not stated	Not stated	Not stated	Gold species remained mononuclear during CO oxidation as demonstrated by EXAFS spectroscopy	[12, 13]
18	Au/CeO ₂	<5	303–333	54 ± 8^a	$(5.6 \pm 0.2) \times 10^{-2}$	Lower limit based on total number of Au atoms	0.19	0.18	-0.4	Catalyst with mononuclear gold species activated during CO oxidation at 353 K while clusters formed. Values reported in this table correspond to steady-state conditions at 303 K	[12, 13]
19	Au/TiO ₂	<15	243–310	19 ^a	3.4×10^{-2}	Lower limit based on total number of Au atoms	Zero	0.25	Not stated	Authors attributed increase in catalytic activity to decrease in gold particle size	[14]
20	Au/TiO ₂			18 ^a	1.2×10^{-1}						
21	Au/TiO ₂			58 ^a	Not stated						
22	Au/TiO ₂			56 ^a	9.6×10^{-6}						
23	Au/TiO ₂	<15	190–250	75 ^a	3.7×10^{-2}	Based on surface metal atoms determined assuming fcc structure, amount of gold loading determined by ICP, X-ray fluorescence and TEM	Not stated	Not stated	Not stated	Various synthesis methods were used in the preparation of Au/TiO ₂ catalysts.	[15]
24	Au/TiO ₂		Not stated	27 ^a	3.7×10^{-2}						
25	Au/TiO ₂		364–526	19 ^a	3.4×10^{-2}						
26	Au/TiO ₂		323–434	18 ^a	1.2×10^{-1}						
27	Au/TiO ₂		Not stated	20 ^a	6.8×10^{-2}						
28	Au/TiO ₂		Not stated	27 ^a	2.6×10^{-1}						
29	Au/TiO ₂		444–750	56 ^a	9.6×10^{-6}						
30	Au/TiO ₂		Not stated	57 ^a	8.3×10^{-6}						
31	Au/TiO ₂		450–1,060	58 ^a	Not stated						

Table 3 continued

Entry number	Catalyst	Conversion (%)	Temperature range (K) for activation energy	Apparent activation energy (kJ/mol)	TOF (s ⁻¹)	Details about TOF calculations	Reaction order			Comments	References
							CO	O ₂	CO ₂		
32	Au/TiO ₂	Not stated	Not stated	Not stated	Not stated	Not stated	e	e	Not stated	Authors suggested that CO ₂ desorption appears to be rate-limiting step, suggesting negative reaction order in CO ₂ . Another finding is that carbon oxide species formed on the surface of Au/TiO ₂ ; authors suggested these were only spectators	[16]
33	Au/MgO	Not stated	Not stated	Not stated	$(5 \times 10^{-2}) - (2.5 \times 10^{-1})$	Based on surface metal atoms determined by constant-current topographic images	Not stated	Not stated	Not stated	CO supported on crystalline surfaces of TiO ₂ (a low-surface-area model support).	[17]
34	Unsupported nanoporous gold	~100	Not stated	Not stated	3.4×10^{-2}	Not stated	Not stated	Not stated	Not stated	Nanoporous gold made by dealloying of silver from silver/gold alloy. Potential roles of silver not described. Authors claimed that metallic gold plays a catalytic role in CO oxidation	[18]
35	Nanoporous gold foams	60–100	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated	Authors carried out similar experiments with catalyst having higher loadings of silver. These samples had activities almost the same as others. Authors ruled out role of silver in CO oxidation catalysis	[19]
36	Au/MgO	1	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated	Not stated	Authors claimed that catalytic activity and activation of gold correlated with F centers.	[20]
37	Au/MgO	3								Authors suggested the possibility that reduced Ti defect sites at the boundary between gold clusters and TiO ₂ determine shape and electronic properties of gold clusters	[21]
38	Au/MgO	12								Authors claimed strong metal-support interactions responsible for catalytic activity of Au/TiO ₂ . Model catalyst: support was thin TiO ₂ film on Mo(112).	[21]
39	Au/MgO	22								Authors concluded that desorption of CO _{2(a)} is rate-limiting step in CO oxidation.	[22]
40	Au/TiO ₂	Not stated	Not stated	Not stated	$(7.1 \times 10^{-1}) - (2 \times 10^1)^r$	Lower limit based on total number of Au atoms	Not stated	Not stated	Not stated	TOF calculated as rate of removal of adsorbed CO by reaction with oxygen	[21]
41	Au/TiO ₂	Not stated	Not stated	Not stated	4.3×10^{-2}	Lower limit based on total number of Au atoms	Not stated	Not stated	Not stated	Apparent activation energy calculated for CO _g + O ₂ → CO _{2,g} (g = gas phase a = adsorbed).	[22]
42	Au/TiO ₂	Not stated	294–385 K	11.4 ± 2.8 ^e	Not stated	Based on surface metal atoms determined by low energy ion spectroscopy (LEIS) and XPS	1.1 ± 0.1 ^h	1 ⁱ	Not stated	Proposed rate-determining step is decomposition of carbonate intermediates	[23]
43	Au/TiO ₂	<10	263–338	34.3 ^a	3.5×10^{-2}	Based on surface metal atoms determined by TEM assuming fcc structure	0.05	0.24	Not stated	Authors concluded CO oxidation is structure sensitive. Rate of CO oxidation independent of or only slightly dependent on P _{CO} and P _{O2} . Authors proposed that CO ₂ formation results from decomposition of bidentate carbonate species	[24]

Table 3 continued

Entry number	Catalyst	Conversion (%)	Temperature range (K) for activation energy	Apparent activation energy (kJ/mol)	TOF (s ⁻¹)	Details about TOF calculations	Reaction order			Comments	References
							CO	O ₂	CO ₂		
44	Au/Fe ₂ O ₃			35.1 ^a	3.0×10^{-2}		0	0.05			
45	Au/Co ₃ O ₄			16.3 ^b	Not stated		0.05	0.27			
46	Au/Fe ₂ O ₃	<20	Not stated	29 ^d	1.3–3 ^j	Lower limit based on total number of Au atoms	Not stated	Not stated	Not stated	Dominant reaction pathway concluded to involve adsorption of a mobile, molecular oxygen species on support, dissociation at the gold–support interface and reaction on gold particles and/or at the interface with CO adsorbed on the gold	[25]
47	Au/Fe ₂ O ₃			Not stated	2.9–6.7						
48	Au/Fe ₂ O ₃			Not stated	3.2–3.4						
49	Au/NiO _x			Not stated	1.3 ^j						
50	Au/CoO _x			Not stated	1.8 ^j						
51	Au/TiO _x			21 ^d	1.6 ^j						
52	Au/Mg(OH) ₂			Not stated	0.5–0.9 ^j						
53	Au/MgO			Not stated	0.3 ^j						
54	Au/Al ₂ O ₃			Not stated	0.35 ^j						
55	Au/Al ₂ O ₃	13–23	273–329	10	1.6	Steady-state isotopic transient kinetics analysis used to evaluate the intrinsic turnover frequency	Not stated	Not stated	Not stated	Oxygen exchange proposed to occur between supports and CO ₂ . Labeled oxygen found in H ₂ O exiting reactor appeared to originate from ¹⁸ O associated with CO ₂ reactant	[26]
56	Au/TiO ₂									Authors concluded that dissociative adsorption of O ₂ not reversible and observed that oxygen in CO ₂ was exchanged by oxidation of C ¹⁶ O with ¹⁸ O ₂ of the support	
57	Au/TiO ₂	5–20	303–353	72 ^d , 20 ^d	Not stated	Not stated	Not stated	Not stated	Not stated	Catalysts deactivated during CO oxidation at both 303 and 353 K. Deactivation of catalyst correlated with and assigned to buildup carbonates on support	[27]
58	Au/TiO ₂	5–20	303–353	33 ± 3	1.6 ^k	Not stated	Not stated	Not stated	Not stated	Authors concluded that the formation of a reaction inhibiting carbonate adlayer is the main origin or deactivation	[28]
59	Au/TiO ₂	5–20		36 ± 4	1.2 ^k						
60	Au/TiO ₂	5–20		34 ± 4	1.6 ^k						
61	Au/TiO ₂	5–20		31 ± 3	2.2 ^k						
62	Au/TiO ₂	5–20		28 ± 3	2.0 ^k						
63	Au/TiO ₂	1–2	260–294	28	Not stated	Not stated	Zero	0.18–0.20	Not stated	Catalyst was thiol monolayer-protected gold clusters prepared from dendrimer templates and deposited onto high-surface-area titania, followed by removal of thiol in H ₂ /N ₂ . Authors concluded that the monolayer-protected gold clusters are comparable in terms of gold particle size, rate laws, and apparent activation energies, to the standard catalysts available from the World Gold Council (WGC); however, these catalysts are 50% more active than the ones from WGC	[8]

Table 3 continued

Entry number	Catalyst	Conversion (%)	Temperature range (K) for activation energy	Apparent activation energy (kJ/mol)	TOF (s ⁻¹)	Details about TOF calculations	Reaction order		Comments	References
							CO	O ₂ / CO ₂		
64	Au/Al ₂ O ₃	10	298–377	12	0.02 at 298 K 0.04 at 373 K	The turnover frequency is the reaction rate per Au atom in the catalyst normalized by the fraction of metal exposed	0.32	0.36	Reaction orders in CO and O ₂ were affected by H ₂ O added to the feed—the reaction order in CO decreased to 0.18 and that in O ₂ increased to 0.48	[29]
65	Au/ <i>z</i> -Fe ₂ O ₃	<5	324–343	13.4	Not stated	Not stated	Not stated	Not stated	Authors concluded that dry CO oxidation is much more facile on Au0 than on oxidized gold clusters	[6]
66	Au/ <i>z</i> -Fe ₂ O ₃	<5	560–573	32.6						
67	Au/ <i>z</i> -Fe ₂ O ₃	<5	560–573	9.9						
68	Au/CeO ₂	<5	Not stated	29.5						
69	Au/CeO ₂	<5	Not stated	50.8						
70	Au/CeO ₂	<5	Not stated	39.9						
71	Au/Al ₂ O ₃	22	298–373	2.7	0.25	Not stated	Not stated	Not stated	Al ₂ O ₃ support was one-dimensional nanofibers	[30]
72	Au/Al ₂ O ₃	<5		23.7	0.07				Al ₂ O ₃ was commercially available	
73	Au/Al ₂ O ₃	Not stated	238–500	22	3×10^{-2} – 2×10^{-1}	Values per surface Au atom	Not stated	Not stated	Reaction rates enhanced by moisture. The degree of rate enhancement depends on type of support.	[31]
74	Au/SiO ₂	Not stated	Not stated	Not stated	1×10^{-3} – 4×10^{-2}				Effect of moisture becomes significant only when > 200 ppm H ₂ O present for Au/Al ₂ O ₃ whereas activity for Au/SiO ₂ diminishes considerably with a decrease in moisture to about 0.3 ppm. The activity of Au/TiO ₂ at about 3,000 ppm H ₂ O is so high that it gives complete conversion of CO	
75	Au/TiO ₂	Not stated	200–263	25–26	3×10^{-1}	–Saturation of CO conversion			Authors suggested intrinsic rate of CO oxidation nearly independent of the support, suggesting that the ability of Au/metal oxide to activate O ₂ is a key feature in determining the global reaction rate	[32]
76	Au/TiO ₂	<37	196–360	29	3.4×10^{-1}	Calculated dividing the global reaction rate by the dispersion of gold.	0.2	0.25		
77	Au/Al ₂ O ₃	<20	196–360	8	1.8×10^{-1}	Fraction of exposed gold was estimated from the inverse of the surface-average gold particle size determined by STEM	0.15	0.52		

Table 3 continued

Entry number	Catalyst	Conversion (%)	Temperature range (K) for activation energy	Apparent activation energy (kJ/mol)	TOF (s ⁻¹)	Details about TOF calculations	Reaction order			Comments	References
							CO	O ₂	CO ₂		
78	Au/TiO ₂	Not stated	Not stated	Not stated	1.4 ± 0.2	Based on the reaction order of adsorbed CO species	Not stated	Not stated	Not stated	Authors concluded CO adsorbed on gold is reactive species; they proposed hydroxycarbonyl as an intermediate	[33]
79	Au/MgO	4–15	Not stated	Not stated	(2–8) × 10 ⁻²	Based on total number of Au atoms	Not stated	Not stated	Not stated	Authors concluded that both Au(I) and Au(0) present in working catalysts	[34]

^a Apparent activation obtained from Arrhenius plot

^b No specific values for were given for individual catalysts; only a range of values of reaction order was provided

^c The values of temperature at which the reaction orders were determined fall between 310 and 360 K

^d Method to obtain value of apparent activation energy not stated in paper

^e Noncompetitive absorption

^f Units are: molecules CO₂/(Au site s)

^g Apparent activation energy was determined from rates of titration of adsorbed oxygen (O₁) with gas-phase CO

^h Reaction order with respect to CO partial pressure

ⁱ Reaction order with respect to O₂ coverage

^j TOF was calculated using exposed gold only

^k Values are those corresponding to initial activities

including values of TOF and how they were determined, reaction orders, and apparent activation energies.

We believe that these tables provide the most complete available statement of kinetics of CO oxidation catalyzed by supported gold.

3 Generalizations Based on the Data

Table 2 is a summary of the catalysts tested for CO oxidation; the catalysts were investigated at temperatures in the range of 203–373 K. Haruta [35] referred to a low-temperature regime (typically, ~210 K) and a high-temperature regime (typically, >300 K). The O₂ partial pressures were varied between 4 and 200 mbar, and the CO partial pressures between 10 and 40 mbar. The results indicate orders of reaction in CO and in O₂ in the range 0.0–0.6. The reaction order in CO has been approximated as zero by some researchers [24]. Correspondingly, numerous researchers have postulated that CO is adsorbed on the gold; some [4] have suggested that CO is bonded to gold at the gold-support interface.

The roles of oxygen in the gold-catalyzed CO oxidation are evidently not fully elucidated. Some authors have postulated that oxygen adsorbed on the gold [4] or at the gold-support interface [36] may play a role. In contrast, Guzman et al. [37] reported evidence of the involvement of reactive oxygen species (such as superoxides) on their CeO₂ support; the influence of the presence of reactive oxygen species on some supports but not on others (e.g., γ-Al₂O₃ [38]) would suggest that the form of kinetics would differ from one support to another, but there are too few data to test this statement.

A few reports of the influence of CO₂ on the rate indicate that it inhibits the reaction; according to one report [16, 22], the desorption of CO₂ from Au/TiO₂ is rate limiting under some conditions. Others [39] have reported that CO₂ (rather than O₂) is the oxidizing agent of gold in supported gold catalysts, implying that the gold in the catalytic sites cycles between more than one oxidation state.

Haruta's group [40] reported a detailed investigation of the influence of water in the reactant stream on CO oxidation catalyzed by TiO₂⁻, Al₂O₃⁻, and SiO₂⁻-supported gold. Water in low concentrations increases the activity of the catalyst.

The most thorough investigation of the kinetics of CO oxidation catalyzed by supported gold was reported by Vannice's group [9]; the catalyst support was TiO₂. The authors tested several catalysts that had been subjected to various pretreatments, and kinetics parameters are reported for each (entry numbers 1–9 in Tables 1, 2, 3).

Many of the most active supported gold catalysts for CO oxidation are supported on TiO₂ or on various oxides of iron

or of cerium. Turnover frequencies (rates of reaction per accessible gold site; Table 3) span a wide range, between 10^{-6} and 10^{-1} s^{-1} . There is one report of an intrinsic turnover frequency—that is, per active site [41] (entry numbers 55, 56, 64, 76, and 77, Tables 1, 2, 3)—determined in transient measurements with isotopically labeled reactant ^{13}CO for Au/ γ - Al_2O_3 ; the value is $1.6 \times 10^{-1} \text{ s}^{-1}$ at 296 K and CO and O_2 partial pressures of 24.2 mbar each.

Only a few values of apparent activation energies of CO oxidation catalyzed by gold have been reported, and the information about the conditions under which they were determined is often lacking. The apparent activation energies range from values that are essentially indistinguishable from 0 to 138 kJ/mol (Table 3).

Most reports of catalyst deactivation and how it occurs (e.g., [11]) do not include kinetics data, but the work of Vannice's group [9] is exceptional, providing kinetics data for various catalysts before and after deactivation (Table 2).

Supported gold catalysts typically undergo rapid deactivation during CO oxidation, and this complication has hindered the collection of kinetics data. For example, the initial conversion observed with a zeolite-supported gold catalysts was about 40%, and this decreased to <5% within 15 min of operation in a once-through flow reactor at 298 K [42]. An Au/ TiO_2 [27] catalyst, on the other hand, showed an initial conversion at 303 K of nearly 100%, and the conversion had declined to 10% after 2,000 min of operation in a flow reactor when O_2 was present in stoichiometric excess; but the decline in activity was more rapid when the O_2 was not present in stoichiometric excess. Other authors have also observed that the rate of catalyst deactivation was less when the reaction took place in an O_2 -rich atmosphere [25].

It is clear that the available data do not lend themselves to conclusive integration and that much work remains to be done to consolidate the literature and to represent CO oxidation catalyzed by supported gold quantitatively.

4 Conclusions

The results summarized here show that the literature of CO oxidation catalyzed by supported gold is extensive but fragmented and not easily generalized; it is not easy to make meaningful comparisons of various supported gold catalysts for this reaction, and much work remains to be done to consolidate the literature of CO oxidation catalyzed by supported gold.

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References

- Hutchings GJ (2005) *Catal Today* 100:55
- Haruta M, Kobayashi T, Sano H, Yamada N (1987) *Chem Lett* 405
- Hashmi S, Hutchings GJ (2006) *Angew Chem Int Ed* 45:7896
- Mihaylov M, Knözinger H, Hadjiivanov K, Gates BC (2007) *Chem Ing Tech* 79:795
- Bond GC, Louis C, Thompson DT (2006) *Catalytic series V.6: catalysis by gold*. World Scientific Imperial College Press, London
- Deng W, Carpenter C, Yi N, Flytzani-Stephanopoulos M (2007) *Topics Catal* 44:199
- Kung MC, Davis RJ, Kung HH (2007) *J Phys Chem C* 111:11767
- Long CG, Gilbertson JD, Vijayarathavan G, Stevenson KJ, Pursell CJ, Chandler BD (2008) *J Am Chem Soc* 130:10103
- Lin SD, Bollinger M, Vannice MA (1993) *Catal Lett* 17:245
- Haruta M, Yamada N, Kobayashi T, Ijima S (1989) *J Catal* 301
- Gardner S, Hoflund GB (1991) *Langmuir* 7:2135
- Aguilar-Guerrero V, Gates BC (2007) *Chem Comm* 3210
- Aguilar-Guerrero V, Gates BC (2008) *J Catal* 260:351
- Haruta M (2004) *J New Mat Electrochem Systems* 7:163
- Bamwenda GR, Tsubota S, Nakamura T, Haruta M (1997) *Catal Lett* 44:83
- Chang B, Jang BW, Dai S, Overbury SH (2005) *J Catal* 236:392
- Valden M, Lai X, Goodman DW (1998) *Science* 281:1647
- Xu C, Su J, Xu X, Liu P, Zhao H, Tian F, Ding Y (2007) *J Am Chem Soc* 129:42
- Zielasek V, Jürgens B, Schulz C, Biener J, Biener MM, Hamza AV, Bäumer M (2006) *Angew Chem Int Ed* 45:8241
- Yan Z, Chinta S, Mohamed AA, Fackler JP, Goodman DW (2005) *J Am Chem Soc* 127:1604
- Goodman DW (2005) *Catal Lett* 99:1
- Clark JC, Dai S, Overbury SH (2007) *Catal Today* 126:135
- Bondzie VA, Parker SC, Campbell CT (1999) *Catal Lett* 63:143
- Haruta M, Tsubota S, Kobayashi T, Kageyama H, Genet MJ, Delmon B (1993) *J Catal* 144:175
- Schubert MM, Hackenberg S, van Veen AC, Muhler M, Plzak V, Behm RJ (2001) *J Catal* 197:113
- Calla JT, Davis RJ (2006) *J Catal* 241:407
- Denkwitz Y, Zhao Z, Hörmann U, Kaiser U, Plzak V, Behm RJ (2007) *J Catal* 251:363
- Denwitz Y, Geserik J, Hörmann U, Plzak V, Kaiser U, Hüsing N, Behm RJ (2007) *Catal Lett* 119:199
- Calla JT, Davis RJ (2005) *Ind Eng Chem Res* 44:5403
- Han Y, Zhong Z, Ramesh K, Chen F, Chen L (2007) *J Phys Chem C* 111:3163
- Date M, Okumura M, Tsubota M, Haruta M (2004) *Angew Chem Int Ed* 43:2129
- Calla JT, Bore MT, Datye AK, Davis RJ (2006) *J Catal* 238:458
- Henao JD, Caputo T, Yang JH, Kung MC, Kung HH (2006) *J Catal* 238:8689
- Guzman J, Gates BC (2004) *J Catal* 229:26
- Haruta M (2008) In: Corain B, Schmid G, Toshima N (eds) *Relevance of metal nanoclusters in catalysis and materials science: the issue of size control*, ch 9. Elsevier, Amsterdam, p 183
- Bond GC, Thompson DT (1999) *Catal Rev Sci Eng* 41:319
- Guzman J, Carrettin S, Fierro-Gonzalez JC, Hao Y, Gates BC, Corma A (2005) *Angew Chem Int Ed* 117:4856
- van Bokhoven JA, Louis C, Miller JT, Tromp M, Safonova OV, Glatzel P (2006) *Angew Chem Int Ed* 45:465
- Mihaylov M, Ivanova E, Hao Y, Hadjiivanov K, Gates BC, Knözinger H (2008) *Chem Comm* 175
- Daté M, Okumura M, Tsubota S, Haruta M (2004) *Angew Chem Int Ed* 43:21
- Calla JT, Davis RJ (2005) *J Phys Chem B* 109:2307
- Fierro-Gonzalez JC, Gates BC (2004) *J Phys Chem B* 108:16999