Catalysis Letters Vol. 92, Nos. 3–4, February 2004 (© 2004)

Deactivation of gold catalysts supported on sulfated TiO_2-ZrO_2 mixed oxides for CO oxidation during catalytic decomposition of chlorodifluoromethane (HCFC-22)

Suk Yin Lai*, Hongxia Zhang, and Ching Fai Ng

Department of Chemistry and Center for Surface Analysis and Research, Hong Kong Baptist University, Kowloon Tong, Hong Kong

Received 3 June 2003; accepted 28 October 2003

Gold deposited on sulfated TiO_2-ZrO_2 with sodium hydroxide existed in the form of isotropic particles of 11 nm or less in diameter, whereas deposition with aqueous ammonia yielded larger anisotropic crystallites. The gold on sulfated TiO_2-ZrO_2 catalyst prepared by deposition with sodium hydroxide was active for the oxidation of carbon monoxide at room temperature in the presence of water vapor. However, the selectivity of the catalysts to carbon dioxide during the decomposition of chlorodifluoromethane in the presence of water vapor was increased by only a small extent compared to those without gold nanoparticles. The gold nanoparticles were deactivated for CO oxidation by HF and HCl formed during the hydrolysis of HCFC-22.

KEY WORDS: HCFC decomposition; CO oxidation; gold nanoparticles; sulfated titania-zirconia.

1. Introduction

Chlorofluorocarbons (CFCs), once widely used as solvents and refrigerants, have been found to be the main culprits for the destruction of the ozone layer [1]. Under the Montreal Protocol and its subsequent amendments, the production and use of CFCs was completely stopped in the developed countries. The use of hydrochlorofluorocarbons (HCFCs), of lower ozone-depleting potential compared to the fully halogenated analogs, is to be curtailed and eventually completely phased out [2].

In order to solve the problems related to the use of these ozone-depleting substances, means of converting the stockpile of CFCs into useful and less environmentally harmful substances and means of destruction of these compounds for dilute sources that are not economically recovered and reused are necessary. We have investigated the catalytic hydrolytic destruction of CFC-12 using solid catalysts [3,4]. Sulfated TiO_2-ZrO_2 mixed oxide, prepared by the treatment of a TiO_2-ZrO_2 mixed oxide with concentrated sulfuric acid and then calcination at 650 °C, was found to be very active and selective toward the decomposition of dichlorodifluoromethane into carbon dioxide.

Although less harmful, HCFCs nonetheless contribute to the depletion of the ozone layer as well as to global warming. Hence, we have extended our investigation to the destruction of HCFCs by catalytic decomposition. In the work reported here, chlorodifluoromethane (HCFC-22) was used as a prototype compound representative of the HCFCs. The catalytic destruction of this compound on different single and mixed oxides of transition metals has been investigated by Li *et al.* [5]. Over most transition metal oxides, much CHF_3 and CO were formed in addition to CO_2. Our preliminary experiment using sulfated TiO_2-ZrO_2 as catalyst showed that CO rather than CO_2 was the major product. The introduction of oxidizing function into the catalyst, so that the toxic carbon monoxide can be oxidized into carbon dioxide at the same time would be desirable.

Gold has been known for a long time as an inert metal that does not possess much catalytic activity. However, the pioneering work of Haruta *et al.* showed that nanoparticles of gold are catalytically highly active for CO oxidation [6]. In the last decade, numerous studies on the catalytic activity of gold have been undertaken [7–31] and these works have been reviewed in the literature [32,33]. Aida *et al.* reported that gold supported on different transition metal oxides can decompose methyl chloride oxidatively into CO and CO_2 [7]. The catalysts that were found to be most selective toward CO_2 contained transition metal oxides that are also good oxidation catalysts. The contribution of gold appeared to be not very large. With methyl chloride, hydrolysis yields hydrocarbons rather than CO as the main carbon containing products. Gold is less active toward the oxidation of hydrocarbons than the oxidation of CO [31]. In this work, the catalytic effect of gold was studied again to test whether the excellent

---

* To whom correspondence should be addressed.
E-mail: laisy@hkbu.edu.hk

1011-372X/04/0200–0107/0 © 2004 Plenum Publishing Corporation

activity of gold for CO oxidation can be utilized for the complete destruction of chlorodifluoromethane.

2. Experimental

2.1. Catalyst preparation

The TiO_2-ZrO_2 mixed oxides were prepared using the method reported by Navio *et al.* [34]. $TiCl_4$ and $ZrOCl_2$ at the mole ratio of 7 : 3 were individually dissolved in methanol, cooled in an ice bath and then mixed together and stirred for 40 min. 28% H_2O_2 to the amount of 0.47 mL for each gram of $TiCl_4$ was added to the solution. Hydrolysis was then induced by slow addition of 28% aqueous ammonia solution until the pH of the solution was about 8. The viscous gel was stirred for another hour and then allowed to age overnight. The precipitated hydrous mixed oxide was then filtered and washed with deionized water until no chloride could be detected in the washing liquid. The sample was dried at 90 °C overnight. A portion of the sample was calcined in air at 650 °C for 8 h. The sample was denoted as TZ. Another portion of the uncalcined sample was impregnated with an aqueous solution of ammonium sulfate, dried and then calcined at 650 °C for 8 h. The amount of sulfate added was calculated to give a $SO_4^=$: (Ti + Zr) mole ratio of 5 : 95. This sulfated sample was denoted as TZNS.

Gold was added to the mixed oxide by the method of deposition–precipitation. The sulfated or nonsulfated mixed oxide was stirred for 1 h at room temperature in an aqueous solution of $HAuCl_4$, the pH of which was adjusted to about 9 with concentrated ammonia solution or NaOH solution. The amount of gold salt added was sufficient to give a gold loading of 3% by weight when completely deposited on the oxide substrate. The catalyst precursor was then filtered, dried and finally calcined in air at 400 °C for 2 h. The supported gold catalysts prepared by deposition–precipitation with ammonia on TiO_2-ZrO_2 and sulfated TiO_2-ZrO_2 were denoted as Au/TZ-DA and Au/TZNS-DA respectively. The corresponding samples prepared by deposition–precipitation using sodium hydroxide were denoted as Au/TZ-DS and Au/TZNS-DS. A portion of Au/TZNS-DS was impregnated with 16% H_2SO_4, dried and calcined at 400 °C for 4 h. This sample was denoted as Au/TZNS-DS-HS.

2.2. Catalyst characterization

The gold content in the catalysts was determined by AAS using a Varian AA-10 instrument after extraction with aqua regia. The titanium to zirconium ratio of the mixed-oxides was determined by EDX with a Joel T330-A scanning electron microscope operating at 20 kV. The crystal phases in the samples were determined using a Rigaku D-Max powder X-ray diffractometer with Cu Kα radiation. The particle size of gold was determined by X-ray diffraction (XRD) line broadening from the Au(111) peak at $d = 2.34$Å and Au(200) peak at $d = 2.03$Å. Selected samples were examined using a Philips CM20 transmission electron microscope at 200 kV electron beam energy. The surface area of the catalysts was determined by the BET method using nitrogen adsorption at 77 K using a NOVA 1200 automatic adsorption apparatus. The samples were outgassed under vacuum at 300 °C for 2 h before the measurement. The surface composition of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) using a Shengyang SKL-12 electron spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer.

2.3. Catalytic activities

The activity of the catalysts was tested using a laboratory scale fixed-bed flow reaction system. 0.2 g of catalyst was packed into a Pyrex glass reactor and used for each catalytic run. For CO oxidation, CO gas with a flow rate of 1.5 mL min^{-1} was mixed with a 100 mL min^{-1} flow of synthetic air. The mixture was saturated with water vapor at room temperature before being fed into the reactor. For the HCFC-22 hydrolysis reaction, the reactant stream was a mixture of HCFC-22 at 1 mL min^{-1} flow rate and synthetic air at 100 mL min^{-1} flow rate that was saturated with water vapor. Prior to the reaction, the catalyst was activated by heating in a trace of HCFC-22 at the reaction temperature for 30 min. A Shimadzu GC 8A gas chromatograph equipped with a methanizer, a flame ionization detector and a Porapak Q column was used for the analysis of the $CHClF_2$, CO, CO_2 and CHF_3 in the reactor effluent. No attempt to quantify HCl and HF were made since these reactive gases tended to react with the glass reactor and the gas pipeline in the gas chromatograph, and could not be determined accurately.

3. Results and discussion

3.1. Catalyst characterization

The specific surface area, gold loading and gold particle size determined by XRD line broadening of the catalysts are shown in table 1. The TiO_2-ZrO_2 mixed oxides existed mainly in the columbite phase. A small amount of anatase phase was present. SEM-EDX did not reveal the presence of separate particles of different composition. The bulk Ti:Zr atom ratio of the samples was measured from at least five different regions and the average value was found to be 7.0 : 3.0 for the sample TZ and 6.8 : 3.2 for the sample TZNS, similar to the

Table 1
Composition and specific surface area of the catalysts

Catalyst	Au loading (%)	S_{BET} ($m^2\ g^{-1}$)	Au particle diameter (nm)	
			Au(111)	Au(200)
TZ	0.0	73.8	–	–
TZNS	0.0	75.6	–	–
Au/TZ-DA	2.4	61.8	26	19
Au/TZ-DS	1.3	55.6	8	8
Au/TZNS-DA	2.9	98.1	29	16
Au/TZNS-DS	1.6	66.5	9	11
Au/TZNS-DS-HS	1.6	63.6	8	7

Table 2
Surface composition of the catalysts in terms of mole ratio

Catalysts		Ti:Zr	Au/(Ti + Zr)	F/(Ti + Zr)	Cl/(Ti + Zr)
Au/TZ-DA	Fresh	5.8 : 4.2	0.018	0	0
	Spent	6.0 : 4.0	0.031	0.35	0.20
Au/TZNS-DA	Fresh	5.7 : 4.3	0.022	0	0
	Spent	5.2 : 4.8	0.029	0.50	0.20
Au/TZ-DS	Fresh	6.0 : 4.0	0.022	0	0
	Spent	6.0 : 4.0	0.028	0.28	0.19
Au/TZNS-DS	Fresh	6.0 : 4.0	0.023	0	0
	Spent	6.0 : 4.0	0.034	0.30	0.20

composition of the precursor solution. Addition of ammonium sulfate to the hydrous mixed oxide did not enhance the surface area of the mixed oxide significantly.

Precipitation–deposition with ammonia led to higher gold loading and larger gold particles with anisotropic crystallite shape, whereas those prepared by deposition–precipitation with sodium hydroxide were smaller and more isotropic. The treatment with 16% sulfuric acid resulted in significant change in neither the gold loading nor the gold particle size.

Using XPS, the chemical states and the surface composition of the different elements were determined [35]. To correct for charging effect, all the binding energies were referenced to the main C 1s peak at 284.8 eV. Only one type of chemical species was found for the elements Zr, Ti and Au. These corresponded to that of the oxides of zirconium and titanium and to metallic gold. No partially oxidized gold was found. Chlorine was not detected on the fresh catalysts, showing that the washing was sufficient to remove the residual chloride from the catalyst precursor. Sodium was detected on the catalysts prepared by deposition–precipitation with sodium hydroxide.

The surface composition of the catalysts was calculated in terms of mole ratio, using the total amount of the Ti and Zr atoms for the support as the reference. The result for the fresh catalysts and the catalysts that had been used for the HCFC-22 decomposition reaction (spent catalysts) are shown in table 2. Slight surface enrichment in zirconium was found on the catalysts. Although the gold loading on the catalysts prepared by deposition with ammonia was higher, the surface gold concentration was slightly lower than that observed for the catalysts prepared by deposition with sodium hydroxide, supporting the inference from X-ray diffraction line broadening that lower gold dispersion was obtained by deposition with ammonia. After the HCFC-22 decomposition reaction, fluorine and chlorine were detected, with binding energy corresponding to metal fluoride and chloride. The surface gold concentration increased slightly after the HCFC-22 reaction. This can be accounted for by the preferential loss of the oxides by the formation of volatile halides with HCl and HF during the catalytic reaction and by the preferential deposition of halides on the mixed oxide substrate rather than on gold.

3.2. CO oxidation activities

The conversion for the CO oxidation reaction at different temperature over the catalysts is shown in figure 1. Blank run with silica gel in the reactor up to 350 °C did not reveal measurable CO oxidation. Only the supported gold catalysts exhibited low-temperature CO oxidation activities. For catalysts that showed room temperature activity, the rate of CO oxidation at 30 °C was calculated and given in table 3, together with the temperature required for 100% CO oxidation over the catalysts. The CO oxidation activities decreased in the order Au/TZNS-DS > Au/TZ-DS > Au/TZNS-DA > Au/TZNS-DS-HS ≈ Au/TZ-DA > TZNS > TZ. For

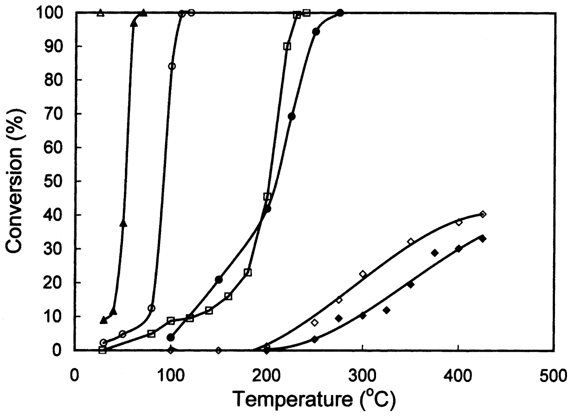

Figure 1. Activity of the catalysts for CO oxidation. ◆ – TZ, ● – Au/TZ-DA, ▲ – Au/TZ-DS, ◇ – TZNS, – Au/TZNS-DA, △ – Au/TZNS-DS, □ – Au/TZNS-DS-HS.

both the TZ and TZNS series of catalysts, the sample prepared by deposition–precipitation with ammonia was much less active compared to those prepared by deposition–precipitation with sodium hydroxide. Treatment of the catalyst after gold deposition by sulfuric acid resulted in large decrease in the activity for CO oxidation.

Gold supported on both TiO_2 and ZrO_2 had been found to exhibit room-temperature oxidation of CO when highly dispersed, with the activity being higher when TiO_2 was used as the support [8,22,27,32,36]. The presence of high concentration of water vapor was reported to suppress the CO oxidation activity of gold supported on TiO_2 [13,28,37]. Our results show that when gold was deposited on TiO_2-ZrO_2 using sodium hydroxide, the resulting catalysts could oxidize CO at room temperature in air saturated with water vapor.

Of the two catalysts prepared by deposition with NaOH, Au/TZNS-DS showed higher activity, effecting 100% CO conversion at 25 °C. Au/TZ-DS, which was derived from nonsulfated TiO_2-ZrO_2 required a higher temperature of 70 °C for the complete oxidation of CO. The higher activity of Au/TZNS-DS cannot be accounted for by the difference in gold loading since Au/TZNS had only 23% higher gold loading than Au/TZ-DS. Neither can it be attributed to the enhancement effect of sulfate. The surface sulfur and sodium content of some of the catalysts determined with XPS are shown in table 3. Although a surface sulfur concentration of 1.2% was found on the sulfated mixed oxide TZNS, it dropped to ca. 0.1% on Au/TZNS-DA and was completely absent on Au/TZNS-DS. Under the condition required for the deposition–precipitation of gold, sulfate would be stripped from the support surface by the basic gold salt solution. When sulfate was put back onto the catalysts by impregnation with 16% H_2SO_4, the activities of the catalysts for CO oxidation were much reduced. It has been reported by Ruth *et al.* that cofeeding 0.05% SO_2 during CO oxidation over a Au/TiO_2 suppressed activity dramatically [38]. The data reported here shows that sulfate also deactivates gold for the CO oxidation reaction.

It is well known that for gold to be catalytically active, it has to be prepared in a highly dispersed state. Quantum size effect of small gold particles had been invoked to account for the high activity of small gold particles on transition metal oxides [18]. On the other hand, Bollinger and Vannice observed that doping TiO_x species on gold powder could result in a catalyst with high activity [13]. The consensus now is that activation of CO on the gold surface and O_2 on the active metal oxide support are prerequisites for CO oxidation. This accounts for the high activity of gold nanoparticles in close contact with the support.

While XRD line broadening allows a large volume of catalyst to be sampled, crystallites of dimension less than 5 nm are not amenable to detection by XRD and the measured average particle size is biased toward the larger particles. To characterize the gold particles better, the samples Au/TZ-DS and Au/TZNS-DS were studied by transmission electron microscopy (TEM) and selected TEM micrographs are shown in figure 2. From the TEM micrographs it can be seen that the substrate mixed oxides exist in the form of small crystallites about 20 nm in diameter. Some gold particles ranging from 3 to 20 nm in diameter can be observed as darker spots. Owing to the similarity in particle size between the substrate oxides and the gold, it is difficult to distinguish whether some of the larger dark particles are gold or are produced by overlapping of the oxide particles. Hence, statistically valid gold particle size

Table 3
CO oxidation activity of the catalysts

Sample	Temperature for 100% CO conversion (°C)	Rate of CO oxidation at 30°C (μmol s^{-1} g^{-1})
TZ	> 350	–
Au/TZ-DA	275	–
Au/TZ-DS	70	0.46
TZNS	> 350	–
Au/TZNS-DA	100	0.11
Au/TZNS-DS	< 25	> 5.11
Au/TZNS-DS-HS	240	–

Table 4
Surface sodium and sulfur concentration on selected catalysts

Catalyst	TZNS	Au/TZNS-DA	Au/TZ-DS	Au/TZNS-DS	Au/TZNS-DS-HS
S/(Ti+Zr)	0.069	0.007	0	0.000	0.070
Na/(Ti+Zr)	0	0	0.066	0.047	Not determined

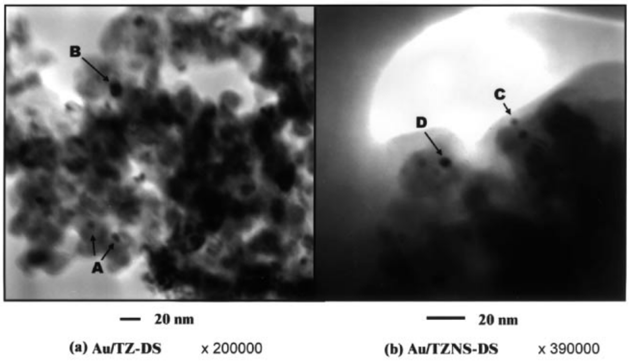

Figure 2. Transmission electron micrographs of gold catalysts prepared by precipitation–deposition with sodium hydroxide.

distribution measurement was not attempted. At a magnification of 200 000, gold particles of diameter about 6 nm (A) and up to 15 nm (B) can be found over the sample Au/TZ-DS. At higher magnification, smaller gold particles can be detected. On the TEM micrograph of Au/TZNS-DS, in addition to gold of diameter about 5 nm (D), gold particles as small as 3 nm (C) are observed. The smaller gold particles can be found on both catalysts but are more abundant on the sample Au/TZNS-DS. It was reported by Gluhoi *et al.* that alkali metal oxide enhanced the activity of gold by inhibiting gold particle sintering [39]. Since sodium was found on both catalysts and its concentration was actually lower on Au/TZNS-DS, the difference in sodium content is unlikely to be the most important factor accounting for the stabilization of the smaller gold particles on Au/TZNS-DS. The removal of sulfate from the sulfated mixed oxide surface during the deposition of gold probably created defective oxide sites that facilitated the deposition of small gold particles, making Au/TZNS-DS more active for CO oxidation.

By adjusting the pH of the $HAuCl_4$ solution with aqueous ammonia, it was hoped that the deposition of Na^+ on the catalysts, which severely decreased the acidity and hydrolytic activity of the mixed oxide could be avoided. However, the gold particle size produced was much larger and, consequently, the CO oxidation activity was much more inferior.

3.3. HCFC-22 decomposition

The conversion of HCFC-22 at different temperatures over the catalysts is shown in figure 3. The temperatures at which complete HCFC-22 conversion was achieved and the selectivity of the catalysts for the different products at 100% conversion (or at 375 °C, the maximum temperature studied for the samples Au/TZ-DS and Au/TZNS-DS) are shown in table 5. Consistent with our previous result [4], the sulfated titania-zirconia was more active than the nonsulfated titania-zirconia. Addition of gold resulted in reduction in the activity of the catalysts. The deactivation was attributed to the removal of acid sites from the catalyst surface and was more severe for the samples prepared by deposition–precipitate using sodium hydroxide. Posttreatment with 16% sulfuric acid restored the activity to some extent. However, the high activity for the TZNS could not be achieved.

Some enhancement in the oxidation of CO to CO_2 took place for all the gold-loaded samples. However, the CO_2 selectivity is much lower than would be expected from the CO oxidation activity on the gold-loaded catalysts.

The catalytic conversion of HCFC-22 in the presence of oxygen and water vapor is postulated to occur according the following reaction scheme:

$$CHClF_2 + H_2O \rightarrow CO + HCl + 2HF$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (1)$$

Side reaction with HF led to the formation of CHF_3.

$$CHClF_2 + HF \rightarrow CHF_3 + HCl \qquad (2)$$

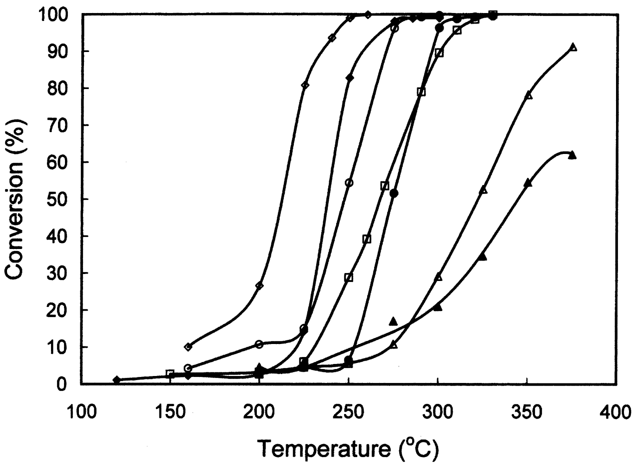

Figure 3. Activity of the catalysts for HCFC-22 reaction. ◆ – TZ, ● – Au/TZ-DA ▲ – Au/TZ-DS, – TZNS, ○ – Au/TZNS-DA △ – Au/TZNS-DS, □ – Au/TZNS-DS-HS.

Table 5
Selectivity of the catalysts for the HCFC-22 reaction at 100% conversion

Catalyst	Temperature for 100% HCFC-22 conversion (°C)	Selectivity to CO (%)	Selectivity to CO_2 (%)	Selectivity to CHF_3 (%)
TZ	300	77	0	23
Au/TZ-DA	330	51	12	37
Au/TZ-DS[a]	> 375	43	17	40
TZNS	260	71	0	29
Au/TZNS-DA	300	58	11	31
Au/TZNS-DS[b]	> 375	56	11	34
Au/TZNS-DS-HS	330	58	14	28

[a] Selectivity at 375 °C, at which the HCFC-22 conversion was 62%.
[b] Selectivity at 375 °C, at which the HCFC-22 conversion was 91%.

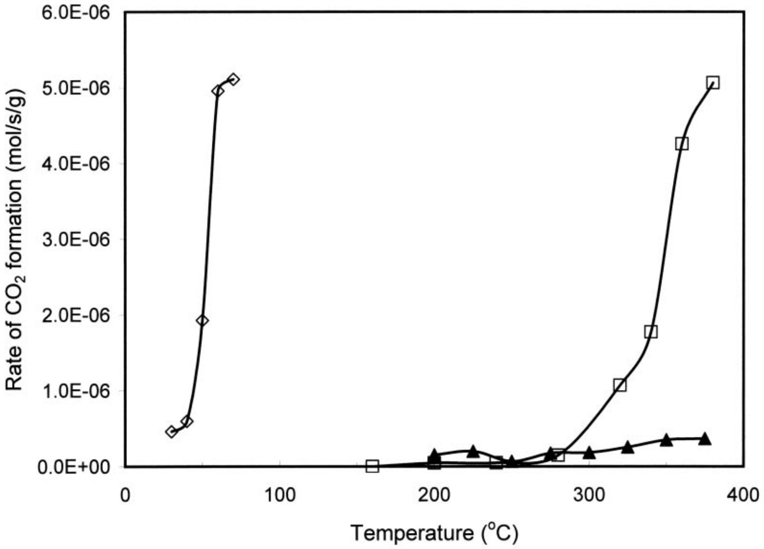

Figure 4. Activity for CO oxidation over the fresh and spent Au/TZ-DS catalysts. ◇ CO oxidation over the fresh catalyst, □ CO oxidation over the spent catalyst, ▲ CO oxidation during HCFC-22 decomposition.

For the effective destruction of HCFC-22, a catalyst should be active for the hydrolysis of chlorofluorocarbons as well as the oxidation of carbon monoxide, but inactive for the fluorination reaction. Consistent with our previous observation, increasing the acidity of the catalyst by promotion with sulfate enhances the reactivity of the TiO_2-ZrO_2 catalysts for the HCFC-22 decomposition. Although both TZ and TZNS possess some CO oxidation activity, it is too low to be effective under our experimental condition.

Despite the large difference in CO oxidation activity, the effectiveness for the conversion of CO to CO_2 on the different gold catalysts during the HCFC-22 hydrolysis reaction was remarkably similar. The CO_2 yield was much lower than that expected from the measured CO oxidation activity. It has been suggested that chloride might have an inhibitory effect on the CO oxidation activity of gold [9]. Since HF and HCl were coproducts of the HCFC-22 hydrolysis reaction, the catalysts could be poisoned for CO oxidation. To confirm this, the catalyst Au/TZDS was tested for its CO oxidation activity after the catalysts was used for HCFC-22 decomposition (spent catalyst). The rate of CO_2 formation over the fresh and spent catalysts for CO oxidation, together with the rate of CO_2 formation over the catalyst during HCFC-22 decomposition at different temperature, is shown in figure 4. The much lower CO oxidation activity found on the spent catalyst is strong evidence of the poisoning effect of HCFC-22 decomposition products. According to Oh *et al.*, the inhibitory effect of chloride for CO oxidation over Au/Al_2O_3 was due to Cl^--enhanced sintering of gold and due to the poisoning effect of Cl^- adsorbed on Au^+ [40]. While recognizing the limitation of TEM for our samples, we attempted to detect any change in particle size on the spent Au/TZ catalyst by TEM (figure 5). In addition to the larger gold particles (e.g. E), smaller gold particles 3–4 nm in diameter (F, G) could still be detected but these

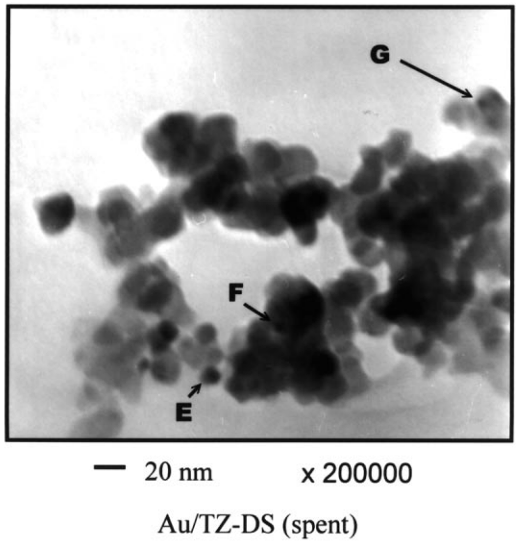

Figure 5. Transmission electron micrograph of the catalyst Au/TZ-DS after the catalyst was used for the HCFC-22 decomposition and CO oxidation reactions.

were less abundant compared to the fresh Au/TZ sample, suggesting that indeed some metal sintering occurred. At the same time, it is believed that halide poisoning of the support for O_2 activation also occurred. The rate of CO_2 formation on the spent catalyst above 300 °C was much higher than that at the same temperature during the HCFC-22 hydrolysis reaction. This shows that the deactivation was partially reversible and the catalyst recovered some CO oxidation activity during CO oxidation at high temperature by desorption or redistribution of the adsorbed halides.

4. Conclusions

Au/TiO_2-ZrO_2 catalysts prepared by deposition–precipitation using NaOH were found to be active for room temperature CO oxidation in moist air. Deposition–precipitation with aqueous ammonia produced catalysts with larger gold particle size and lower CO oxidation activities. Promoting the acidity of the Au/TiO_2-ZrO_2 catalyst by impregnation with 16% H_2SO_4 reduced CO oxidation activity. The catalysts were deactivated for CO oxidation by the HCl and HF formed during the hydrolysis reaction of HCFC-22 The addition of gold can only enhance the selectivity of the decomposition of HCFC-22 in the presence of water and oxygen to CO_2 by a small extent.

Acknowledgments

This work was funded by the Research Grant Council of Hong Kong under Grant No. HKBU 2041/00P. The City University of Hong Kong is gratefully acknowledged for providing us with the facilities for the transmission electron microscopic study.

References

[1] M.J. Molina and F.S. Rowland, Nature 249 (1974) 910.
[2] The Montreal Protocol on Substances that Deplete the Ozone Layer as either adjusted and/or amended in London 1990, Copenhagen 1992, Vienna 1995, Montreal 1997, Beijing 1999. Secretariat for The Vienna Convention for the Protection of the Ozone Layer & The Montreal Protocol on Substances that Deplete the Ozone Layer, 2000.
[3] C.F. Ng, S. Shan and S.Y. Lai, Appl. Catal., B: Environ. 16 (1998) 209.
[4] S.Y. Lai, W. Pan and C.F. Ng, Appl. Catal., B: Environ. 24 (2000) 207.
[5] G. Li, I. Tatsumi, M.-o. Yoshihiko and T. Yusaku, Appl. Catal., B: Environ. 9 (1996) 239.
[6] M. Haruta, N. Yamada, T. Kobayashi and S. Ijima, J. Catal. 115 (1989) 301.
[7] T. Aida, R. Higuchi and H. Niiyma, Chem. Lett. (1990) 2247.
[8] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, J. Catal. 144 (1993) 175.
[9] S.D. Lin, M. Bollinger and M.A. Vannice, Catal. Lett. 17 (1993) 245.
[10] A. Baiker, M. Maciejewski, S. Tagliaferri and P. Hug, J. Catal. 151 (1995) 407.
[11] F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, J. Phys. Chem. 100 (1996) 3625.
[12] W.S. Epling, G.B. Hoflund, J.F. Weaver, S. Tsubota and M. Haruta, J. Phys. Chem. 100 (1996) 9929.
[13] M.A. Bollinger and M.A. Vannice, Appl. Catal., B: Environ. 8 (1996) 417.
[14] F.E. Wagner, S. Galvagno, C. Milone, A.M. Visco, L. Stievano and S. Calogero, J. Chem. Soc., Faraday Trans. 93 (1997) 3403.
[15] A.P. Kozolva, S. Sugiyama, A.I. Kozolov, K. Asakura and Y. Iwasawa, J. Catal. 176 (1998) 426.
[16] W.-X. Zhang, Y.-G. Tao, M.-J. Jia and T.-H. Wu, Chem. J. Chin. Univ. 19 (1998) 1317.
[17] D.A.H. Cunningham, W. Vogel, H. Kageyama, S. Tsubota and M. Haruta, J. Catal. 177 (1998) 1.
[18] M. Valden and D.W. Goodman, Isr. J. Chem. 38 (1998) 285.
[19] F. Boccuzzi, G. Cerrato, F. Pinna and G. Strukul, J. Phys. Chem., B 102 (1998) 5733.
[20] J.-D. Grunwaldt and A. Baiker, J. Phys. Chem., B 103 (1999) 1002.
[21] R. Finch, M., N.A. Hodge, G.J. Hutchings, A. Meagher, Q.A. Pankburst, M.R.H. Siddiqui, F.E. Wagner and R. Whyman, Phys. Chem. Chem. Phys. 1 (1999) 485.
[22] J.-D. Grunwaldt, M. Maciejewski, O.S. Becker, P. Fabrizioli and A. Baiker, J. Catal. 186 (1999) 458.
[23] L. Guczi, D. Horváth, Z. Pászti, L. Tóth, Z.E. Horváth, A. Karacs and G. Petõ, J. Phys. Chem., B 104 (2000) 3183.
[24] M. Olea, M. Kunitake, T. Sido and Y. Iwasawa, Phys. Chem. Chem. Phys. 3 (2001) 627.
[25] T.K. Sau, a. Pal and T. Pal, J. Phys. Chem., B 105 (2001) 9266.
[26] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa and M. Haruta, J. Catal. 202 (2001) 256.
[27] M. Maciejewski, P. Fabrizioli, J.-D. Grunwaldt, O.S. Becker and A. Baiker, Phys. Chem. Chem. Phys. 3 (2001) 3846.
[28] M. Daté and M. Haruta, J. Catal. 201 (2001) 221.
[29] J. Guzman and B.C. Gates, J. Phys. Chem., B (2002) 7659.
[30] R. Zanella, S. Giorgio, C.R. Henry and C. Louis, J. Phys. Chem., B 106 (2002) 7634.
[31] R. Grisel, K.-J. Weststrate, A. Gluhoi and B.E. Nieuwenhuys, Gold Bulletin 35 (2002) 39.
[32] M. Haruta, Catal. Today 36 (1997) 153.
[33] G.C. Bond and D.T. Thompson, Catal. Rev.—Sci. Eng. 41 (1999) 319.
[34] J.A. Navio, F.J. Marchena, M. Macias and P.J. Sanchez-Soto, J. Mater. Sci. 27 (1992) 2643.

[35] J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, J. Chastain and R.C. Long Jr. (eds) (Physical Electronics Inc., Eden Prairie, 1995).
[36] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, Catal. Lett. 51 (1998) 53.
[37] J.-D. Grunwaldt, J. Catal. 181 (1999) 223.
[38] K. Ruth, M. Hayes, R. Burch, S. Tsubota and M. Haruta, Appl. Catal., B: Environ. 24 (2000) L133.
[39] A.C. Gluhoi, M.A.P. Dekker and B.E. Nieuwenhuys, J. Catal. 219 (2003) 197.
[40] H.S. Oh, J.H. Yang, C.K. Costello, Y.M. Wang, S.R. Bare, H.H. Kung and C.C. Kung, J. Catal. 210 (2002) 375.