available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article

The roles of hydroxyapatite and FeO_x in a Au/FeO_x-hydroxyapatite catalyst for CO oxidation

ZHAO Kunfeng^{a,b}, QIAO Botao^a, ZHANG Yanjie^a, WANG Junhu^{a,*}^a Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 31 January 2013

Accepted 25 March 2013

Published 20 July 2013

Keywords:

Gold

Iron oxide

Hydroxyapatite

Carbon monoxide

Sintering resistance

ABSTRACT

A FeO_x-modified hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂)-supported gold catalyst is highly active and stable during CO oxidation at low temperature, and it is also sinter-resistant to calcination at temperature up to 600 °C. This work used catalyst characterization and activity tests to investigate the roles of the HAP support and FeO_x promoter in CO oxidation. XPS results suggested that a strong interaction between the HAP support and the Au and FeO_x nanoparticles gave the sintering resistance. In situ DRIFT studies revealed that the addition of FeO_x changed the nature of the reaction mechanism and intermediates to promote catalytic activity. TEM and Mössbauer examination of the spent catalysts in combination with the in situ DRIFT results suggested that the better stability of Au/FeO_x-HAP originated from its better prevention of carbonate accumulation.

© 2013, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Supported gold catalysts have attracted interest for various catalyzed reactions, including (preferential) oxidation of CO (in H₂), water-gas shift, (selective) oxidation, (selective) hydrogenation, and epoxidation of propene [1–3]. A major barrier to the application of supported gold catalysts is that under reaction conditions, the Au particles tend to sinter, which leads to a dramatic decrease in activity. To address this problem, the strategies that have been developed include taking advantage of the confinement effect of mesoporous materials [4,5], utilizing mixed or surface-modified oxide supports [6–8], developing new supports [9,10], and preparing supported Au-M bimetallic alloy or core-shell structured catalysts [11–13]. These strategies can improve the anti-sintering ability of supported gold catalysts at high temperature, but they usually cause other problems such as the use of an expensive precursor [4], com-

plicated preparation [5,11], decrease of low temperature activity [8,10,12,13], and even deactivation on stream [7].

Recently, it was found that certain anions such as PO₄³⁻ and OH⁻ can effectively stabilize the gold nanoparticles against aggregation to provide a new strategy to synthesize sinter-resistant gold catalysts [7,9,14–16]. More recently, materials based on hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂), which contain abundant PO₄³⁻ and OH⁻ groups, have attracted attention as recyclable catalysts and catalyst carriers [17] for their structural flexibility [18] and bifunctionality of their base and acid sites [19]. Therefore, using HAP-based materials as the support to enhance the stability of gold nanoparticles appears attractive and effective. In fact, it was found that a HAP-supported gold catalyst showed good structural and reactive stability for CO oxidation [10,20–22]. However, its activity was relatively low as compared with those of reducible oxide-supported gold catalysts. This may be due to the poorer

*Corresponding author. Tel: +86-411-84379159; Fax: +86-411-84685940; E-mail: wangjh@dicp.ac.cn

This work was supported by the Chinese Academy of Sciences for “100 Talents” Project, the National Natural Science Foundation of China (11079036), and the Natural Science Foundation of Liaoning Province (20092173).

DOI: 10.1016/S1872-2067(12)60590-7 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 34, No. 7, July 2013

ability of HAP to activate O_2 because the adsorption and activation of O_2 is a critical step for CO oxidation on gold. Therefore, we expected that a suitable modification with a reducible oxide can improve the activity and sinter-resistant properties of HAP-supported gold catalysts. FeO_x has been extensively used as an additive to improve the activity of supported Pt catalysts for CO (preferential) oxidation [23–26]. In the past few years, the role of FeO_x for O_2 activation has been revealed [27–30].

Based on these developments above, we have designed a FeO_x -modified HAP-supported gold catalyst with high activity, good stability, and good sinter-resistance [31]. In this work, we extended the reaction study and characterization in order to understand the effects of the HAP support and FeO_x modifier on the activity of the Au/ FeO_x -HAP catalyst. HAP was found to stabilize the Au nanoparticles and the size and phase of the FeO_x modifier. FeO_x was found to significantly promote the activity of the Au/ FeO_x -HAP catalyst for CO oxidation by changing the nature of the reaction mechanism and intermediates. The better stability of Au/HAP and Au/ FeO_x -HAP was due to their better prevention of carbonate accumulation rather than their better sintering resistance.

2. Experimental

2.1. Catalyst preparation

The method used to prepare the Au/ FeO_x , Au/HAP, and Au/ FeO_x -HAP catalysts was reported in a previous work [31]. FeO_x is denoted as F, and the FeO_x samples freeze-dried and further calcined at 400 °C for 5 h are denoted as F-FD and F-400, respectively. FeO_x -HAP (and HAP) are denoted as FH (and H), and the FeO_x -HAP (and HAP) samples freeze-dried and further calcined at 400 °C for 5 h are denoted as FH-FD (and H-FD) and FH-400 (and H-400), respectively. Other FH samples with different FeO_x contents were also synthesized, and unless they are specially labeled, FH represents FeO_x -HAP with 8.4 wt% of Fe. Gold was deposited on the three F-400, H-400, and FH-400 supports by a deposition-precipitation method to give nominal 5 wt%. The catalysts dried at 60 °C (denoted as Au/F-60, Au/H-60, and Au/FH-60 depending on the support) were further calcined at 400 °C for 3 h (denoted as Au/F-400, Au/H-400, and Au/FH-400) and 600 °C for 3 h (denoted as Au/F-600, Au/H-600, and Au/FH-600).

2.2. Catalytic activity

The catalytic activity was evaluated in a fixed-bed reactor. Catalyst powder (100 mg) diluted with 130 mg SiC was loaded into a U-shape quartz reactor and was purged with He for 30 min. Then, the feed gas containing 1% CO, 1% O_2 , and balance He was flowed through the reactor at a flow rate of 33.3 ml/min (space velocity of 20000 ml/(g_{cat}·h)). The effluent gas was analyzed by an online gas chromatograph (HP 6890N) equipped with a TDX-01 column and a thermal conductivity detector using He as carrier gas. The CO conversion was calculated based on the difference between inlet and outlet concentrations. The stability measurements under reaction conditions

were performed at 24 °C, and 50 mg catalyst (resulting in a space velocity of 40000 ml/(g_{cat}·h)) was used to avoid reaching 100% CO conversion. For measuring the specific reaction rate, the catalytic CO oxidation reaction was conducted in a differential mode where the CO conversion was kept below 20%. To do this, an amount of the sample (3–167 mg) with a size of 200 mesh was diluted with SiC (300–400 mg, ~200 mesh). For each run at a specific reaction temperature (24 °C), the CO conversions at 20, 40, and 60 min were averaged and used for calculation of the specific rate.

2.3. Catalyst characterization

The actual Au and Fe loadings were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The Brunauer-Emmett-Teller (BET) specific surface area was measured by nitrogen adsorption at –196 °C on a Micromeritics ASAP 2010 apparatus. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250 X-ray photoelectron spectrometer with monochromated Al $K\alpha$ anode. All binding energies were calibrated by using contaminant carbon as an internal standard (C 1s = 284.5 eV). The high resolution transmission electron microscopy (HRTEM) images were observed on a JEOL JEM-2010 microscope operated at 200 kV. The ^{57}Fe Mössbauer spectra were recorded at –193 °C with a Janis gas flow low temperature system or at room temperature on a Topologic 500A spectrometer. The $^{57}Co(Rh)$ source was moving in a constant acceleration mode. All of the spectral analyses were conducted assuming a Lorentzian line shape for computer deconvolution and fitting. The Doppler velocity of the spectrometer was calibrated with respect to α -Fe foil at room temperature. The free recoil fraction was assumed to be the same for all iron species. In this way, Mössbauer parameters such as the isomer shift (IS), electric quadrupole splitting (QS), full line width at half maximum (W), magnetic hyperfine field (B_{hf}), and relative resonance areas of the different components of the absorption patterns (peak area) were determined. The in situ diffuse reflectance infrared Fourier transform spectra (DRIFT) were collected by an Equinox 55 spectrometer (Bruker) with a resolution of 4 cm^{–1} at 20 °C. Before the measurement, 40 mg catalyst powder was loaded into a reaction cell and then purged with He (30 ml/min) for 30 min. The CO adsorption spectra were recorded after the catalyst was exposed to 3% CO-97% He (31 ml/min) for 20 min. Then O_2 was introduced (forming 3% CO + 6% O_2 He balanced mixture, 33 ml/min) and the CO + O_2 spectra were also recorded after 20 min exposure. Temperature-programmed desorption (TPD) of CO_2 was performed on a Micromeritics Autochem 2910 apparatus equipped with a thermal conductivity detector to evaluate the surface basicity of the catalysts. About 100 mg of catalyst was heated in a flow of dry He (30 ml/min) to 200 °C and held for 30 min. Then the catalyst was cooled to 50 °C and exposed to CO_2 pulse gas for adsorption until saturated. Desorption of CO_2 was analyzed online with a temperature rise to 800 °C (heating rate 10 °C/min) in He flow (30 ml/min).

3. Results and discussion

3.1. Sinter-resistant Au/FH catalyst

From the activity measurement at 24 °C [31], the as-synthesized catalyst, Au/FH-60, has a moderate specific rate ($1.740 \text{ mol}_{\text{CO}}/(\text{g}_{\text{Au}}\cdot\text{h})$) as compared with that of Au/F-60 ($3.780 \text{ mol}_{\text{CO}}/(\text{g}_{\text{Au}}\cdot\text{h})$) and Au/H-60 ($0.246 \text{ mol}_{\text{CO}}/(\text{g}_{\text{Au}}\cdot\text{h})$), which was due to the co-existence of FeO_x and HAP. After calcination at 400 °C, the HAP-containing catalysts exhibited anti-sintering properties. The specific rates of Au/H-400 and Au/FH-400 decreased to 0.155 and $0.630 \text{ mol}_{\text{CO}}/(\text{g}_{\text{Au}}\cdot\text{h})$, respectively, while specific rate of Au/F-400 decreased sharply to $0.161 \text{ mol}_{\text{CO}}/(\text{g}_{\text{Au}}\cdot\text{h})$. The activities of the catalysts calcined at 600 °C further confirmed this with specific rates of 0.009, 0.038, and $0.071 \text{ mol}_{\text{CO}}/(\text{g}_{\text{Au}}\cdot\text{h})$ for Au/F-600, Au/H-600, and Au/FH-600, respectively.

The TEM results [31] gave visual evidence of the sintering resistance. All the gold nanoparticles were highly distributed on the catalysts dried at 60 °C and could hardly be seen. After calcination at elevated temperature, e.g. at 400 and 600 °C, gold nanoparticles on HAP-containing catalysts (Au/H and Au/FH) aggregated to ~ 2.5 and ~ 4.5 nm, while that on Au/F aggregated to ~ 2.5 and ~ 8 nm, respectively. The stability of catalysts calcined at 400 °C was tested at 24 °C with the space velocity of $40000 \text{ ml}/(\text{g}_{\text{cat}}\cdot\text{h})$ to avoid reaching 100% CO conversion [31]. Au/FH-400 with the decrease of CO conversion from near 100% to 90% after 80 h exhibited excellent stability in comparison with Au/F-400 that decreased from 96% to 54% and Au/H-400 that decreased from 37% to 13% during the same period. These results indicated that HAP contributed to the sintering resistance of Au/FH, and FeO_x mainly accounted for the high activity. It is the combination of HAP and FeO_x that made Au/FH a highly active catalyst for CO oxidation even after calcination at as high as 600 °C.

To further investigate the effect of FeO_x on the catalysis of CO oxidation, Au/FH catalysts with various Fe contents were prepared and calcined at different temperatures. Their activities were also measured (Fig. 1). The T_{50} (the temperature at which 50% CO conversion is achieved) data are summarized in Table 1. For all Au/FH-60 catalysts, the activity generally increased with the increase of Fe content and they were more active than Au/H-60, indicating that FeO_x definitely played a critical role in improving the activity for CO oxidation. For catalysts after calcination at 600 °C, the slightly lower activity of Au/FH-600 with 17.5 wt% Fe than that of Au/FH-600 with 12.6 wt% Fe combined with the lowest activity of Au/F-600 proved that an excess of FeO_x caused a decrease of sintering resistance.

3.2. Physicochemical characterization

All three F, H, and FH supports have relatively large surface areas after they were calcined at 400 °C [31]. The surface area decreased with further calcination at 600 °C to different degrees: 2/3 decrease for FeO_x (from 84 to $27 \text{ m}^2/\text{g}$) and 1/2 decrease for HAP (from 109 to $60 \text{ m}^2/\text{g}$) and FeO_x -HAP (from 130 to $70 \text{ m}^2/\text{g}$). The smaller decrease for the HAP and

Fig. 1. CO conversion on Au/FH catalysts with various Fe contents. Feed gas $\text{CO}:\text{O}_2:\text{He} = 1:1:98$, GHSV = $20000 \text{ ml}/(\text{g}_{\text{cat}}\cdot\text{h})$, catalyst 100 mg.

FeO_x -HAP supports indicated that they are more sinter-resistant compare to the FeO_x support.

The gold loadings measured by ICP-AES were much less than the nominal 5 wt% loading (3.7, 2.1 and 3.2 wt% for Au/F, Au/H, and Au/FH, respectively). This indicates the loss of Au during the deposition process, in accord with previous reports [32,33], in which the same deposition precipitation method was used. It should be noted that the Au loadings of Au/F-600 and Au/FH-600 were higher than that of Au/H-600. This is probably related to the lower isoelectric point of HAP [34,35] than that of Fe_2O_3 [36], suggesting that Au is easier deposited on the surface of FeO_x with our preparation conditions.

The results of the Au 4f XPS analysis (Fig. 2 and Table 2) revealed that on all the catalysts dried at 60 °C, there were two kinds of gold species with Au 4f_{7/2} binding energies (B.E.) of 84.0–84.1 eV and 85.5–85.9 eV, which were due to Au^0 and $\text{Au}^{\delta+}$, respectively. The ratio of $\text{Au}^{\delta+}/\text{Au}^0$ on Au/F-60 was significantly lower than those on Au/H-60 and Au/FH-60. After calcination at 400 and 600 °C, the gold species on the Au/F cat-

Table 1

T_{50} of Au/FH catalysts with various Fe contents.

Fe (wt%)	$T_{50}/^\circ\text{C}$		
	Au/FH-60	Au/FH-400	Au/FH-600
0 [31]	25	4	40
2.1	-16	-8	27
4.9	-23	-23	31
8.4	-26	-29	9
12.6	-31	-30	1
17.5	-31	-32	7
70 [31]	-46	-16	92

Fig. 2. Au 4f XPS spectra of Au/F, Au/H, and Au/FH calcined at different temperatures.

alysts changed into the metallic state (B.E. = 83.4 eV), in accord with reported results [37,38]. However, for the Au/H and Au/FH catalysts, besides Au⁰ (B.E. = 83.5–83.7 eV) there were some positively charged gold species (85.5/85.6 eV for Au/H and 85.1 eV for Au/FH). Considering that Au oxide on a FeO_x support would decompose completely under calcination, the positively charged Au would be due to a strong interaction between Au and HAP.

The Fe 2p XPS spectra of catalysts containing various amounts of Fe are presented in Fig. 3. The binding energies of Fe 2p_{3/2} are 710.2 and 710.8 eV for Au/F and Au/FH, respectively. This result indicated that the Fe mainly existed as Fe³⁺ because the binding energy of Fe 2p_{3/2} for Fe²⁺ is lower than 710 eV [39]. The spin-orbit splitting energies are 13.6 and 13.4 eV for the Au/F and Au/FH catalysts, respectively, both of

which are larger than that reported for Fe₃O₄ (13.2 eV), suggesting there was no Fe²⁺ [40]. In addition, the slightly higher binding energies for the Au/FH catalysts would suggest that there is also a strong interaction between FeO_x and HAP.

In our previous work, the shape change of the room temperature ⁵⁷Fe Mössbauer spectra for Au/F and Au/FH treated at different temperatures showed that the introduction of HAP enhanced the sinter-resistant ability of FeO_x [31]. The room temperature ⁵⁷Fe Mössbauer spectra of FeO_x in the catalysts

Fig. 3. Fe 2p XPS spectra of Au/F and Au/FH calcined at different temperatures.

Table 2

Surface distribution of gold species on the catalysts.

Catalyst	B. E. of Au 4f _{7/2} (eV)	Au ^{δ+} /Au ⁰
Au/F-60	84.0, 85.9	0.25
Au/F-400	83.4	—
Au/F-600	83.4	—
Au/H-60	84.1, 85.5	0.75
Au/H-400	83.7, 85.5	0.33
Au/H-600	83.5, 85.6	0.18
Au/FH-60	84.1, 85.7	0.67
Au/FH-400	83.6, 85.1	0.43
Au/FH-600	83.6, 85.1	0.32

Fig. 4. ^{57}Fe Mössbauer spectra of F, FH, Au/F, and Au/FH at $-193\text{ }^{\circ}\text{C}$. Au/F-600 was tested at room temperature. $\gamma\text{-Fe}_2\text{O}_3$ was fitted with $W_{1,6} = W_{2,5} + C = W_{3,4} + 2C$, and $\alpha\text{-Fe}_2\text{O}_3$ was fitted with $W_{1,6} = W_{2,5} = W_{3,4}$, where W is the full linewidth at half maximum, and C is a constant.

showed paramagnetic relaxation patterns but could not differentiate between $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ [31]. To characterize the crystal phase of FeO_x , $-193\text{ }^{\circ}\text{C}$ ^{57}Fe Mössbauer spectra were further obtained. The results are shown in Fig. 4 and Table 3, which revealed that the as-synthesized FeO_x existed as $\gamma\text{-Fe}_2\text{O}_3$. $400\text{ }^{\circ}\text{C}$ calcination (F-400, Au/F-60, and Au/F-400) resulted in a mixture of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$, and when the calcination temperature reached $600\text{ }^{\circ}\text{C}$, $\gamma\text{-Fe}_2\text{O}_3$ was transformed to $\alpha\text{-Fe}_2\text{O}_3$ completely. For the FH series, all samples calcined below $400\text{ }^{\circ}\text{C}$ were $\gamma\text{-Fe}_2\text{O}_3$, and even after calcination at $600\text{ }^{\circ}\text{C}$, 64% of FeO_x existed as $\gamma\text{-Fe}_2\text{O}_3$. The low temperature ^{57}Fe Mössbauer spectra showed that the introduction of HAP not only enhanced the sinter-resistant ability of FeO_x but also stabi-

lized the $\gamma\text{-Fe}_2\text{O}_3$ crystalline phase to elevated temperature, which gave high activity [41,42]. The influence of HAP on the maghemite-to-hematite phase change of a $\text{FeO}_x\text{-HAP}$ composite support was investigated in our previous work [43].

The catalysts after the stability test (Au/XX-400-S, XX = F, H, FH) were also characterized by TEM and ^{57}Fe Mössbauer spectroscopy. The TEM results [31] had shown that the gold particles on all the catalysts had aggregated slightly, with diameter increase from 2.7 to 3.2 nm, 2.4 to 2.9 nm, and 2.2 to 2.7 nm for Au/F-400, Au/H-400, and Au/FH-400, respectively. Obviously, particle aggregation was not the main reason for catalyst deactivation during reaction because the particles were all in the optimum size range ($< 5\text{ nm}$). Furthermore, the aggregation

Table 3

^{57}Fe Mössbauer parameters of F, FH, Au/F, and Au/FH at $-193\text{ }^{\circ}\text{C}$.

Sample	Oxidation state of iron	IS ^a (mm/s)	QS ^b (mm/s)	B_{hf} (T)	Spectral area ^c (%)	Crystal phase
F-FD	Fe^{3+}	0.31		49	41	$\gamma\text{-Fe}_2\text{O}_3$
F-400	Fe^{3+}	0.31		44	59	$\gamma\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.32		43	54	
	Fe^{3+}	0.32		48	24	
	Fe^{3+}	0.36		52	22	
Au/F-60	Fe^{3+}	0.32	-0.18	47	23	$\gamma\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.31		42	55	$\alpha\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.36	-0.18	52	22	
	Fe^{3+}	0.32		48	26	
Au/F-400	Fe^{3+}	0.31		43	44	$\alpha\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.36	-0.18	52	30	
	Fe^{3+}	0.26	-0.21	51	100	
	Fe^{3+}	0.31		48	30	
FH-FD	Fe^{3+}	0.35		42	32	$\gamma\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.33		44	37	
	Fe^{3+}	0.31		48	44	
	Fe^{3+}	0.28		41	56	
Au/FH-60	Fe^{3+}	0.30		48	41	$\gamma\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.38		40	59	
Au/FH-400	Fe^{3+}	0.31		48	49	$\gamma\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.37		38	51	
	Fe^{3+}	0.30		50	28	
Au/FH-600	Fe^{3+}	0.31		46	36	$\gamma\text{-Fe}_2\text{O}_3$
	Fe^{3+}	0.36	0.37	53	36	

^a Isomer shift relative to $\alpha\text{-Fe}$ foil at room temperature. ^b Electric quadrupole splitting. ^c Uncertainty is $\pm 5\%$ of reported value. ^d Room temperature.

Fig. 5. ^{57}Fe Mössbauer spectra of Au/F-400 and Au/FH-400 at $-193\text{ }^{\circ}\text{C}$ after stability test.

extents were similar, but their activity decreases were different. The ^{57}Fe Mössbauer spectra (Fig. 5 and Table 4) showed that the phases of FeO_x were nearly unchanged for Au/F-400 and Au/FH-400.

3.3. Mechanism

The characterization results, especially the TEM images, showed clearly that HAP plays a special role in stabilizing the Au nanoparticles against sintering [31]. This can be ascribed to the functional groups such as OH^- and/or PO_4^{3-} on its surface because the use of OH^- and PO_4^{3-} groups to stabilize Au nanoparticles has been proved previously [7,9,14–16]. The XPS results suggested that the interaction between Au and the HAP support is strong because the Au species on the HAP and FeO_x -HAP supports were partially positive even after calcination at 400 and 600 $^{\circ}\text{C}$, which implies that HAP stabilizes Au nanoparticles by its strong interaction with Au (most probably through its OH^- and/or PO_4^{3-} groups). The ^{57}Fe Mössbauer spectra indicated that HAP can also stabilize the size and crystal phase of the FeO_x modifier. The Fe 2p XPS results for the Au/F and Au/FH catalysts suggested that there is also a strong interaction between FeO_x and HAP. All these results provide

Table 4

^{57}Fe Mössbauer parameters of Au/F-400 and Au/FH-400 at $-193\text{ }^{\circ}\text{C}$ after stability test.

Sample*	IS (mm/s)	QS (mm/s)	B_{hf} (T)	Spectral area (%)	Crystal phase
Au/F-400-S	0.35		49	18	$\gamma\text{-Fe}_2\text{O}_3$
	0.32		44	54	
	0.37	-0.18	52	27	
Au/FH-400-S	0.31		48	45	$\gamma\text{-Fe}_2\text{O}_3$
	0.38		38	55	

* Oxidation state of iron is Fe^{3+} .

clear evidence that HAP stabilized the species dispersed on it through a strong interaction with them.

There is no doubt from the above results that HAP stabilized Au nanoparticles against sintering for calcination at as high as 600 $^{\circ}\text{C}$. However, Au catalysts supported on HAP were less active for CO oxidation as shown by our activity results and previous reports [10,20–22]. For CO oxidation over supported Au catalysts, it is generally accepted that O_2 activation is the key step because O_2 cannot easily adsorb on Au. Reducible supports that can activate O_2 are necessary for highly active supported Au catalysts. Therefore, the use of a support that can provide active O or a modifier that can improve O_2 activation is an effective method to improve the activity of a supported Au catalyst. In the current study, FeO_x was used as the modifier to improve the catalytic activity of HAP-supported Au catalyst, and the results showed that it works well. The investigation of the effect of FeO_x content further confirmed the promoter role of FeO_x .

In an attempt to understand the promotion by FeO_x and the deactivation of the catalysts during reaction, we performed in situ DRIFT experiments with the Au/F-400, Au/H-400, and Au/FH-400 catalysts (see Fig. 6). For all three catalysts, an absorption peak at 2101–2111 cm^{-1} was observed, which can be ascribed to CO adsorption on a Au^0 site [44,45]. For the Au/H-400 catalyst, the CO adsorption showed a blue shift from 2106 to 2111 cm^{-1} after the introduction of O_2 , indicating that both CO and O_2 were adsorbed on the Au site and the reaction occurred by a competitive Langmuir-Hinshelwood mechanism [46]. For the Au/F and Au/FH catalysts, the almost unchanged

Fig. 6. In situ DRIFT spectra of Au/F-400, Au/H-400, and Au/FH-400 catalysts at 20 $^{\circ}\text{C}$. Pretreatment: 40 mg of catalyst powder was purged with He (30 ml/min) for 30 min; CO adsorption: 3% CO-97% He (31 ml/min); CO + O_2 adsorption: 3% CO + 6% O_2 + 91% He (33 ml/min).

Fig. 7. TPD profiles of CO_2 adsorbed on the catalysts calcined at 400 °C. Catalyst (100 mg) was pretreated at 200 °C for 30 min in a flow of dry He (30 ml/min); CO_2 adsorbed at 50 °C and desorbed to 800 °C with a rate of 10 °C/min in He flow (30 ml/min).

position of the CO adsorption on Au^0 suggested that the reaction followed a non-competitive Langmuir-Hinshelwood mechanism [28] or redox mechanism [47] and that O_2 was activated on the support [29,48]. In addition, for Au/H-400, three peaks at 1614, 1430, and 1218 cm^{-1} were observed, which can be ascribed to a bicarbonate from the reaction of adsorbed CO_2 with a OH^- group [49–51]. The peaks at 2975, 2880, 1702, and 1550 cm^{-1} observed on the Au/F and Au/FH catalysts were typical peaks for formate adsorption [50,52], indicating that CO reacted with the OH^- groups of FeO_x and formed very reactive adsorbed formates [50]. It can be seen that in the 1200–1800 cm^{-1} region, the 1415 and 1443 cm^{-1} peaks ascribed to monodentate or polydentate carbonates were more prominent for Au/F than for Au/FH, suggesting that carbonate accumulation caused by CO_2 adsorption was more prevalent on Au/F than on Au/FH. The accumulation of the carbonate species is an important cause for deactivation in CO oxidation, especially for FeO_x supported catalyst [53,54].

The surface basicity of the catalysts was evaluated by the TPD of CO_2 (Fig. 7). The desorption temperature and peak area of CO_2 are the criteria for the strength and amount of basic sites, respectively [55]. It can be seen that for all catalysts, there were two CO_2 desorption peaks, one at about 95 °C and another broad peak from 200 to 600 °C, which was centered at 289 °C for Au/F-400 and 274 °C for Au/H-400 and Au/FH-400. For the CO_2 desorption peak at 95 °C, the peak area of Au/FH and Au/H was larger than that of Au/F, indicating that the Au/FH and Au/H catalysts have more weak surface basic sites than Au/F. For CO_2 desorption at high temperature, the lower CO_2 desorption temperature and peak area of Au/FH and Au/H than those of Au/F suggested that Au/FH and Au/H have fewer strong surface basic sites than Au/F. These results showed that Au/FH and Au/H have a more facile CO_2 desorption, which agrees well with the DRIFT results.

In addition, the TEM images of the catalysts after the stability test showed that sintering of the Au nanoparticles was not obvious [31]. Therefore, deactivation was not caused by Au sintering. Activity loss is more usually attributed to unreactive carbonate species blocking active sites, and not to the growth of

Fig. 8. A typical HRTEM image of the Au/FH-400 catalyst.

Au nanoparticles during reaction [2]. Therefore, according to the TEM, in situ DRIFT, and CO_2 -TPD results, we can suggest that the excellent stability of Au/FH-400 and Au/H-400 should be ascribed to their prevention of carbonate accumulation.

The characterization and activity results showed clearly that the HAP support plays a vital role in stabilizing the Au nanoparticles against sintering by a strong interaction between Au and HAP while the FeO_x modifier promotes the activity by changing the nature of the reaction mechanism and intermediates. This, however, requires that the Au nanoparticles must be in contact directly with both the HAP and FeO_x species. Thus, it is probable that the Au nanoparticles were anchored on the junction of HAP and FeO_x . To confirm this, the Au/FH-400 catalyst was examined with HRTEM. A typical image is presented in Fig. 8, in which it can be seen that the Au nanoparticles were anchored on the junction of FeO_x ($\gamma\text{-Fe}_2\text{O}_3$ (211)) and HAP (101).

4. Conclusions

A $\text{Au/FeO}_x\text{-HAP}$ catalyst is highly active and stable during CO oxidation, and it is also sinter-resistant to calcination at elevated temperature (to 600 °C). In the $\text{Au/FeO}_x\text{-HAP}$ catalyst, the HAP support (most probably reacting with the OH^- and/or PO_4^{3-} groups on its surface) plays a unique role in stabilizing the Au nanoparticles as well as the size and phase of FeO_x by a strong interaction with these. FeO_x significantly promotes the catalytic activity for CO oxidation by changing the nature of the reaction mechanism and intermediates. The better stability of the $\text{Au/FeO}_x\text{-HAP}$ and Au/HAP catalysts originated from their better prevention of carbonate accumulation rather than a better sintering resistance. The understanding of the stabilizing mechanism of the HAP support and promotion mechanism of FeO_x will be helpful for the further development of highly active and sinter-resistant catalysts for applications at high temperature.

Acknowledgements

The authors would like give special thanks to Dr. Long Hao and Prof. Junhua Dong (Institute of Metal Research, Chinese

Academy of Sciences) for giving assistance to the XPS data collection.

References

- [1] Wang D H, Cheng D Y, Hao Z P, Shi X C. Nano-Gold Catalysts and Their Applications. Beijing: National Defence Ind Press (王东辉, 程代云, 郝郑平, 史喜成. 纳米金催化剂及其应用. 北京: 国防工业出版社), 2006. 14
- [2] Bond G C, Louis C, Thompson D T. Catalysis by Gold. London: Imperial College Press, 2006. 337
- [3] Bond G C, Louis C, Thompson D T. Catalysis by Gold—Phenomenon-Principle-Application. Xu B Q, Yang X Z, Wang D H transl. Beijing: Science Press (邦德, 路易斯, 汤普森. 黄金的催化作用——现象·原理·应用. 徐柏庆, 杨绪壮, 王东辉译. 北京: 科学出版社), 2008. 253
- [4] Zhu H G, Liang C D, Yan W F, Overbury S H, Dai S. *J Phys Chem B*, 2006, 110: 10842
- [5] Zhang H L, Yan X J, Li W C. *Chin J Catal* (张慧丽, 阎晓洁, 李文翠. 催化学报), 2009, 30: 1085
- [6] Yan W F, Mahurin S M, Pan Z W, Overbury S H, Dai S. *J Am Chem Soc*, 2005, 127: 10480
- [7] Ma Z, Brown S, Overbury S H, Dai S. *Appl Catal A*, 2007, 327: 226
- [8] Zhang H L, Ren L H, Lu A H, Li W C. *Chin J Catal* (张慧丽, 任丽会, 陆安慧, 李文翠. 催化学报), 2012, 33: 1125
- [9] Yan W F, Brown S, Pan Z W, Mahurin S M, Overbury S H, Dai S. *Angew Chem, Int Ed*, 2006, 45: 3614
- [10] Ma Z, Yin H F, Overbury S H, Dai S. *Catal Lett*, 2008, 126: 20
- [11] Liu X Y, Wang A Q, Wang X D, Mou C Y, Zhang T. *Chem Commun*, 2008: 3187
- [12] Yu K, Wu Z C, Zhao Q R, Li B X, Xie Y. *J Phys Chem C*, 2008, 112: 2244
- [13] Li L C, Wang C S, Ma X X, Yang Z H, Lu X H. *Chin J Catal* (李力成, 王昌松, 马璇璇, 杨祝红, 陆小华. 催化学报), 2012, 33: 1778
- [14] Brown M A, Carrasco E, Sterrer M, Freund H J. *J Am Chem Soc*, 2010, 132: 4064
- [15] Qi C X, Su H J, Guan R G, Xu X F. *J Phys Chem C*, 2012, 116: 17492
- [16] Veith G M, Lupini A R, Dudney N J. *J Phys Chem C*, 2009, 113: 269
- [17] Zhang Y J, Wang J, Yin J, Zhao K F, Jin C Z, Huang Y Y, Jiang Z, Zhang T. *J Phys Chem C*, 2010, 114: 16443
- [18] Vallet-Regí M, González-Calbet J M. *Prog Solid State Chem*, 2004, 32: 1
- [19] Tsuchida T, Kubo J, Yoshioka T, Sakuma S, Takeguchi T, Ueda W. *J Catal*, 2008, 259: 183
- [20] Phonthammachai N, Zhong Z Y, Guo J, Han Y F, White T J. *Gold Bull*, 2008, 41: 42
- [21] Domínguez M I, Romero-Sarria F, Centeno M A, Odriozola J A. *Appl Catal B*, 2009, 87: 245
- [22] Huang J, Wang L C, Liu Y M, Cao Y, He H Y, Fan K N. *Appl Catal B*, 2011, 101: 560
- [23] Liu X S, Korotkikh O, Farrauto R. *Appl Catal A*, 2002, 226: 293
- [24] Shou M, Tanaka K-i, Yoshioka K, Moro-oka Y, Nagano S. *Catal Today*, 2004, 90: 255
- [25] Siani A, Alexeev O S, Captain B, Lafaye G, Marécot P, Adams R D, Amiridis M D. *J Catal*, 2008, 255: 162
- [26] Tomita A, Shimizu K-i, Kato K, Tai Y. *Catal Commun*, 2012, 17: 194
- [27] Fu Q, Li W X, Yao Y X, Liu H Y, Su H Y, Ma D, Gu X K, Chen L M, Wang Z, Zhang H, Wang B, Bao X H. *Science*, 2010, 328: 1141
- [28] Liu K, Wang A Q, Zhang W S, Wang J, Huang Y Q, Shen J Y, Zhang T. *J Phys Chem C*, 2010, 114: 8533
- [29] Liu L Q, Zhou F, Wang L G, Qi X J, Shi F, Deng Y Q. *J Catal*, 2010, 274: 1
- [30] Liu K, Wang A Q, Zhang W S, Wang J, Huang Y Q, Wang X D, Shen J Y, Zhang T. *Ind Eng Chem Res*, 2011, 50: 758
- [31] Zhao K F, Qiao B T, Wang J, Zhang Y J, Zhang T. *Chem Commun*, 2011, 47: 1779
- [32] Wolf A, Schüth F. *Appl Catal A*, 2002, 226: 1
- [33] Moreau F, Bond G C, Taylor A O. *J Catal*, 2005, 231: 105
- [34] Zhang J X, Maeda M, Kotobuki N, Hirose M, Ohgushi H, Jiang D L, Iwasa M. *Mater Chem Phys*, 2006, 99: 398
- [35] Fu H L, Rahaman M N, Day D E, Brown R F. *J Mater Sci: Mater Med*, 2011, 22: 579
- [36] Kittaka S. *J Colloid Interface Sci*, 1974, 48: 327
- [37] Qiao B T, Deng Y Q. *Appl Catal B*, 2006, 66: 241

Graphical Abstract

Chin. J. Catal., 2013, 34: 1386–1394 doi: 10.1016/S1872-2067(12)60590-7

The roles of hydroxyapatite and FeO_x in a Au/FeO_x-hydroxyapatite catalyst for CO oxidation

ZHAO Kunfeng, QIAO Botao, ZHANG Yanjie, WANG Junhu *

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences

The hydroxyapatite stabilizes gold and FeO_x nanoparticles by a strong interaction with these, while FeO_x promotes the catalytic activity by changing the nature of the reaction mechanism and the intermediates.

- [38] Qiao B T, Zhang J, Liu L Q, Deng Y Q. *Appl Catal A*, 2008, 340: 220
- [39] Moulder J F, Stickle W F, Sobol P E, Bomben K D. Handbook of X-Ray Photoelectron Spectroscopy. 2nd Ed. Eden Prairie: Perkin-Elmer Corporation, Physical Electronics Division, 1992. 80
- [40] Banerjee I, Kholam Y B, Balasubramanian C, Pasricha R, Bakare P P, Patil K R, Das A K, Bhoraskar S V. *Scripta Mater*, 2006, 54: 1235
- [41] Kozlova A P, Sugiyama S, Kozlov A I, Asakura K, Iwasawa Y. *J Catal*, 1998, 176: 426
- [42] Mizera J, Spiridis N, Socha R, Grabowski R, Samson K, Korecki J, Grzybowska B, Gurgul J, Kepinski L, Malecka M A. *Catal Today*, 2012, 187: 20
- [43] Zhao K F, Liu X, Jin C Z, Yu F H, Rykov A, Wang J, Zhang T. *Hyperfine Interact*, 2013, 218: 1
- [44] Tripathi A K, Kamble V S, Gupta N M. *J Catal*, 1999, 187: 332
- [45] Li M J, Wu Z L, Ma Z, Schwartz V, Mullins D R, Dai S, Overbury S H. *J Catal*, 2009, 266: 98
- [46] Liu K, Wang A Q, Zhang T. *ACS Catal*, 2012, 2: 1165
- [47] Li L, Wang A Q, Qiao B T, Lin J, Huang Y Q, Wang X D, Zhang T. *J Catal*, 2013, 299: 90
- [48] Lin J, Qiao B T, Liu J Y, Huang Y Q, Wang A Q, Li L, Zhang W S, Allard L F, Wang X D, Zhang T. *Angew Chem, Int Ed*, 2012, 51: 2920
- [49] Baltrusaitis J, Jensen J H, Grassian V H. *J Phys Chem B*, 2006, 110: 12005
- [50] Smit G, Zrncevic S, Lazar K. *J Mol Catal A*, 2006, 252: 103
- [51] Daniells S T, Overweg A R, Makkee M, Moulijn J A. *J Catal*, 2005, 230: 52
- [52] Glisenti A. *J Chem Soc, Faraday Trans*, 1998, 94: 3671
- [53] Qiao B T, Wang A Q, Yang X F, Allard L F, Jiang Z, Cui Y T, Liu J Y, Li J, Zhang T. *Nat Chem*, 2011, 3: 634
- [54] Qiao B T, Wang A Q, Lin J, Li L, Su D S, Zhang T. *Appl Catal B*, 2011, 105: 103
- [55] Hattori H. *Chem Rev*, 1995, 95: 537

Au/FeO_x-羟基磷灰石催化CO氧化反应中羟基磷灰石和FeO_x的作用

赵昆峰^{a,b}, 乔波涛^a, 张彦杰^a, 王军虎^{a,*}

^a中国科学院大连化学物理研究所, 辽宁大连116023

^b中国科学院大学, 北京100049

摘要: 近期我们报道了Au/FeO_x-羟基磷灰石(HAP, Ca₁₀(PO₄)₆(OH)₂)催化剂应用于CO氧化反应的研究结果, 该催化剂不仅具有很高的低温CO氧化活性和反应稳定性, 同时也具有很好的高温抗烧结性能, 即使600 °C焙烧后依然能够维持很好的CO氧化反应活性. 为了进一步研究Au/FeO_x-HAP催化CO氧化反应中HAP和FeO_x的作用, 本文对该催化剂进行了更加深入的表征. X射线光电子能谱结果表明, HAP能与Au和FeO_x形成强相互作用, 进而在高温条件下稳定Au和FeO_x纳米粒子. 根据原位漫反射红外结果, FeO_x则主要通过改变反应路径和中间产物的方式起到促进催化剂CO氧化活性的作用. 结合透射电镜, 穆斯堡尔谱和原位漫反射红外结果可知, Au/FeO_x-HAP催化剂良好的反应稳定性源于其优异的抗碳酸盐累积能力.

关键词: 金; 氧化铁; 羟基磷灰石; 一氧化碳; 抗烧结

收稿日期: 2013-01-31. 接受日期: 2013-03-25. 出版日期: 2013-07-20.

*通讯联系人. 电话: (0411)84379159; 传真: (0411)84685940; 电子信箱: wangjh@dicp.ac.cn

基金来源: 中国科学院“百人计划”; 国家自然科学基金(11079036); 辽宁省自然科学基金(20092173).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).