Journal of Catalysis 273 (2010) 167–176

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Ultra-low-gold loading Au/CeO$_2$ catalysts for ambient temperature CO oxidation: Effect of preparation conditions on surface composition and activity

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ARTICLE INFO

Article history:
Received 1 March 2010
Revised 17 May 2010
Accepted 19 May 2010
Available online 20 June 2010

Keywords:
Au/CeO$_2$ catalyst
CO oxidation
Au^0/Au$^{\delta+}$ ratio
Water-derived species

ABSTRACT

A series of 0.06–0.09 wt% Au/CeO$_2$ catalysts for CO oxidation at ambient temperature were prepared under different preparation conditions and characterized by BET, XRD, XPS, HRTEM and FT-IR techniques. Experiment results showed that with acid material as support, the catalyst prepared by raising the pH of the acid support suspension before introduction of the HAuCl$_4$ solution exhibits the highest activity because of the higher Au^0/Au$^{\delta+}$ ratio existing on the surface. The optimum calcination temperature of the support CeO$_2$ and the drying temperature of the catalyst, which affect strongly the amount of water-derived species and the activity, were found to be 873 and 333 K, respectively. Base pretreatment for acid CeO$_2$ support leads to the decrease in Au$^{\delta+}$ and favors the preparation of an excellent catalyst with the specific rate raised from 2.92 to 10.06 mol g_{Au}^{-1} h^{-1}. Possible active center model and its formation process were proposed.

1. Introduction

Au catalyst, which had historically been considered catalytically less active than other transition metals, has attracted a tremendous interest in the last decades [1–4]; the reactivity of it depends on the gold cluster size, and extremely high gold dispersion was found to be in favor of the improvement of its catalytic activity [5]. Au/CeO$_2$ catalysts have been reported to be highly active catalysts for CO oxidation at ambient temperature, where nanoscale ceria being used as a support favors the dispersion of active contents and shows the capacity of Ce to switch between Ce^{3+} and Ce^{4+} [6–8]. However, the active centers in this system are still unclear [9–13].

Au^0/Au$^{\delta+}$ ratio is one of the important parameters on the catalyst surface composition, and the respective role of Au^0 and Au$^{\delta+}$ remains controversial for the CO oxidation reaction. Guzman et al. [14] have shown that the activity of Au supported on ceria decreases with decreasing Au$^{\delta+}$/Au^0 ratio. Venezia et al. [15] suggested the catalysts without Au^0 had the highest activity, while Chen and Goodman [10] proposed only metallic gold as active species. Han et al. [16] attributed the high catalytic activity of their catalyst to the coexistence of Au^0 and Au$^{\delta+}$. Another key parameter on the catalyst surface composition is the amount of water-derived species. The positive influence of moisture in reactant gas on the catalytic activity of gold has been reported [17–23]. Date and Haruta [24] quantitatively investigated the influence of moisture over a wide range of concentrations from 0.1 to 6000 ppm and found that the amount of moisture adsorbed on the catalyst influences the activity rather than the moisture content in the gas phase. In addition, Au/CeO$_2$ is also an efficient catalyst for WGS reaction and during the process for exploring the reactive intermediate, the dissociation of water to OH$_{ad}$ group seems to be necessary [25–28]. Therefore, the appropriate amount of water-derived species on the catalyst surface seems to be an important factor giving rise to high catalytic activity of the catalyst for ambient temperature CO oxidation.

However, surface composition could be sensitively affected by catalyst preparation conditions, and an understanding of the chemical basis for this is essential. There have been many comparative studies on the preparation of Au catalyst. In recent years, Al-Sayari et al. [29] compared Au/ZnO and Au/Fe$_2$O$_3$ catalysts prepared by two coprecipitation methods and demonstrated that the catalyst performance is highly dependent on pH and aging time. Moreau et al. [30] have made an in-depth study of the critical effect of the pH during the deposition–precipitation preparation (hereinafter denoted as DP). Of the numerous variations in the seemingly simple catalyst preparation procedure, little attention had been given to the function of residual acid materials on CeO$_2$ produced during the calcination process of Ce(NO$_3$)$_3$·6H$_2$O at different temperatures. Different manners applying to control the pH during

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doi:10.1016/j.jcat.2010.05.008

the deposition–precipitation process have been described in the literatures [31–34]. The varieties of the preparation conditions make the comparison of gold supported from each other often problematic and sometimes impossible. The effect of the calcination of the catalysts is another issue to be concerned and yet controversial, as some consider it to be necessary [35–37]; while others regard it as detrimental [38].

Furthermore, as most reported gold catalysts contain more than 1 wt% gold, the high price of gold and low availability limits their application. In the present work, a series of Au/CeO_2 catalysts with gold contents varying from 0.06 to 0.09 wt% were prepared and characterized by BET, XRD, HRTEM, XPS and FT-IR techniques. The influences of preparation conditions on the surface composition and the activity of Au/CeO_2 catalysts were particularly addressed, including the calcination temperature of CeO_2 support, the way to control the pH value and the drying temperature of the catalyst without calcination step. Based on the investigation results, possible active center model and its formation process were proposed.

2. Experimental

2.1. Catalyst preparation

CeO_2 was prepared by direct thermal decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ at different temperatures under atmosphere. Theoretically calculating 0.1 wt% Au/CeO_2 catalysts were prepared by following four DP methods, but the actual Au content was determined via inductively coupled plasma atom emission spectroscopy (ICP-AES).

2.1.1. Preparation method A

An appropriate amount of $HAuCl_4$ aqueous solution with given concentration was mixed with desired amount of CeO_2 under stirring to produce a suspension, which was then heated to 343 K; the pH value of the suspension was progressively raised by drop-wise addition of NaOH (0.1 M) to 9; after 60 min of agitation, the resulted suspension was cooled and filtered; the solid obtained was washed thoroughly with distilled water and then dried at 333 K for 16 h to produce catalyst A.

2.1.2. Preparation method B

Appropriate quantity of CeO_2 support was suspended in de-ionized water to produce a suspension. The temperatures and the pH values of both the suspension and $HAuCl_4$ aqueous solution were separately raised to 343 K and 9 by the addition of NaOH, respectively, then mixed them together and reacted for 60 min, followed by cooling and filtering. Finally, the catalyst B was obtained by drying the solid at 333 K for 16 h.

2.1.3. Preparation method C

Under stirring, NaOH solution was added by drop-wise to the suspension of CeO_2 at room temperature until the pH value of the suspension reached 9; then the base suspension of CeO_2 thus prepared was heated to 343 K, followed by introducing a solution of $HAuCl_4$ into the base suspension of CeO_2, the pH of which was decreased partially by NaOH reversely addition, the pH value of the reaction system was kept at 9 throughout the preparation. After reacting for 60 min, the mixing suspension was cooled and filtered; the solid obtained was washed thoroughly with distilled water and then dried at 333 K for 16 h to produce catalyst C.

2.1.4. Preparation method D

The preparation process of catalyst D followed the preparation method C, but the pH of $HAuCl_4$ was raised to 9 first, and then desired amount of CeO_2 was added to $HAuCl_4$ solution.

2.2. Catalyst characterization

The specific surface area (S_{BET}), pore volume (V_{pore}) and pore diameter (D_{pore}) of the samples were determined by means of BET method on a Quantachrome Autosorb-1 instrument at 77 K with N_2 as adsorbent.

Powder X-ray diffraction (XRD) spectra were measured on a Panalytical X'Pert PRO X-ray diffractometer using Cu Kα1 radiation. The XRD patterns were referenced to the powder diffraction files (ICDD-FDP data base) for identification.

The HRTEM images of the samples were obtained using a Phillips Analytical FEI Tecnai 30 electron microscope operating at 300 kV. The samples were ground to fine powder, which was then mixed with acetone to make a suspension. A drop of the suspension was placed on a lacey carbon nickel grid, subsequently dried at room temperature for measurement.

XPS characterization was performed on a PHI-Quantum 2000 spectrometer. Samples in powder form were pressed into a wafer for analysis. The adventitious carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energy (Bes).

The FT-IR spectra of the samples were measured by the KBr pellet method on a Nicolet Nexus FT-IR spectrophotometer in the wavenumber range 4000–500 cm^{-1}.

2.3. Catalytic activity measurement

The activity test of the catalyst was carried out in a quartz tubular fixed-bed reactor with 0.2 g of the catalyst per pass under the reaction conditions of atmosphere pressure, 298 K and GHSV = 18,000 h^{-1}; the composition of the reactant includes 1% CO, 1% O_2 and 98% N_2. The products were analyzed by on-line gas chromatograph equipped with a carbon molecular sieve (1 m × 3 mm) and a 5A molecular sieve (2 m × 3 mm) columns in parallel connected to a thermal conductivity detector.

3. Results and discussion

3.1. The acid–base property of the support

During the preparation process of the Au/CeO_2 catalyst with the support calcined at 673, 873 and 1073 K, it was found that the addition of CeO_2 always led to a decrease in the pH at different extents, and the dosages of NaOH used to maintain a constant pH value of the reaction system were different. In order to measure the acid–base property of the above three supports, the following experiments were designed: 1 g of the support CeO_2-673 was suspended in 20 ml de-ionized water under vigorous stirring at 343 K for 2 h, and the pH value of the suspension was measured by pH Meter, and so did the supports CeO_2-873 and CeO_2-1073. The results show that the pH values of the supports CeO_2-673, CeO_2-873 and CeO_2-1073 were 3.1, 4.6 and 6.2, respectively, which imply that lower calcination temperature such as 673 K will increase the amount of acid species as residual on the CeO_2 support, resulting in smaller pH value during the catalyst preparation process. On the other hand, high calcination temperature made $Ce(NO_3)_3 \cdot 6H_2O$ decomposing nearly completely and small amount of acid species left on CeO_2-1073.

3.2. Catalyst characterization

Comparing with other catalysts, the Au/CeO_2-673 sample prepared by method A has prominent gold deposition efficiency (Table 1). In method A, before the addition of NaOH, the interaction of $HAuCl_4$ and CeO_2 had conducted during the process of raising the suspension temperature from 298 to 343 K, so CeO_2 calcined at

Table 1
Physiochemical properties (determined by ICP, XRD and BET) and activities of the samples.

Sample	Au content (wt%)	d_{CeO_2} (nm)	S_{BET} (m^2/g)	D_{pore} (nm)	V_{pore} (cm^3/g)	Specific rate (mol g_{Au}^{-1} h^{-1})
CeO_2-673	–	–	86	7.3	0.17	–
CeO_2-873	–	–	66	7.2	0.14	–
CeO_2-1073	–	–	6	10.7	0.02	–
Au/CeO_2-673[a]	0.09	9.2	–	–	–	2.92
Au/CeO_2-873[a]	0.06	11.6	–	–	–	8.47
Au/CeO_2-1073[a]	0.06	55.1	–	–	–	3.76
Au/CeO_2-673[b]	0.07	9.2	–	–	–	6.31
Au/CeO_2-673[c]	0.07	9.2	–	–	–	6.20
Au/CeO_2-673[d]	0.08	9.2	–	–	–	3.45
Au/CeO_2-673-base pretreatment[a]	0.06	9.2	–	–	–	10.06

[a] Catalyst prepared by method A.
[b] Catalyst prepared by method B.
[c] Catalyst prepared by method C.
[d] Catalyst prepared by method D.

low temperature supplied a strong acid surrounding (pH = 3.1) and much of the $HAuCl_4$ compound had already deposited under this lower pH condition. Moreau et al. [30] had reported the same situation on Au/TiO_2 catalyst and explained that under higher pH condition surface will be negatively charged, resulting in an electrostatic repulsion of gold-containing anions, this probably accounts for the fall in the gold content; while at lower pH, the gold content is high owing to the attraction between the gold-containing anions and the positively charged surface.

Fig. 1 shows the XRD patterns of CeO_2 support and ultra-low-gold loading Au/CeO_2 catalysts prepared by method A with the supports calcined at different temperatures. From Fig. 1, no diffraction peaks corresponding to metallic gold ($2\theta = 38.2°$, 44.4° and 64.5°) or gold oxides ($2\theta = 25.5°$, 30.2° and 32.5°) can be detected, suggesting that the gold particles are highly dispersed on the surface of CeO_2 support, or the amount of gold species is too small to be detected by XRD technique. The XRD pattern of the catalyst with the support calcined at 673 K exhibits broad and diffuses peaks, which indicates small crystallites and very disordered structure existing. With increasing the calcination temperatures of the supports, the peak intensity gradually increases, and the corresponding half-widths of the peaks become narrow, suggesting that CeO_2 particle sintering, ordering of structure, crystallite growth all increase. This appears to be the pattern of CeO_2 support as a function of calcination temperature in the presence of the active content Au. According to Debye–Scherrer equation, particle sizes of CeO_2 after calcinations have been measured and listed in Table 1.

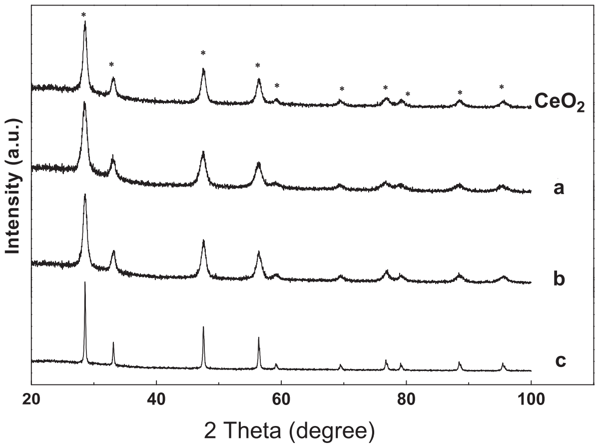

Fig. 1. XRD patterns of CeO_2 support and the catalysts Au/CeO_2 with the CeO_2 support calcined at different temperatures: (a) Au/CeO_2-673, (b) Au/CeO_2-873, (c) Au/CeO_2-1073.

BET measurement results (Table 1) show that specific surface area dropped significantly with increasing the support calcination temperature, which is consistent with the rapid growth of CeO_2 crystallite specified by XRD diffractograms.

HRTEM measurements were performed on ultra-low-gold loading catalysts Au/CeO_2-673, Au/CeO_2-873 and Au/CeO_2-1073, but no reflection related to gold size was detected from these catalysts although the presence of Au in this sample has been confirmed by the following XPS characterization results. In order to examine the size of Au particles, the same method was used to prepare the above three catalysts but the gold content was also increased to 1 wt%, and the HRTEM images are shown in Fig. 2. It was found that their respective gold particle average diameter measured with 200 particles is close to each other, suggesting the differences in Au nano-particle sizes with the support calcining are not great, since the catalysts were prepared by depositing gold on an already preformed ceria support and just dried at 333 K without any further pretreatment, such as calcined at higher temperature, so the effect of this particle size on the catalytic activity is negligible. This result agrees well with previous data, which showed the gold particle size is independent of the support surface area [25]. Moreover, for the ultra-low-gold loading catalysts, the lower surface density of gold on the support probably limits the growth of gold, hence combined with the XRD results, these observations indicate that, neither aggregation nor sintering of the gold particles occurs during the ultra-low-gold loading catalyst preparation process, and the amount of gold species is smaller than that detectable by HRTEM technique. Menegazzo et al. have used the quantitative low temperature CO chemisorption data and the FT-IR analysis to determine the concentration of gold sites able to chemisorb CO on 0.47 wt% Au/ZrO_2 catalyst (DP), which also has not shown any gold particles on its HRTEM spectra, and the results suggest a high metal dispersion existed on such a low-gold loading catalyst and almost all the atoms are exposed on the surface [39].

Au 4f, Ce 3d and O 1s XPS spectra of the ultra-low-gold loading catalysts Au/CeO_2-673, Au/CeO_2-873 and Au/CeO_2-1073 prepared by method A are presented in Fig. 3a–c, respectively, and the contents of $Au^{\delta+}$ (Au^+ or/and Au^{3+}), Ce^{3+} and ($OH + H_2O$) in the catalysts as a function of calcination temperatures of the supports are summarized in Table 2. The first doublet at 84.0 and 87.7 eV is the characteristic of Au^0, and the peaks at 84.6, 86.3, 88.6 and 89.9 eV are attributed to $Au^{\delta+}$. The amount of positively charged gold species in the three samples decreased in the following order: Au/CeO_2-673 > Au/CeO_2-873 > Au/CeO_2-1073, especially, metallic gold is the only gold species observed from the Au/CeO_2-1073 catalyst. The catalyst with the support calcined at low temperature has more $Au^{\delta+}$ species compared to that with the support calcined at high temperature when they were all prepared by method A,

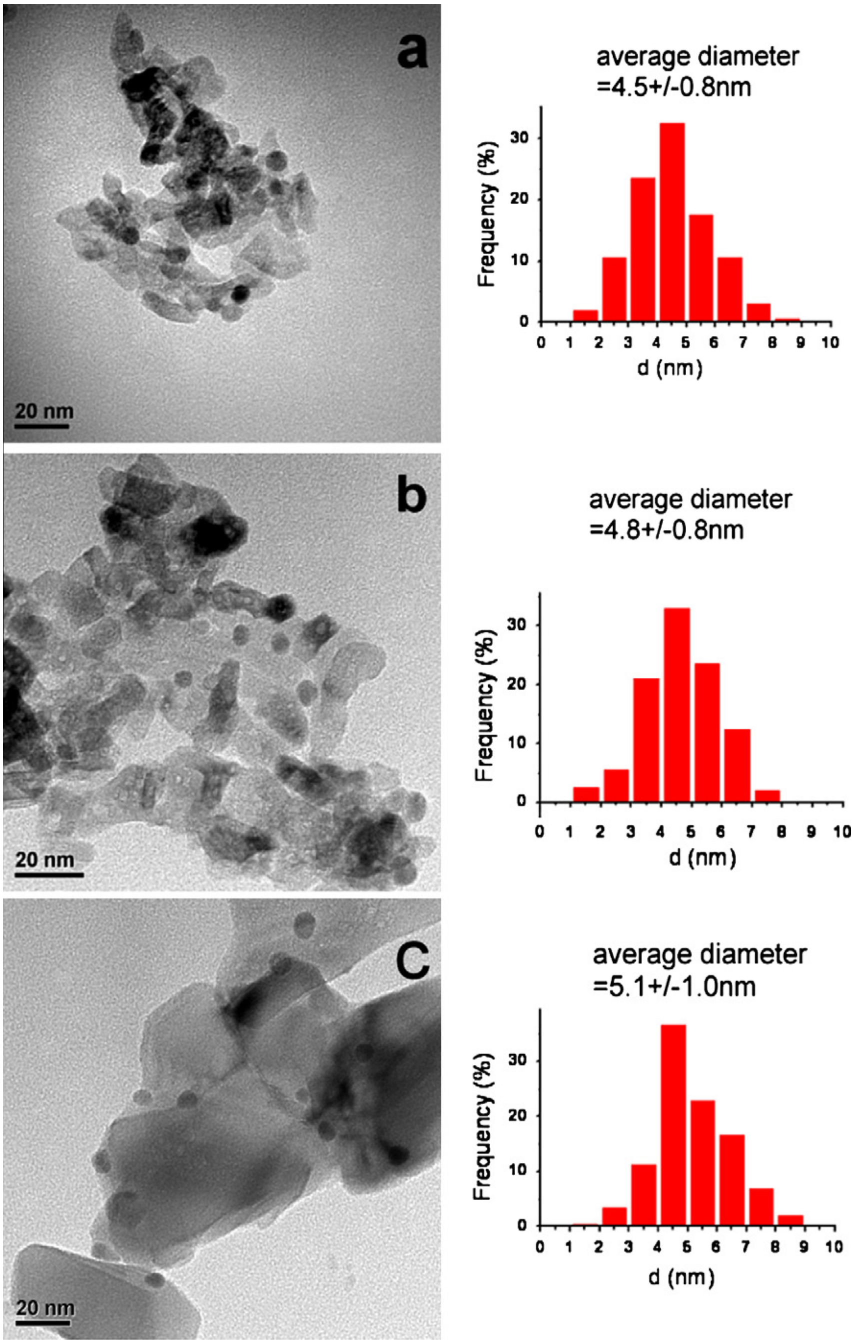

Fig. 2. High-resolution transmission electron microscopic images of the catalysts with 1 wt% gold content: (a) Au/CeO_2-673, (b) Au/CeO_2-873, (c) Au/CeO_2-1073.

this could be explained by that the residual acid species produced during the support calcination process and small ceria particle size favor the formation of $Au^{\delta+}$, which will be further discussed in 3.8. Elegant leaching experiment was applied to analyze the role of Au^0 and $Au^{\delta+}$ in the WGS reaction [40,41], in which Au nano-particles were removed from the catalyst by cyanide leaching, and the activities before and after leaching were compared. Changing the calcination temperature of the support during the preparation of the catalysts with various $Au^0/Au^{\delta+}$ ratios seems to be another simple way to probe the effects of Au^0 and $Au^{\delta+}$.

Fig. 3b shows the XPS spectra in the Ce 3d region. *V* and *U* correspond to $3d_{5/2}$ and $3d_{3/2}$ spin-orbital components, and the signals V', U' are characteristics of Ce^{3+}. The amount of Ce^{3+} decreases with the increase in the calcination temperature of the support, which may deduce that the calcination at high temperature under atmosphere annihilates the surface oxygen vacancies on CeO_2. The O 1s spectra shown in Fig. 3c indicate the presence of two different oxygen species, the peak at ca. 529 eV is attributed to lattice oxygen, and a distinct shoulder at ca. 531 eV corresponds to a mixture of hydroxyl groups and adsorbed water on the surface of the catalyst. It is worthwhile noting that a higher fraction of surface hydroxyl groups and adsorbed water on the sample with the support calcined at lower temperature can be retained in comparison with that calcined at higher temperature. Since the catalysts were dried at 333 K, a relative low temperature, Au/CeO_2-673 and Au/CeO_2-873 have higher surface area and smaller pore size, which made the evaporation of the water from the small pore structure of CeO_2 more difficult, thus the number of water-derived species in-

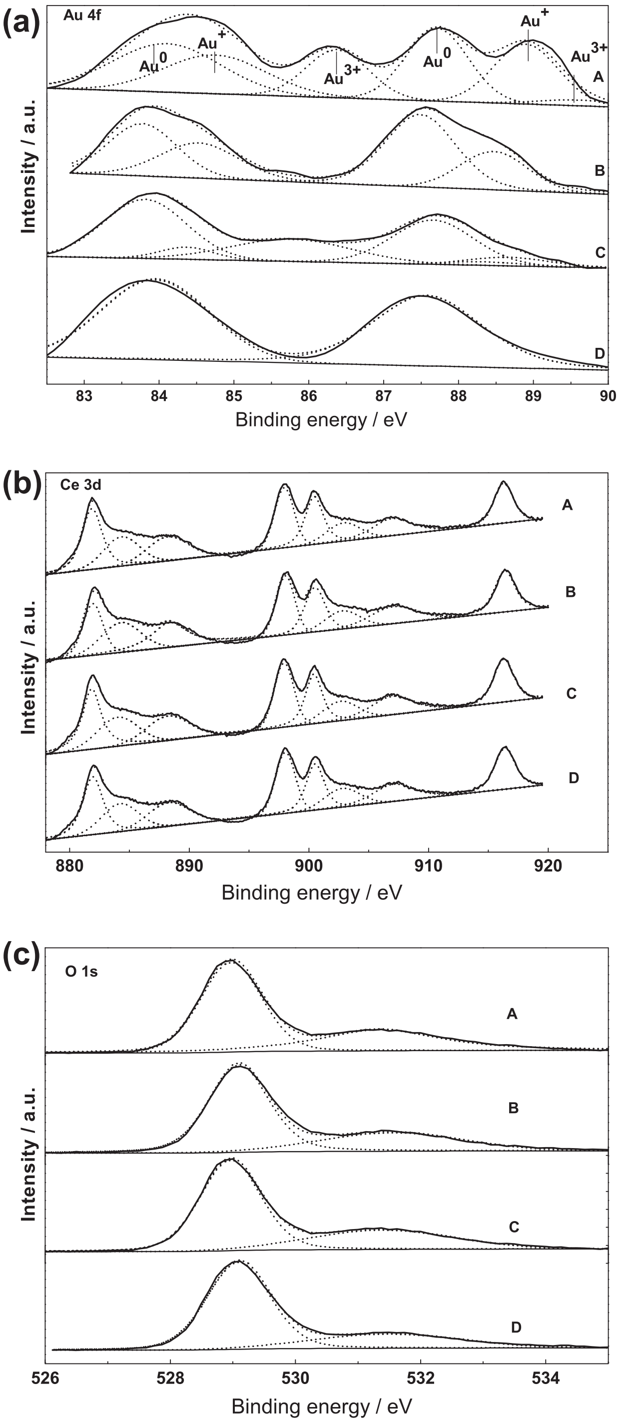

Fig. 3. XPS spectra of the Au(4f), Ce(3d) and O(1s) regions recorded on (A) Au/CeO_2-673, (B) Au/CeO_2-673 after CO oxidation at ambient temperature, (C) Au/CeO_2-873, (D) Au/CeO_2-1073.

Table 2
Relation of species distribution on the surface of the catalysts with calcination temperatures of the supports.

Catalyst	$Au^{\delta+}$ (%)	OH + H_2O (%)	Ce^{3+} (%)
0.09 wt% Au/CeO_2-673	52	38	23
0.09 wt% Au/CeO_2-673[a]	39	31	25
0.06 wt% Au/CeO_2-873	13	32	22
0.06 wt% Au/CeO_2-1073	0	26	21

[a] Catalyst after CO oxidation reaction at ambient temperature.

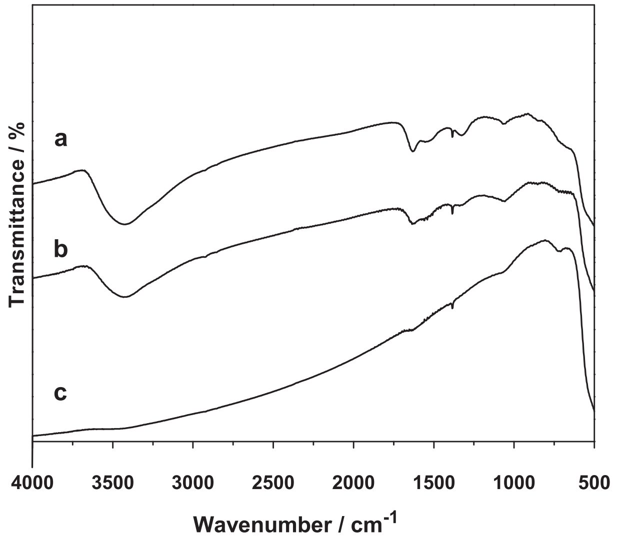

Fig. 4. FT-IR spectra of the catalyst: (a) Au/CeO_2-673, (b) Au/CeO_2-873, (c) Au/CeO_2-1073.

creases with higher surface area. In addition, FT-IR spectra of the three catalysts are shown in Fig. 4. A broad peak around 3420 cm^{-1} is assigned to the adsorbed water or hydrogen-bonded OH groups on ceria [25], and a relatively sharp band at 1637 cm^{-1} corresponds to the O–H bending mode [42]. The FT-IR measurement result shows that there are a large amount water-derived species on the surface of Au/CeO_2-673 and Au/CeO_2-873 and a significant reduction in the absorbance of them for Au/CeO_2-1073.

Au^{3+} is known to be readily reduced (forming Au^+ and subsequently Au^0). After reaction, the amount of Au^{3+} on the Au/CeO_2-673 catalyst decreased significantly and was followed by a large increase in Au^0 content, but Au^+ still kept at a relatively high level. The disappearance of Au^{3+} may indicate that the interaction between gold and support was weakened. On the other hand, the reaction induced the increase in Ce^{3+}, suggesting that the lattice oxygen participated in CO oxidation reaction; meanwhile, the oxygen vacancy formed.

3.3. Effect of support calcination temperature on catalyst activity

A series of ultra-low-gold loading Au/CeO_2 catalysts with the support calcined at 673, 873 and 1073 K were prepared by method A, and their activity profiles for CO oxidation as a function of time on stream at ambient temperature are shown in Fig. 5. The conversion of CO over the Au/CeO_2-1073 catalyst was found to be 35%, which was measured after 5 min on stream and sustained for 1 h. The catalysts Au/CeO_2-673 and Au/CeO_2-873 showed poor activities in the first 5 min, but their CO conversion increased with the time passing, especially over the catalyst Au/CeO_2-873, the conversion of CO increased drastically and achieved 70% after 1-h reaction, which is higher than that by 35% over the catalyst Au/CeO_2-1073.

On the basis of the earlier experimental results and XPS data, we can infer that Au^0 species make great contribution to the catalytic activity and too much $Au^{\delta+}$ species result in the lower initial activity. Hao et al. [43] reported a similar result that the Au/MgO catalyst prepared by adsorption of $Au(CH_3)_2(acac)$ (acac is acetylacetonate) on partially dehydroxylated MgO was not active initially for CO oxidation at room temperature, but the sample was activated by treatment in flowing Helium at 473 K, during which the original mononuclear Au(III) species decomposed and the gold was reduced to zerovalent. In addition, although the XPS data have

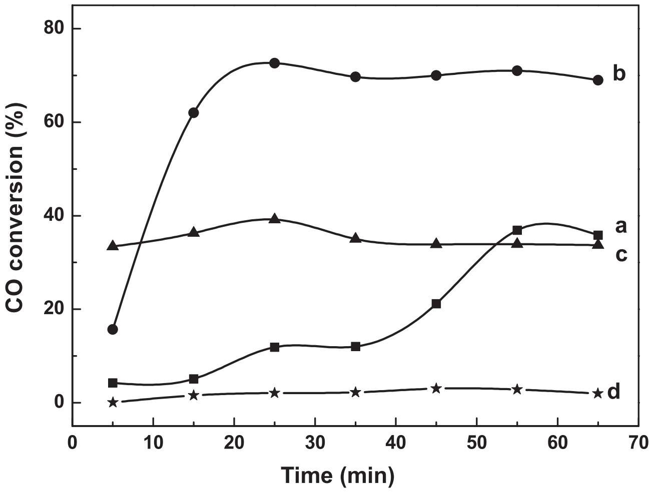

Fig. 5. Activity profiles of dried catalysts prepared by method A for CO oxidation at ambient temperature: (a) Au/CeO_2-673, (b) Au/CeO_2-873, (c) Au/CeO_2-1073, (d) Au/CeO_2-1073 after H_2 reduction.

showed that the catalyst Au/CeO_2-1073 contained only zerovalent gold, the participation of cationic gold in the catalyst cannot be excluded because this catalyst did not show any activity at room temperature after reduction in pure H_2 at 333 K for 3 h (Fig. 5d). We speculate that the cationic gold may present at the interface between Au and support, and the amount of them is too small to be detected by XPS, but they could act as dopants to activate the oxygen on the surface. Shapovalov and Metiu [44] have used density functional theory calculation to show that doped oxides required small amount of expensive metals to weaken the bond between the surface oxygen atoms and the oxide, facilitating CO oxidation. Even though the catalyst Au/CeO_2-1073 has higher initial activity, its final activity is lower than the catalyst Au/CeO_2-873, which may be explained by the smallest surface area (6 m^2/g) of it. Many experimental papers have emphasized that the activity of the gold-supported catalyst seems to be enhanced when the support has a higher surface area [16,45,46]. Date and Haruta [24] had proposed that the support should have such surface area as large as possible, at least more than 50 m^2/g.

The origin of the low reactivity of the dried Au/CeO_2-673 and Au/CeO_2-873 catalysts at low temperature may be due to another factor that non-optimal level of water-derived species retained on the catalysts. For the non-calcined catalysts in many cases, the catalytic performance was observed to increase with time on stream, and the calcined catalysts did not show this effect, and they always give very high activities at the beginning of the experiment. However, the catalyst Au/CeO_2-1073 prepared under the same conditions as those preparing the other two catalysts had the highest initial reactivity. The comparison of the XPS data and the FT-IR spectra of the three catalysts show that the amount of hydroxyl groups and adsorbed water increased in the following order: Au/CeO_2-1073 < Au/CeO_2-873 < Au/CeO_2-673. In addition, the water-derived species are not only attributed to those adsorbed on the support (Ce-H_2O and/or Ce-OH) but also adsorbed on the gold species ($Au^{\delta+}$-OH), so excess water-derived species may block the active sites or competitively adsorb with CO and O_2 on the same site at the beginning of the CO oxidation reaction. In contrast, the optimal amount of water-derived species on the surface may be established for the catalyst Au/CeO_2-1073. Another supporting evidence is that there was a H_2O peak detected by gas chromatography, which appeared only after the dose sampling in the first 5 min of the reaction process and disappeared in the following time for both Au/CeO_2-673 and Au/CeO_2-873, but this situation did not occur in the whole reaction process for Au/CeO_2-1073.

Calcined catalysts exhibit very high initial activities, indicating their activation time is very short. Widman et al. [47] have studied the initial catalytic behavior by applying quantitative temporal analysis of products (TAP) techniques, the results shown that the activity of the calcined catalyst increased with time during the first 30 pulses activation process (the pulse width was around 3 s). They also demonstrated that the formation of an oxygen vacancy caused by the reaction of CO with surface oxygen atom (most favorably adjacent to $Au^{\delta+}$) is the key point during the activation period; meanwhile removing surface oxygen atom located near the dopant makes $Au^{\delta+}$ turn into Au^0. Differently, there are many adsorbed water and hydroxyl groups covering on the surface of dried catalysts, so the reactant gas may need to carry away some water-derived species (detected by gas chromatography), and then CO reacts with the surface oxygen atoms to form the necessary oxygen vacancies and reduce $Au^{\delta+}$ to Au^0; therefore, the initial activity increased with increasing Au^0/$Au^{\delta+}$ ratio, and the excess water-derived species prolong the activation process. However, Guzman et al. [14] have shown that the activity of Au supported on ceria decreased with increasing the Au^0/$Au^{\delta+}$ ratio, this contrary situation was detected by IR spectroscopy characterizing CO adsorption at room temperature first and then introducing O_2 to start reaction, because the activation process of the catalyst without much more water-derived species on the surface could be finished by the pretreatment with CO, the contrary situation may present the deactivation behavior rather than activation. For the water gas shift reaction, water was introduced together with the reactant gas and then dissociate to hydroxyl groups on the calcined catalyst [25], which is different from that the hydroxyl groups have existed on the surface before the introduction of reactant gas for dried catalysts in this work, therefore, the activation time could not be prolonged. After an instantaneous activation process, which is difficult to be observed for calcined catalysts, the activity gradually decreased with time on stream during the deactivation process.

$Au^{\delta+}$ could increase the surface oxygen atom mobility, but if it gives oxygen too easily it will not be effective in taking oxygen from the gas phase [44]. Compared with Au/CeO_2-873, too much $Au^{\delta+}$ (52%) also inhibited the final catalytic activity of the catalyst Au/CeO_2-673. When CO was adsorbed on $Au^{\delta+}$; meanwhile, several kinds of carbonates species could be formed, some of them easily decompose to CO_2, but other carbonates are fairly stable and will be present on the surface during the catalytic reaction [44]. Even though Au^+-OH helps the stable carbonate species to decompose [48,49] (CO inserts into Au^+-OH to form Au-hydroxycarbonyl, which is oxidized to a bicarbonate by an active oxygen; the decomposition of bicarbonate would produce CO_2 and Au^+-OH, completing a reaction cycle), it is worth noting that an active oxygen is very necessary during oxidation process, otherwise, carbonate could accumulate on the active sites. Too much $Au^{\delta+}$ species could suppress the durative supplement of the active oxygen, so stable carbonate species accumulating on the active sites of Au/CeO_2-673 led to the poor final activity. From the earlier XPS data, it was found that most Au^+ species were still detected after reaction, suggesting that they could not be reduced completely by CO because of the stable carbonate.

3.4. Effect of drying temperature of the catalysts on the activity

The presence of water was known to be crucial for the reaction of CO oxidation over supported gold catalyst. Date and Haruta have quantitatively investigated the effects of moisture in the reactant gas for CO oxidation over the catalyst Au/TiO_2, and found that the optimum concentration of moisture for the reaction is ~200 ppm [24]. Tabakova et al. have found that the presence of moisture is crucial for the reaction over the catalyst Au/TiO_2 at 90 K [28]. Bond and Thompson have reported that the reaction mechanism for CO oxidation involves hydroxyl species [50]. However, many studies focused on the water coming from the reactant gas rather than the catalysts themselves possessing; therefore, most of reported catalysts were often calcined or non-calcined but dried at above 373 K. Just as that said by Date and Haruta [24], the amount of moisture adsorbed on the catalyst influences the activity rather than the moisture content in the gas phase, we expect to improve the catalyst activity by obtaining an optimum amount of water-derived species on the surface, which could replicate the effect of the water coming from the reactant gas, thus the activities of the Au/CeO_2-1073 catalysts dried at 313, 333 and 373 K were compared. Based on the XPS result, it can be inferred that a large amount of $Au^{\delta+}$-OH still remained on the surface of Au/CeO_2-673 and Au/CeO_2-873, and drying these catalysts at 373 K may result in the thermal decomposition of $Au^{\delta+}$-OH species or the recombination of –OH groups, in such a way that $Au^{\delta+}$ species transformed to Au^0, thus the changes of the activity could not only be attributed to the effect of water-derived species or the Au^0/$Au^{\delta+}$ ratio. On the contrary, Au^0 was the main gold species on the surface of Au/CeO_2-1073 rather than $Au^{\delta+}$-OH, and the sintering of Au particles does not occur at so low temperatures; therefore, the change of the activity can be chiefly attributed to the amount of water-derived species adsorbed on the support (Ce-H_2O and/or Ce-OH). Fig. 6 shows the effect of water-derived species on the activities of the catalysts Au/CeO_2-1073 dried at 313, 333 and 373 K. The activities of the catalysts were found to be particularly sensitive to drying temperature, and the catalyst with poor activity was just dried at 373 K. Drying at moderate temperature, 333 K, tends to give a catalyst with higher activity. From the earlier results, an inference can be drown that the low temperature oxidation of CO over gold catalyst involves water-derived species on the surface, and the optimal amount of it could be attained by drying the catalyst at 333 K. Recently, Goodman and coworkers [51] have reported that the water-derived species caused two effects: (1) the decrease in CO coverage; and (2) the appearance of stable carbonate species, since both effects inhibit CO oxidation, the promotional effects of water-derived species can be rationalized by its effects on molecular oxygen adsorption and activation; even though the specific activation mechanism has not been drawn, previous experimental [18] and theoretical studies [52] have also shown that the addition of water does promote O_2 adsorption and activation. Dried at 313 K, large amount of water-derived species effectively blocks the adsorption sites for CO and O_2, despite the potential ability of Au^+-OH species, which help the stable carbonate species to decompose, the coverage of O_2 adsorption sites checks the possibility to supply active oxygen atoms, giving rise to retarding the further oxidation reaction, so the two inhibiting effects are dominant; however, dried at 373 K, just as the calcined catalysts, the lack of the water-derived species make it impossible to exhibit the promotional effects on molecular oxygen adsorption and activation.

3.5. Effect of the methods for controlling the pH on the catalyst activity

During the deposition–precipitation process, someone raised the pH of $HAuCl_4$ solution before introduction of the support [31] or raised the pH of the support suspension before introduction of $HAuCl_4$ solution [32], the other added base solution to a mixed solution of $HAuCl_4$ and support [33] or added base solution to $HAuCl_4$ solution and a support suspension respectively before mixing them [34]. Fig. 7 shows the dependence of CO conversion on the methods for controlling the pH value during the preparation of the catalysts. The catalyst Au/CeO_2-673 made by method A exhibits the lowest catalytic activity. Based on the equilibrium constants reported by Nechayev and Nikolenko [53], at pH 6–8, the form of material $AuCl_3{\cdot}H_2O$ existing at pH 3–4 transforms mainly into the form of $AuCl(OH)_3^-$. In method A, before the addition of NaOH, the interaction of $HAuCl_4$ and CeO_2 had conducted during the process of raising the suspension temperature from 298 to 343 K, so CeO_2 calcined at low temperature supplied strong acid surroundings (pH = 3.1) for $HAuCl_4$ to form $AuCl_3{\cdot}H_2O$, which would be adsorbed on the surface of CeO_2 and possibly reacted with CeO_2 on the surface as Fig. 8 [30]. Electrostatic attraction effect mentioned in Section 3.1 caused the high gold uptake. Even through the subsequent NaOH addition and washing process may eliminate some chlorine, the difficult dissociation of Au-Cl still made some $Au^{\delta+}$ species presenting on the surface of the resulting catalyst as the form of $Au^{\delta+}$-Cl, which is another reason for attributing the lowest final activity to incompletely reduce $Au^{\delta+}$ species. The detrimental effect of chlorine has been reported [30], perhaps assisting the growth of gold particle and affecting the particle morphology during calcinations. In this work, the detrimental effect was not detected by HRTEM since the catalyst was just dried at 333 K without calcinations, but $Au^{\delta+}$-Cl increase the amount of $Au^{\delta+}$ species on the surface.

Higher activities were obtained for the catalysts prepared by method B and C, where the pH of the CeO_2 suspension was raised first to neutralize some residual acid material before introducing

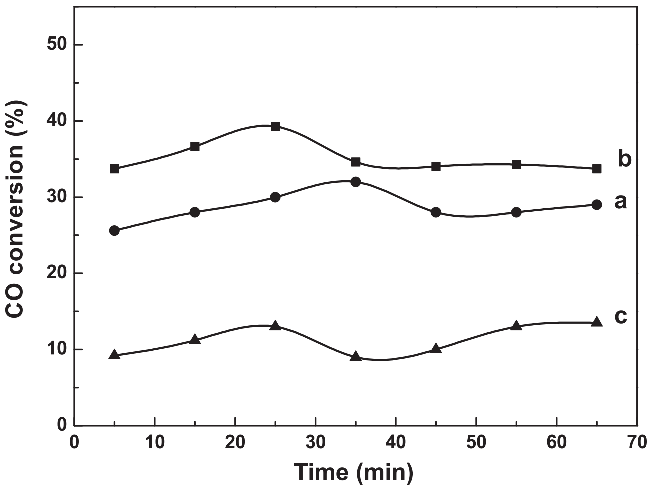

Fig. 6. Activities of Au/CeO_2-1073 catalysts prepared by method A: (a) dried at 313 K, (b) dried at 333 K, (c) dried at 373 K.

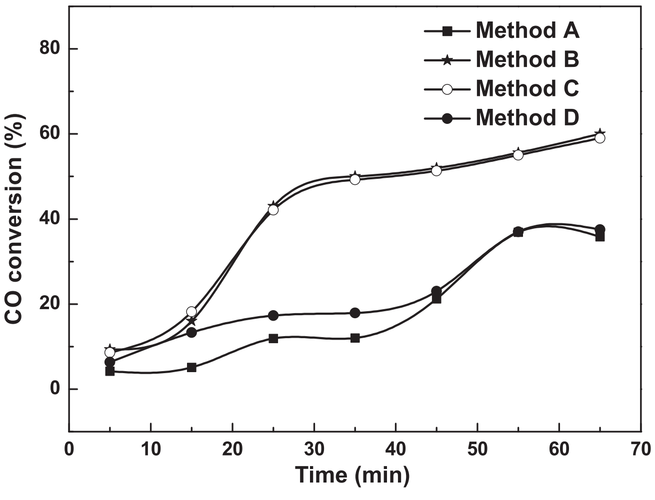

Fig. 7. Activities of the dried Au/CeO_2-673 catalysts prepared by methods A, B, C and D.

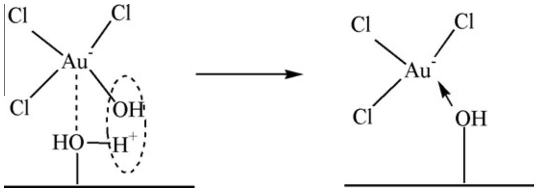

Fig. 8. Adsorption of gold anions at positively charged surface.

$HAuCl_4$ solution. In method D, the pH of gold solution was raised to 9 first, in which $Au(OH)_4^-$ is dominant species, but the pH of the solution was slightly affected by CeO_2 addition. On the earlier results, it seems that the effect of the methods for controlling the pH value on the activity can be mainly attributed to the environment of $HAuCl_4$ supplied by CeO_2 or base solution; therefore, a further experiment was made, in which theoretically calculating 0.1 wt% Au was loaded on CeO_2-1073 K by using methods A–D (Fig. 9). As seen from Fig. 9, the effect of the method for controlling the pH value on the conversion of CO over the catalysts Au/CeO_2-1073 was not as significant as that over the Au/CeO_2-673 catalysts. Because $Ce(NO_3)_3{\cdot}6H_2O$ could decompose relatively completely at 1073 K, little acid material was left over the CeO_2. As for CeO_2-1073, no matter how to control the pH value, $AuCl(OH)_3^-$ or $Au(OH)_4^-$ was the major species during the preparation process, and no acid environment was supplied by residual acid material; therefore, the catalysts prepared by the four different methods have the similar activities.

In summary, for the catalysts with acid material as support, the activities highly depend on the methods for controlling the pH value, and the best catalyst was prepared by raising the pH of the acid support suspension before introduction of the $HAuCl_4$ solution. However, for the catalysts with neutral support, the effect of the methods for controlling the pH value on the catalyst activity is slight. Consequently, for the preparation of a high efficient catalyst with acid material as support, methods B and C are more recommendable.

3.6. New method to improve the catalyst activity

From preliminary results, it can be found that the neutral support CeO_2-1073 could promote the initial activity of gold catalyst because of the large amount of Au^0 formed on the surface, but low surface area of the support led to the decrease in the activity. In contrast, the catalyst 0.09 wt% Au/CeO_2-673 with the highest surface area and gold deposition efficiency showed a poor activity since the residual acid material reacted with $HAuCl_4$ to form the species of $AuCl_3{\cdot}H_2O$ and the excess $Au^{\delta+}$ species adsorbed on the CeO_2-673 surface. In order to produce a special CeO_2 support with both high surface area and little residual acid material, NaOH was used to neutralize acid material on the support CeO_2-673 with the highest surface area before depositing gold on the support. The base pretreatment of acid support was done as follows: the pH of the CeO_2-673 suspension was raised to 9 by adding NaOH; after stirring at 343 K for 4 h, the support was cooled, filtered, washed with distilled water and finally dried at 373 K for 12 h. In order to compare the catalyst activity with that of the preliminary catalyst 0.09 wt% Au/CeO_2-673 without treating the support by base solution in advance, theoretically calculating 0.1 wt% gold was deposited on this special support by means of the same preparation method A. Meanwhile, the activity of the Au/CeO_2-673 catalyst prepared by method B was another comparative object, and the results are shown in Fig. 10. As expecting, the specific rate in the presence of the catalyst with the support being subjected to base pretreatment was found to be promoted obviously from 2.92 to 10.06 mol g_{Au}^{-1} h^{-1}, which can be attributed to the decrease in the $Au^{\delta+}$ quantity by consumption of the residual acid material, but the conversion of CO over the catalyst prepared by method B was found to be only 59%, suggesting that the base pretreatment efficiency for neutralizing residual acid material of the support is better than that by method B. In addition, even though the base pretreatment could decrease the $Au^{\delta+}/Au^0$ ratio and shorten the activation time, the excess water-derived species resulting by the high surface area and small pore size of CeO_2-673 still inhibit its initial activity. The above deductions could be further confirmed by XPS data (summarized in Table 3). After the base pretreatment for the support, the amount of $Au^{\delta+}$ on the catalyst decreased drastically from 52% to 20%, and the amount of water-derived species just decreased slightly from 38% to 34%.

3.7. Effect of $Au^{\delta+}$, Au^0 and water-derived species on the catalyst activity

In this work, the experimental data and catalysts characterization show that the excellent activity of ultra-low-gold loading cat-

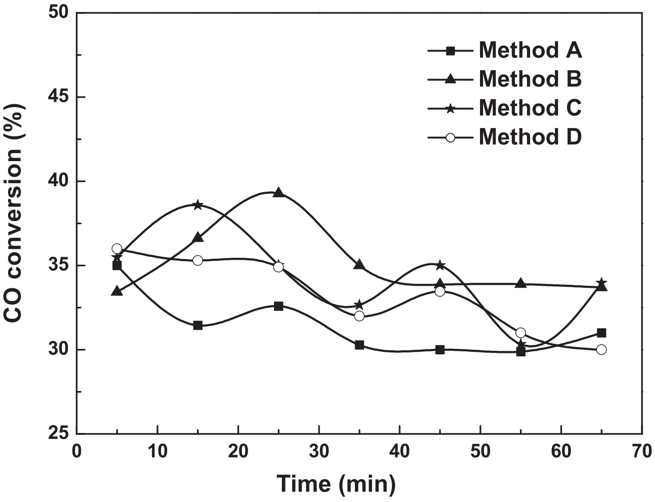

Fig. 9. Activities of the dried Au/(CeO_2-1073 catalysts prepared by methods A, B, C and D.

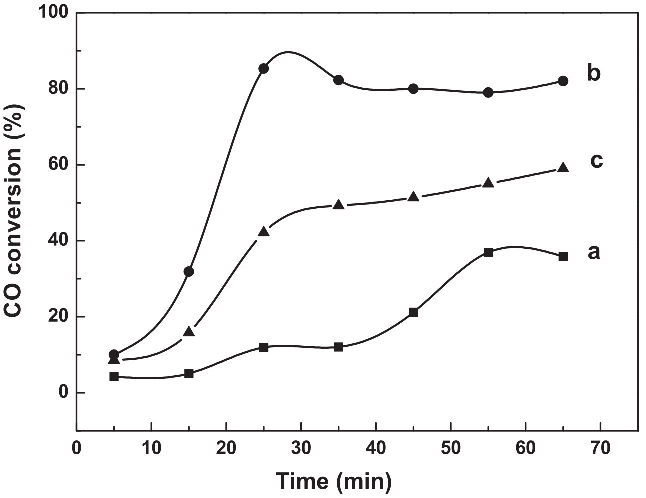

Fig. 10. Activities of the catalysts: (a) Au/CeO_2-673 prepared by method A, (b) Au/CeO_2-673-(base pretreatment) prepared by method A, (c) Au/CeO_2-673 prepared by method B.

Table 3
Relation of species distribution on the surface of the catalysts Au/(CeO_2-673 K) with different preparation methods.

Catalyst	$Au^{\delta+}$ (%)	$OH + H_2O$ (%)	Ce^{3+} (%)
0.09 wt% Au/CeO_2-673[a]	52	38	23
0.07 wt% Au/CeO_2-673[b]	37	36	22
0.06 wt% Au/CeO_2-673-basic pretreatment[a]	20	34	22

[a] Catalyst prepared by method A.
[b] Catalyst prepared by method B.

alyst is contributed by the cooperation of $Au^{\delta+}$, Au^0 and water-derived species.

If only $Au^{\delta+}$ species were the active centers, which weaken Ce-O bond to increase oxygen mobility and to facilitate the formation of oxygen vacancy [9], 0.09 wt% Au/CeO_2-673 with the highest deposition efficiency and abundant $Au^{\delta+}$ species should exhibit the highest activity, but the opposite result was observed. The effect of $Au^{\delta+}$ species makes the surface being a good low temperature oxidant, but this does not mean that it will be a good oxidation catalyst. The oxygen vacancy created when the surface oxidizes CO must be healed by adsorption of oxygen from the gas phase; otherwise, the oxidation reaction will reduce the surface and at some point the oxidation process stops [54]. Over reduction of the support surface is connected to a significantly lower CO oxidation activity [47]. In a good oxidation catalyst, the two conflicting requirements must be well balanced [44]. It must make surface oxygen reactive but not so much that it will hinder the healing of the oxygen vacancies created by the oxidation reaction. By comparing the activities of the catalysts prepared by the three different preparation methods (deposition–precipitation, solvated-metal atom dispersion and coprecipitation) and their initial surface composition detected by XPS, Venezia et al. [15] concluded that the dried catalyst prepared by DP without Au^0 had the highest activity, but note that $Au^{\delta+}$ could be gradually reduced to Au^0 during the reaction process and their XPS also shown the negative shift of the gold binding energies. The lack of Au^0 signal in XPS spectra may be attributed to the high gold content (8 wt%), because the Au^0 signal for dried catalysts (DP) with the gold content in the range of 1–3 wt% has also been detected in some literatures [16,34,55] not only in this work.

On the other hand, if only Au^0 could act as active centers, which weaken the C–O bond and therefore made the further insertion of oxygen easy with release of CO_2 [56], we expect a similar or even more active catalyst could be obtained through the pretreatment of H_2 for 0.06 wt% Au/CeO_2-1073, while the reduction of the catalyst in H_2 strongly reduced its activity. An analogous situation was also reported in the literatures [22,57]. In addition, because of the highest deposition efficiency and surface area for 0.09 wt% Au/CeO_2-673, the amount of Au^0 on the surface of it (0.09 wt% × 48%) is close to that of 0.06 wt% Au/CeO_2-873 (0.06 wt% × 87%), but the activity of the latter with 13% $Au^{\delta+}$ species loading on the surface was much higher than that of 0.09 wt% Au/CeO_2-673, which also indicates the possibility that $Au^{\delta+}$ species are active cannot be excluded, and the required amount of it is not large, especially for the ultra-low-gold loading catalysts. Karpenko et al. [27] shown that the catalyst treated by H_2 at 473 K (containing 19.7% $Au^{\delta+}$) had the highest activity comparing to the untreated catalyst (containing 59.8% $Au^{\delta+}$) and the catalyst treated by H_2 at 673 K (containing 9.7% $Au^{\delta+}$), indicating the proper amount of $Au^{\delta+}$ species is important, which is consistent with us.

However, why could these catalysts exhibit such excellent activities even though the gold uptakes are so low? Another significant parameter contributing to the excellent activities is the optimum amount of water-derived species on the surface, which could prompt the molecular oxygen adsorption and activation [51]. Most of the catalysts reported in the other literatures are calcined or non-calcined but dried at above 373 K, a poor activity result was also observed when 0.06 wt% Au/CeO_2-1073 was just dried at 373 K, which could mainly due to the drastic decrease in the water-derived species on the catalyst.

Accordingly, in this case, the respective role of $Au^{\delta+}$, Au^0 and water-derived species could not be separately treated, and the sole amount of $Au^{\delta+}$ or Au^0 species on the surface of different catalysts could not be used to directly connect with their activities.

3.8. Possible active center model and its formation process

During the catalyst preparation process, $Au^{\delta+}$ species as the form of $Au^{\delta+}$-OH or $Au^{\delta+}$-Cl existed on the surface. When these catalysts were dried at 333 K, large pore structure of the support favors the evaporation of the water, thus the number of the water-derived species increased with the higher surface area. At the same time, some $Au^{\delta+}$ species could be changed to Au^0, but the residual acid materials seemed to make the transformation of $Au^{\delta+}$ difficult because of the difficult dissociation of $Au^{\delta+}$-Cl species, which is one of the main factors resulting in the various $Au^0/Au^{\delta+}$ ratios, and the activity changes. The experiments in Sections 3.5 and 3.6 have confirmed the above conclusion: in order to change the amount of residual acid materials before introducing $HAuCl_4$ solution, a series of catalysts Au/CeO_2-673 with the same support were prepared by different methods and tested, the assay results of the catalysts thus prepared showed different activities; base pretreatment could obviously increase the $Au^0/Au^{\delta+}$ ratio and enhance the activity by neutralizing the residual acid on the surface of CeO_2-673. It was found that after the base pretreatment to CeO_2-673, the amount of $Au^{\delta+}$ species decreased from 52% to 20%, but which is still higher than those of Au/CeO_2-873 (13%) and Au/CeO_2-1073 (0%), so the CeO_2 particle size may be another reason attributing to the different $Au^0/Au^{\delta+}$ ratio. In the case of CeO_2 as support, the oxidation state of Au has been reported to mainly depend on the particle size and morphology of the support, if CeO_2 particle size increases the amounts of $Au^{\delta+}$ and Ce^{3+} decrease [16,25,45,46].

When the dried catalysts were exposed to the reactant gas, CO may need to react with hydroxyl group adsorbed on $Au^{\delta+}$ to produce CO_2 and H_2O, and then react with the surface oxygen atom located near the gold dopant to form oxygen vacancy. After removal of the oxygen atom in its neighborhood, $Au^{\delta+}$ became mobile, then it may migrate, meet other gold species and form metallic cluster, especially for Au^{3+} species, but too much $Au^{\delta+}$ species made the support surface release oxygen atoms so easy that more oxygen vacancies are formed, provoking more difficulties in adsorbing O_2 from the gas, which could result in the stable carbonate accumulating on gold species, such as Au-hydroxycarbonyl. When the steady state reached, appropriate Au^+ species still staying at the dopant sites increase the surface oxygen atom mobility, and Au^0 species weaken the C–O bond to make the further insertion of oxygen easy. On the other hand, some water-derived species adsorbed on the gold species (Au^+-OH) could promote the decomposition of carbonate, the other water-derived species adsorbed on the support could promote the molecular oxygen adsorption and activation, but too much of this kind of water-derived species could cover the adsorption sites of CO and O_2, which, meanwhile, caused the advantage of Au^+-OH species to be limited. The synergetic action of $Au^{\delta+}$, Au^0 and water-derived species for the CO oxidation at ambient temperature has been confirmed, and their respective effect could be putted into full play when they constitute a active center rather than stand alone, but the proper ratio of $Au^{\delta+}/Au^0$ and optimum amount of water-derived species are crucial for obtaining an efficient catalyst.

4. Conclusions

Both the $Au^0/Au^{\delta+}$ ratio and the amount of water-derived species on the catalyst surface were found to be responsible for the activity of CO oxidation at ambient temperature. During the preparation of the catalysts, the methods for controlling the pH value of CeO_2 suspension dramatically affect the activity of the catalysts. CeO_2 support calcined at low temperature supplied a strong acid environment by residual acid material produced during the catalyst preparation process. Direct reaction of $HAuCl_4$ and CeO_2 during the deposition–precipitation process causes the formation of a catalyst with low $Au^0/Au^{\delta+}$ ratio on the catalyst surface and low initial activity. For acid support, raising the pH of the acid support suspension before the introduction of the $HAuCl_4$ solution can increase the $Au^0/Au^{\delta+}$ ratio and improve the activity obviously; however, for neutral support, the effect of the methods for controlling the pH on the catalyst activity is slight. The catalyst with optimal amount of water-derived species can be obtained by drying the catalyst at 333 K without calcination step. The base pretreatment of support is in favor of the preparation of a catalyst with excellent catalytic performance for CO oxidation at ambient temperature.

Acknowledgment

The authors are grateful for the financial support of China Tobacco Fujian Industrial Corporation.

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