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The effect of K addition on Au/activated carbon for CO selective oxidation in hydrogen-rich gas

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The effect of K addition on Au/Activated carbon (AC) catalyst for CO selective oxidation in hydrogen-rich gas was investigated in this paper. It was found that K addition resulted in activity promotion for selective CO oxidation. The results of XRD and XPS characterization indicated that K addition produced the highly dispersed Au species and retarded the sintering of Au species on the catalyst surface during the reaction.

KEY WORDS: selective CO oxidation; Au; activated carbon.

1. Introduction

Hydrogen, as a source of energy for stationary power plants and moving vehicles, will certainly be widely used in decades via fuel cell, for example polymer electrolyte fuel cell (PEFC). However, when hydrogen is produced via the reforming reaction, the gas always contains CO as a poisoning impurity. Therefore, the hydrogen production system must be equipped with a CO removal apparatus. Selective oxidation of CO in H_2-rich gas is one of choices. Ideally, the catalyst should selectively oxidize CO to maintain its concentration less than 5 ppm while make the H_2 un-reacted. Some catalysts have been reported to be active for selective oxidation of CO in H_2-rich mixture, such as supported Pt [1–5], Au [6, 7], Ag [8] Cu [9], Pd, Rh catalysts [10, 11], and metal oxides catalysts [12].

The activated carbon was recently reported as support for Au catalyst in CO oxidation because of its special properties, for example, a high specific surface area(up to 3,000 m^2/g), high stability in acidic and basic media [13], easy modification of textural properties and functional groups, and easy recovery of supported metals by burning off the catalyst. In fact, the Pt–Sn/activated carbon was active for CO oxidation [14–16]. Some papers reported that the activities of Au/AC catalysts were highly dependent on pre-treatment of carbon support [17, 18]. It was known that some alkali metals exhibited significant effects of activity enhancement for CO oxidation in Pt and Pd catalysts [4, 19–24]. It is quite interesting to know the effect of alkali on the Au/activated carbon catalyst for CO selective oxidation.

In this work, we present the observation that the dimension control of Au particle on activated carbon support by addition of K component and the activity improvement for CO selective oxidation.

2. Experimental

2.1. Preparation

Au/AC catalyst was prepared by impregnation of activated carbon with the calculated amount of $HAuCl_4$ aqueous solution. The sample was dried at 383 K for 12 h, and then calcined in air at 573 K for 3 h. The dried sample was washed thoroughly with deionized water, in order to remove the residual chlorine ion. The loading amount of Au was 1 wt%. K-promoted Au/AC catalysts (denoted as K–Au/AC) were prepared by impregnation Au/AC samples with desired amount of KNO_3 aqueous solution. After these procedures, the calcination was carried out again in air at 573 K for 3 h.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) analysis was performed to verify the species present in the catalysts. XRD patterns of the samples were recorded on a Rigaku D/MAX–RB X-ray diffractometer with a target of Cu Kα operated at 50 kV and 40 mA with a scanning speed of 0.5°/min and a scanning angle (2 theta) range of 10–90°. Chemical states of the atoms in the catalyst surface were investigated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 210 Electron

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Spectrometer (Mg Kα radiation; hν = 1253.6 eV). XPS data were calibrated using the binding energy of C_{1s} (284.6 eV) as the standard.

2.3. *Activity measurements*

The measurements of catalytic activity of CO oxidation were performed in a fixed bed reactor (i.d. 5 mm) under atmospheric pressure. Then 200 mg of catalyst was used for each run. The total flow rate of the feed gas was 75 ml min^{-1} (GHSV = 22,500 h^{-1}). The feed gas consisted of 70% of H_2, 2.0% of CO and 1.4% of O_2 in N_2 balance. H_2, CO and O_2 in the reactant and product were analyzed using a gas chromatograph equipped with a Molecular Sieves 13X column and a thermal conductivity detector.

In this paper, the CO conversion was calculated from the variation of the detected CO concentration:

$$\text{CO conversion } (\%) = \{([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/[\text{CO}]_{\text{in}}\} \times 100$$

where $[\text{CO}]_{\text{in}}$ is the inlet CO concentration and $[\text{CO}]_{\text{out}}$ is the outlet CO concentration.

The O_2 conversion is based on oxygen consumption:

$$O_2 \text{ conversion } (\%) = \{([O_2] - [O_2]_{\text{out}})/[O_2]\} \times 100$$

While the oxygen selectivity to CO_2 (S) is defined as follows:

$$S\ (\%) = \{0.5 \times [CO_2]/([\text{CO}] - [\text{CO}]_{\text{out}})\} \times 100$$

3. Results and discussion

3.1. *Catalyst characterization*

3.1.1. *XRD*

The X-ray diffraction (XRD) patterns of various catalysts were shown in figure 1. A broad XRD peak attributed to activated carbon support (around $2\theta = 24°$) was observed on all samples. In the Au/AC and K–Au/AC catalysts, typical peaks of Au crystalline were clearly observed at 2θ = 38.2, 44.4, 64.7 and 77.7°, those peaks were assigned to the diffraction lines of {111}, {200}, {220} and {311} planes of gold. Doping of Au/AC (a) with K led to a progressive decrease of the relative height of the Au diffraction lines for the catalysts calcined at 300°C. As shown in table 1, the peak height and full width at half maximum (FWHM) of the Au (311) phase for K (10%)–Au/AC (sample b) decreased from 2032.97 to 557.15(a.u.), and the FWHM increased from 0.1020 to 0.3011°, correspondingly. Further increase the loading of K to 20% (sample d) resulted in the peak height (to 919.56a.u.). The decrease of the peak height was more pronounced for the catalysts doped with 10% K. These results indicated that the K doping led to an effective increase of the dispersion degree of Au particle. Table 1 presented the crystallite size of these catalysts determined using the Scherrer equation. The average diameter of Au particles in the Au/AC sample was 16 nm, while the diameter of K-doped Au/AC sample was much smaller. When doping amount of K was 5%, the average diameter was 11 nm. When the concentration of K increased, the average diameter of Au particle decreased to 8 nm at the K concentration 10%. Over loading of K resulted in the little larger average diameter of Au particle, but it was still smaller than that of un-doped sample. It seems that K doping results in retardation of the Au particle sintering on the catalyst surface in the K–Au/AC catalyst preparation.

We also synthesized an Au/Ac catalyst by citric acid reduction. Its X-ray diffraction pattern (sample e) was given in figure 1. The main diffraction lines were quite weak and only (111) line could be identified. These results means Au particle dispersion degree in this sample is high. The activity of this sample will be discussed in the following section.

3.1.2. *XPS*

Chemical states of surface atoms in the catalysts after activity tests were investigated by XPS (Figure 2). The binding energies of Au_{4f} in the catalysts are 87.2 eV ($4f_{5/2}$) and 83.8 eV ($4f_{7/2}$), which are almost similar to the data in the previously observation [25, 26] and can be assigned to Au°. The C_{1s}/Au_{4f} intensity ratios and Au atomic content on the surface of different catalysts were shown in table 2. The addition of the K results in the increase of surface Au atomic concentration in sample b and c. Higher [Au AT%] corresponds to the smaller Au particle. For example, sample c exhibited the highest surface Au atomic concentration 0.091% and the smallest average diameter 8 nm. It indicated that suitable K doping led to the smaller average diameter of Au particle.

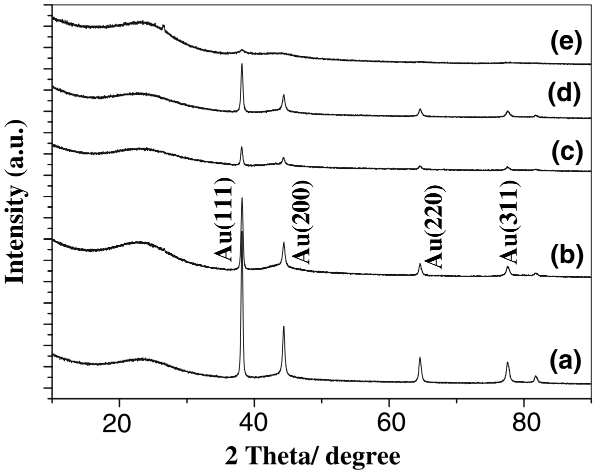

Figure 1. XRD patterns of different catalysts (a) Au/AC; (b) K (5%)–Au/AC; (c) K (10%)–Au/AC; (d) K (20%)–Au/AC; (e) citric acid reduced Au/AC catalyst.

Table 1
Results of XRD analysis for Au (311) over different catalysts

Catalysts	$2\theta/°$	Height (cts)	FWHM (°2Theta)	Crystallite size/nm
Au/AC	77.56	2032.97	0.1020	16
K (5%)–Au/AC	77.62	681.15	0.1632	11
K (10%)–Au/AC	77.56	557.39	0.3011	8
K (20%)–Au/AC	77.58	919.56	0.1428	12

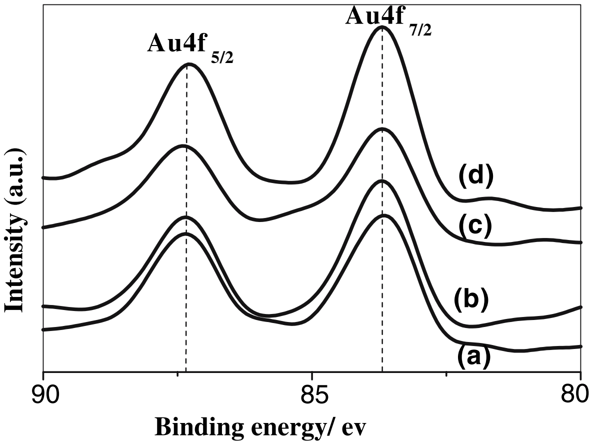

Figure 2. Au 4f binding energies of different catalysts: (a) Au/AC (b) K (5%)–Au/AC; (c) K (10%)–Au/AC; (d) K (20%)–Au/AC.

3.2. *Activity measurements*

3.2.1. *Influence of K content on the activity for CO selective oxidation over various catalysts*

The effect of K loading of the K–Au/AC catalysts on their CO oxidation activity (expressed as conversion of CO in %) in the selective CO oxidation in the presence of excess hydrogen was shown in figure 3. It was found that reaction temperature significantly affected CO conversion, O_2 conversion and CO_2 selectivity in the temperature range from 100 to 300°C. For all the samples, the activity for CO oxidation increased with the increase of the reaction temperature. The CO conversions over Au/AC catalyst were much lower than those over K–Au/AC catalysts. Increase of the K loading from 2 to 10 wt% resulted in a marked increase of the activity. T_{50}, the temperature at which 50% conversion of CO, was lowered from 240 to 110°C for the catalysts containing 2 and 10-wt% K, respectively. CO was not completely oxidized even at 250 °C over 2.0 wt% K sample, while complete CO conversion was observed at ca. 120°C over the 10-wt% K catalyst. Further increase of the K content from 10 to 20-wt% resulted in a higher T_{50} temperatures from 110 to 220 °C. However, the 20-wt% K catalyst remained more active than the 2-wt% K sample. For 10 wt% of K sample, CO was converted completely at 120°C, and the corresponding selectivity of CO_2 reached 70%. These results indicated that increasing the K loading could promote the catalytic activities of the K–Au/AC catalysts.

In order to compare the particle size effect on the activity performance for CO oxidation in the presence of H_2, we also prepared the activated carbon supported Au catalyst with the Au particle size about 5 nm using citric acid as the reducing agent. The gold colloids used in this study were prepared as described in references [27–29]. Typically, preparation of Au colloid of ca. 5 ± 1 nm diameter particles was proceeded by adding 0.5 mL of 1% aqueous $HAuCl_4 \cdot 3H_2O$ to 50 mL of H_2O with vigorous stirring, followed by the addition of 0.5 mL of 1% aqueous citric acid 1 min later. Then 0.5 mL of 0.075% $NaBH_4$ in 1% citric acid was added. And a suitable amount of activated carbon was added and the catalyst was irradiated under infrared lamp. Finally, dried at 110°C for 12 h and calcined at 300°C for 3 h.

Generally speaking, the smaller particle size of Au is, the higher activity of catalyst for CO oxidation is given. However as shown in figure 3, the conversion of CO over K (10%)–Au (1%)/AC reached 100% at 120°C, while the conversion of CO gave completely conversion of CO at 160°C over the citric acid reduced Au/AC catalyst.

The significant increase of activity of CO oxidation over K–Au/AC is might due to providing an "oxygen attractor" of K, which results in very low energy barriers for the CO + O_2 reaction via Eley-Rideal type of

Table 2
XPS data on different catalysts

Catalyst	Centre(Au)	Centre(C1s)	C1s/Au4f	Au[AT]%
Au/AC	83.70	284.12	126.92	0.057
K(5%)–Au/AC	83.64	284.12	84.40	0.082
K(10%)–Au/AC	83.70	284.12	78.76	0.091
K(20%)–Au/AC	83.70	284.12	123.79	0.055

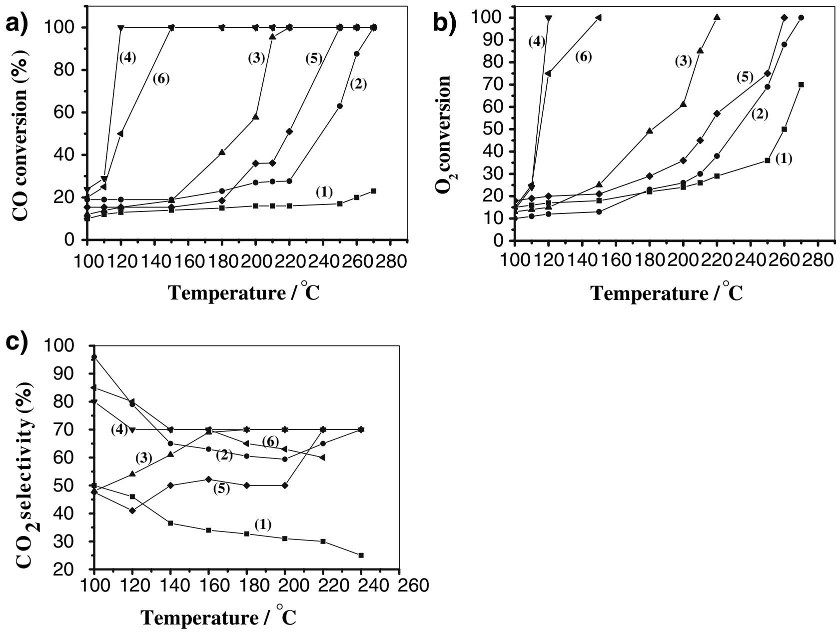

Figure 3. Reaction temperature dependence of CO conversion (a), O_2 conversion (b), and CO_2 selectivity (c) of CO oxidation in H_2-rich gas over K–Au/AC catalysts (CO concentration in the effluent gas over K–Au/AC are: 2.0 vol.% CO, 1.4 vol.% O_2 and 70 vol.% H_2 (N_2 balance). (1)–without K: (2)–2% K; (3)–5% K; (4) – 10% K; (5)–20% K; (6) citric acid reduced Au/AC catalyst.

reaction mechanism [30]. Based on the results, we deduced of the reaction mechanism as follows: On the one hand, the addition of the K resulted in high dispersion of the Au. The higher Au dispersion supplied more adsorption sites for CO and O_2, therefore, the CO and O_2 conversions increased obviously (This conclusion can be supported by the XRD results). Under this condition, the higher affinity towards O_2 at the K-decorated edge was given. On the other hand, K addition decreased the surface acidity of the AC support. When the addition of the K is excess of 10%, further decrease of surface acidity of AC resulted in the strong combination with CO_2. These reasons inhibited the occurrence of CO oxidation. Therefore, the activity of CO oxidation over K (20%)-Au/AC was lower than that of K (10%)–Au/AC sample as shown in figure 3.

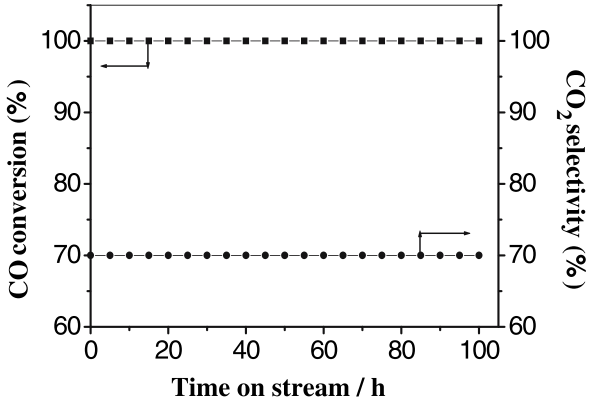

Figure 4. Stability test of catalyst K (10%)–Au/AC for CO oxidation from the mixed gas with large excess H_2, Experimental conditions: 2% CO, 1.4% O_2, 10% H_2O, 70% H_2 and N_2 balance T = 120°C; GHSV = 22,500 h^{-1}; P = 1 atm.1.

3.2.2. *Effect of H_2O on stability of K (10%)–Au (1%)/AC catalyst*

We have checked PROX activities on various catalysts in the gas mixture containing H_2O. A stability test of K (10%)–Au (1%)/AC in 2% CO, 1.4% O_2, 10 % H_2O, 70 % H_2 and N_2 balance was performed at 120°C(see figure 4). Conversions of CO and O_2 reached to 100% in the presence of H_2O. After 100 h test, conversions were still kept at 100% and the selectivities were also kept at 70%. These results indicated that K doped Au/AC catalyst was stable for PROX reaction.

It was reported that Ag supported carbon black(Ag/CB) was active and selective for the oxidation of CO in the presence of excess hydrogen [31]. As shown in table 3 and figure 3, the K–Au/AC catalyst loaded with 1% Au and 10% K gives much better CO conversion and selectivity (100 and 70% respectively) at 393 K under similar conditions. It was known that Pt–Sn/AC[16], Au/ACF [32] and Au/FeOx/ACF [33] catalyst was active for the reaction of CO oxidation, but the ACF-based catalysts showed higher initial activity but deactivated quickly in the reaction medium. The Au/ACF catalyst deactivated more rapidly than the catalysts modified by iron oxide. The K–Au/AC catalyst seems to be less active, but has significant stability.

Table 3
Compare different activated carbon supported catalysts on CO oxidation or CO selective oxidation

Catalysts	Method	Loading (%)	Pretreatment	Reaction conditions	*T* (K)	Catalytic active (%)	Ref
Ag/CB	Imp	Ag% = 4	H_2, 773 K 2 h	0.12 g catalyst, feed gas 1 vol.% CO, 0.5 vol.% 0_2, 98.5 vol.% H_2; flow rate 50 ml/min	362,	CO% = 12	[31]
Ag/Coal (Ag/ACF)	Imp Imp	Ag% = 4	H_2, 773 K, 2 h Reduced at 673 K	0.12 g catalyst, feed gas 1 vol.% CO, 0.5 Vol.% 0_2 and 98.5 vol.% H_2; flow rate 50 ml/min	362	CO% = 4–5	[31] [31]
Pt–Sn/AC	Seq imp	Pt% = 1 Sn% = 0.25	H_2, 673 K	0.25 g catalyst CO: O_2: He ratios as 15:20:65, total feed flow rate of 75 ml/min.	398	CO% = 100	[16]
Au/ACF	Ion exchange	Au% = 1	H_2, 573 K	0.02 g catalyst 1 vol.% CO, O_2/CO = 5, 100 ml/min	298	–	[32]
Au/FeOx /ACF	Ion exchange	Au% = 1.3,	–	0.02 g catalyst 1 vol.% CO, O_2/CO = 5, 100 ml/min	303	–	[33]
Au/AC K–Au/AC	Imp Seq imp	Au% = 1K% = 10		0.2 g catalyst, 70 % H_2, 2.0 % CO, 1.4 % O_2, N_2 balance, total feed flow rate of 75 ml/min	393	CO% = 100	This work

4. Conclusions

It was found that K–Au/AC catalysts are very active and selective for the CO oxidation in the presence of excess hydrogen. The best result was obtained over the 10%K–Au/AC catalyst, corresponding to the smallest Au particle diameter. The catalyst exhibited very high stability in the presence of H_2O. K-doping led to smaller Au particles and improvement of dispersion of Au particles.

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