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Effect of surface properties of activated carbon on CO oxidation over supported Wacker-type catalysts

Li Wang, Yanbo Zhou, Qiufang Liu, Yun Guo*, Guanzhong Lu*

Lab for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science & Technology, Shanghai 200237, China

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ABSTRACT

The effects of chemical pretreatments of the support on CO oxidation over the activated carbon-supported Wacker-type catalyst were studied. Dry oxidation by air at 400 °C and wet oxidation in H_2O_2 and H_3PO_4 aqueous solution were used to modify the physical and chemical properties of activated carbon. The textural and surface characteristics of activated carbons were characterized by nitrogen adsorption, temperature-programmed desorption (TPD) and Boehm titration. The dispersion of active phase and chemical environment of CO oxidation catalysts were investigated by X-ray Photoelectron Spectroscopy (XPS) and temperature-programmed reduction (TPR). CO oxidation results showed that the catalyst prepared using activated carbon with high mesopores and oxygen-functional groups as support performs higher CO oxidation activity at ambient temperature, especially in high relative humidity. XPS and TPR results show that the activated carbon support with enriched oxygen-functional groups would benefit the distribution of active components (Pd^{2+}, Cu^{2+}) on the catalyst surface and the formation of easily reducible Cu^{2+} species.

1. Introduction

Interest on the elimination of CO at low temperature is continually growing because of its importance in practical application and theoretical study, meanwhile catalytic oxidation has been proved to be an efficient and economical method. The potential applications for low temperature CO oxidation were CO_2 laser exhaust abatement, trace CO removal in the enclosed atmospheres, the automotive emission control, and CO preferential oxidation for proton exchange membrane fuel cells (PEMFC) [1]. However, there are problems which arise from the nature of the process streams involved. In addition to the low concentrations of CO, these streams are often water saturated and are at ambient temperature. Hence specific catalysts must be active at low temperature and water tolerant [2].

Supported Wacker catalysts composed of $PdCl_2$–$CuCl_2$ have been reported to be active in CO oxidation at low temperatures, and activated carbon (AC) supports have been reported to be superior to any others, such as alumina, for this catalyst system [3]. Parks and Lee [4] suggested that the active phases of Pd and Cu were Pd^{2+} species containing chlorine and probably carbonyl ligands and solid $Cu_2Cl(OH)_3$ particles, respectively. The redox reactions, involved in the catalysis, are the following:

$$CO + H_2O + PdCl_2 = CO_2 + 2HCl + Pd$$

$$Pd + 2CuCl_2 = PCl_2 + 2CuCl$$

$$2CuCl + 2HCl + 0.5O_2 = 2CuCl_2 + H_2O$$

It is well known that surface properties of activated carbon depend on the nature of precursors and the parameters of the activation process. The porous structure and surface chemistry of activated carbon are important properties in connection with its adsorbent behavior [5]. The surface functional groups further influence in a decisive way the ionic exchange and the catalytic and electronic properties of this carbon material. Much work had been done for modifying the surface chemistry of activated carbons [6]. Among the methods leading to the formation of surface oxygen complexes, two main categories can be distinguished: utilizing oxidizing gases such as oxygen and ozone, and reactions in oxidizing solutions such as nitric acid, alkaline permanganate, hydrogen peroxide, etc.

The objective of this paper is to study the oxidation susceptibility of activated carbons and evaluate the performance of activated carbons as support for CO oxidation. Boehm titration and TPD were applied to evaluate the nature of surface oxygen groups and the variations in their distributions imposed by different oxidation methods. XPS and TPR were used to characterize catalyst and try to interpret the effect of support nature in CO oxidation. The objective

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* Corresponding authors. Tel.: +86 21 64253703; fax: +86 21 64253824.
E-mail addresses: yunguo@ecust.edu.cn (Y. Guo), gzhlu@ecust.edu.cn (G. Lu).

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of the study is to search a method to modify activated carbon as the support of high performance catalyst, which can be used for CO oxidation at ambient temperature, rich oxygen (21%) and high relative humidity (100%), which would be useful in purifying tunnel air.

2. Experimental

2.1. Catalysts preparation

Commercial coconut cell based activated carbon (Tanxing Activated Carbon Co. Ltd., Shanghai) was used for this study. AC was preoxidized in air at 400 °C for 6 h, which was labeled as AC(400). The wet oxidation of AC was carried out by impregnating AC in the aqueous solutions (2N) of H_2O_2, and H_3PO_4 for 48 h at room temperature with gentle shaking, respectively. Then, the samples were filtered and washed with de-ionized water to remove the remaining oxidants. The AC samples impregnated with the oxidation solution were treated in air at 400 °C for 4 h. Wet oxidized carbon samples were labeled as AC(H) by H_2O_2 pretreatment, and AC(P) by H_3PO_4 pretreatment, respectively.

The catalyst was prepared by a wet impregnation method to impregnate supports with an aqueous solution of palladium and copper. The support was dried at 120 °C for 12 h in an oven before impregnation. The metal precursors were $PdCl_2$, $CuCl_2{\cdot}2H_2O$. The loadings of $PdCl_2$ and $CuCl_2$ for all catalysts were 1.7 and 6.5 wt%, respectively.

2.2. CO oxidation test

The conversion of CO oxidation was measured in a fixed-bed reactor with catalysts of 20–40 mesh under atmospheric pressure. The constant reaction temperature of the reactor was achieved by controlling the temperature bath. The reaction gas flows were controlled by mass flow controller, the mixture of air and 1500 ppm CO in nitrogen passed through the catalyst bed at a space velocity (GHSV) of 24,000 h^{-1}. The reaction gas was saturated with water through a saturator enclosed in the temperature bath and fed to the reactor. The conversions of CO on different catalysts were analyzed by an on-line gas chromatography (FuLi 9650, molecular sieve 13X column).

2.3. Characterization of activated carbon and catalysts

Nitrogen isotherms were measured using a ASAP 2010 apparatus (micromeritics) at −196 °C. Before the experiments the samples were heated at 120 °C and then outgassed at this temperature to 10^{-5} Torr. The isotherms were used to calculate the specific surface area (S_{N_2}), micropore volume (V_{mic}), and total pore volume (V_t).

Temperature-programmed desorption (TPD-MS) of samples was carried out in a quartz flow reactor (Φ10 mm × 300 mm) system coupled to a quadrupole mass spectrometer (IPC400, INFICONCo. Ltd.), 200 mg sample was used. The TPD experiments were performed by heating the sample in Ar flow rate (50 ml/min) from 100 °C to 900 °C at a rate of 10 °C/min. Temperature-programmed reduction (TPR) of catalyst precursors was carried out in the same apparatus using 1% hydrogen in argon (20 ml/min) as a reducing gas.

The contents of acidic and basic sites on the surface of samples were determined by the Boehm method [7]. 500 mg sample was placed in 30 ml vial with 0.05N aqueous solutions of NaOH, Na_2CO_3, $NaHCO_3$ and HCl, respectively. After the vials were sealed and shaken for 24 h, the samples were filtrated and 10 ml filtrate was pipetted. Excessive NaOH or HCl was titrated with HCl and NaOH, respectively. The contents of acidic sites were calculated according to the assumption of the base solution, in which NaOH neutralizes the carboxylic, phenolic and lactonic or lactol groups, Na_2CO_3 neutralizes the carboxylic and lactonic or lactol groups, and $NaHCO_3$ neutralizes only carboxylic groups. The content of the surface basic sites was calculated by the amount of HCl reacted with the AC sample.

Table 1
Catalytic Activity of the Pd–Cu/AC samples.

	Sample			
	Pd–Cu/AC	Pd–Cu/AC(400)	Pd–Cu/AC(P)	Pd–Cu/AC(H)
Conversion (%)	45	58	76	65

After 1 g AC sample was immersed in 30 ml de-ionized water to reach equilibrium, pH of the carbon suspension was determined by the pH meter according to the literature [8].

X-ray Photoelectron Spectroscopy (XPS) analysis was performed on Thermo ESCALAB 250 with a monochromatic Al Kα source ($h\nu$ = 1486.6 eV), operating at 150 W. The binding energy (BE) of adventitious C 1s (284.8 eV) was used as a reference.

3. Results and discussion

3.1. Catalytic activity of CO oxidation

The activity of different samples impregnated Pd–Cu for CO oxidation at ambient temperature is presented in Table 1. It is apparent that the catalyst activity is improved evidently by the pretreatment of utilizing oxidizing agents. Compared with untreated activated carbon support, the catalytic activity increased 29%, 44% and 69% supported on the activated carbon oxidized by air, H_2O_2 and H_3PO_4, respectively.

3.2. Pore structure characterization

Pore structure characteristics vary in dependence of modification, which is listed in Table 2. Activated carbon oxidized by air and H_3PO_4 showed the nearly same BET surface area (S_{BET} are 1012 and 1016 m^2/g, respectively), but the air treated one had higher total pore volume than that of H_3PO_4. Activated carbon oxidized by H_2O_2 behaved the biggest BET and total pore volume among them. The contribution of mecro- and macropore volume to the total pore volume was high (about 23%) for the AC(H), the corresponding ratio of AC(400) and AC(P) was nearly the same.

The structure of activated carbon plays an important role in ambient CO oxidation, especially in high relative humidity. Tone et al. [9] investigated the possibility of water vapour lowering the catalytic activity by blocking micropores via capillary condensation in the study of COS hydrolysis. Using the Kelvin equation, at a typical vapour concentration of 30 mol%, the limiting radii of cylindrical pores expected to be affected by capillary condensation of water were calculated to be 0.34 nm or less [10]. The decrease in activity at high water contents probably results from the combination of dilution of the liquid phase and pore filling with liquid, and decreasing the available gas–liquid interfacial surface area.

CO oxidation at high relative humidity (100%) conditions means that pore size distribution can be an important factor in determin-

Table 2
The textural properties of the ACs pretreated by different methods.

Sample	S_{BET} ($m^2\ g^{-1}$)	V_{tol} ($cm^3\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	$V_{mecro+macro}$ ($cm^3\ g^{-1}$)
AC	953	0.393	0.369	0.025
AC(400)	1012	0.545	0.463	0.082
AC(H)	1153	0.568	0.436	0.132
AC(P)	1016	0.472	0.398	0.074

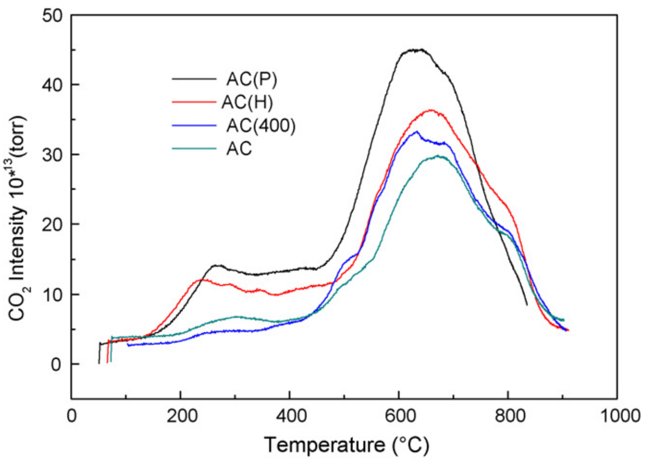

Fig. 1. TPD profiles of CO_2 (m/z = 44).

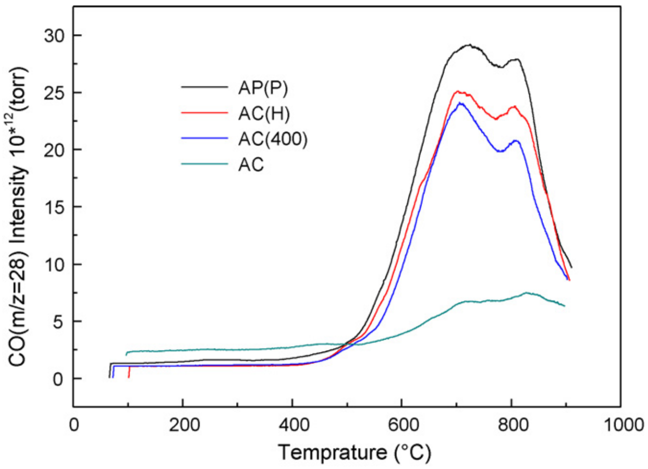

Fig. 2. TPD profiles of CO (m/z = 28).

ing apparent activity in supported liquid phase catalysts not only for the normal pore diffusion reasons but also for access to the liquid phase surface within the pore structure. A heterogeneous carbon (having micro- and mesopores) with chemical surface functionality performs better than apparently neutral, predominantly microporous carbons.

3.3. *Surface chemical properties characterization*

The differences in the surface properties caused by the presence of oxygen-containing functional groups are determined by TPD method. Different TPR profile shape, desorption temperature range and peak position mean different distributions of oxygen groups [11].

It is well known that CO_2 evolution at low temperatures is attributed to acidic groups, while CO produced at higher temperatures is derived from weak acidic and basic groups. CO_2 groups centered at temperatures up to 400 °C come from carboxyls, or lactones at temperatures up to 600 °C. Phenols, ethers, carbonyls and quinones evolve CO between 700 and 1000 °C, and carboxylic anhydrides produce both CO and CO_2 in the temperature range of 350–600 °C [12].

The Ar-TPD profiles of CO_2 and CO are shown in Figs. 1 and 2. Original activated carbon has two CO_2 desorption peaks at about 290 and 510 °C. Modified activated carbon also displayed two desorption peaks at about less than 400 °C and an extensive peak in the range of 500–800 °C. The CO_2 peak at ~400 °C is attributed to the carboxylic acid groups, and the CO_2 peaks at 550 and 670 °C may result from carboxylic anhydrides, lactones or lactols [13].

Compared with the TPD profiles of CO_2, CO was mainly detected at higher temperatures (>600 °C), which may be attributed to the fact that the CO-desorbing functional groups, such as hydroxyl, carbonyl and quinine groups, are more thermally stable than the CO_2-desorbing groups. For the CO desorption peak of original activated carbon, the relative peaks were detected in the temperature range of 500–900 °C. For modified activated carbons, in addition to the intensive peak at 700 °C, there is a small badly resolved peak at about 830 °C. The desorption peak of CO at 700 °C can be assigned to phenolic and carbonyl groups, and the small peak at about 830 °C is attributed to stable oxides like semiquinones, quinones or the same complex at a different environment [14].

TPD result can be used to assess the behavior of the thermally treated samples qualitatively, thus Boehm titration was used to quantify the concentration of different oxygen-containing functional groups. The concentration distributions of the acidic and basic sites on AC obtained by Boehm titration are presented in Table 3.

Compared with the oxidation of air, the wet oxidation can efficiently change the amount of the surface acidic oxygen groups of AC. On the surface of AC(H), there are mainly lactonic and phenolic groups, and the concentration of carboxylic group is lower. This may be due to decrease of the carboxylic groups concentration aroused by the pyrogenation of the carboxylic groups during high temperature treatment, resulting in the reduction of its concentration [15], and/or the formation of lactonic groups through the partial condensation of the carboxylic and phenolic groups to form lactonic groups during an oxidation.

Treatment with air, H_2O_2 and H_3PO_4 can decrease obviously the basic sites on AC such as quinones, chromenes or pyrenes, as compared with the original activated carbon. The treatment with H_3PO_4 solution makes AC to have the maximum amount of the acidic sites and minimum amount of the basic sites. Treatment with H_2O_2 and air at 400 °C can get almost the same acidic sites and basic sites.

The relative amounts of surface oxygen group over ACs show great difference depending on the pretreatment method. The results show that the amounts of lactonic groups are much more than that of carboxylic groups and phenolic groups in all the samples. Compared with AC, AC(H) has smaller amount of the carboxylic group, but phenolic group amount is more than 3 times of that on AC. The amount of lactonic, carboxylic and phenolic groups increased significantly after pretreated by H_3PO_4, especially the increase of phenolic group.

The pH values of AC suspension in de-ionized water are also shown in Table 3. For the original AC, its suspension solution is basic (pH 9.34), but the corresponding pH values are lower than 7

Table 3
The concentration of acid and basic sites obtained by Boehm titration.

Sample	Lactonic	Carboxylic	Phenolic	Total acid sites (mmol/g)	Basic sites (mmol/g)	pH
AC	0.381	0.115	0.112	0.608	1.676	9.34
AC(400)	0.592	0.118	0.308	1.018	0.529	5.08
AC(H)	0.538	0.109	0.352	0.999	0.553	5.35
AC(P)	0.784	0.409	0.443	1.636	0.43	4.51

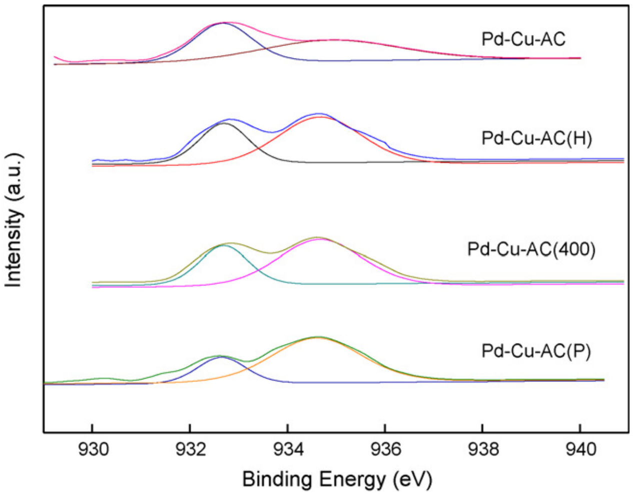

Fig. 3. XPS spectra of Cu $2P_{2/3}$ for different catalysts.

for all the treated carbon samples. The pH value of AC suspension solution is corresponded to the total amount of acidic and basic sites on AC, which showed a good correlation with the amount of the surface oxygen groups on AC. High amount of acidic oxygen groups combined with low amount of basic oxygen groups on AC surface caused lower pH value of AC suspension solution; and vice versa.

The surface oxygen-containing functional groups such as carboxylic, carbonyl, and quinonyl groups are closely related to the hydrophobicity of carbon supports. The different pretreatment ways of activated carbon support might are expected to have a significant influence not only on the dispersion and sintering propensity of Cu particles dispersed on their surface, but also on their reducibility. The surface oxygen-containing functional groups were beneficial in terms of rendering a higher dispersion of Cu-compounds [16]. As the reductive site, these surface functional groups on carbon played an important role in the reduction of Pd(II) and Cu(II) species. A preferential reduction of Cu(II) rather than Pd(II) on the reduction sites has happened because the redox potential of Cu(II) to Cu(I) [0.15 V vs Ag(I)/AgCl] is lower than that of Pd(II) to Pd(0) (0.92 V) [17].

3.4. XPS

$PdCl_2$ and $CuCl_2$ were dispersed on the catalysts in amorphous phase, or their particles were too small to be detected, the characteristic diffraction peak of Pd- or Cu-containing phases was not observed in the XRD patterns. In order to obtain the further information about the active components, XPS was used to characterize the surface composition and chemical state of catalyst.

XPS spectra showed Pd existed in the form of Pd(II). No metallic phase of Pd was detected, although it is reported that $PdCl_2$ would reduce to metallic Pd particles during catalyst preparation. The spectra of Cu 2p are numerically fitted with two Gaussian–Lorentzian features, which are shown in Fig. 3. The peak at the binding energy (BE) of 932.2 eV was attributed to Cu^+, another peak at 934.6 eV was attributed to Cu^{2+}. It indicated that Cu existed in the form of Cu(I) and Cu(II). The relative percentages of these two Cu species are quantified based on the area ratios of Cu^+ and Cu^{2+} peaks.

The surface concentration and distribution of Pd, Cu and Cl species obtained from XPS results are summarized in Table 4. It was showed that the different catalysts exhibited the great difference of surface composition, although the same preparation method and the amounts of catalytic components have been employed in the experiments.

Table 4
Surface compositional results for catalysts obtained by XPS analysis.

Sample	Pd^{2+}	Cu^{2+}	Cu^+	Cl^-	Pd^{2+}/Cu^{2+}	Cl/(Pd + Cu)
Pd–Cu–AC	0.21	0.37	0.30	1.22	0.57	0.83
Pd–Cu–AC(400)	0.24	0.41	0.19	1.4	0.58	0.94
Pd–Cu–AC(H)	0.27	0.46	0.21	1.62	0.59	0.97
Pd–Cu–AC(P)	0.29	0.48	0.13	1.83	0.6	1.1

The active Pd(II) and Cu(II) components are enriched on the surface of activated carbon supports modified by H_3PO_4; whereas Cu(I) is enriched on the surface of original activated carbon supports. The increasing ratio order of Pd(II)/Cu(II) on different surface of carbon supports were Pd–Cu–AC(P) > Pd–Cu–AC(H) > Pd–Cu–AC(400) > Pd–Cu–AC, which is consistence with the order of CO oxidation activity. It would be easily understood by taking account into the CO oxidation mechanism on support Wacker-type catalyst. Parks et al. [18] also found that the reaction rate increased linearly with increasing amounts of $CuCl_2$ relative to $PdCl_2$, a trend that persisted up to the point at which the ratio of Cu/Pd reached a value of 8. It should also be noted that the mole ratio of Cl/(Cu + Pd) on these catalysts was less than 2, which suggested to be due to the lose of Cl^- anions in catalyst preparation. The correlation between the ratio of Cl/(Pd + Cu) on the supports and the activity for CO oxidation indicated that the existence of Cl^- anion is important in stabilizing both active copper phase and the Pd(II) species.

3.5. Temperature-programmed reduction (TPR)

TPR experiments gave useful information concerning the influence of the different AC supports parameters on the reducibility of the Wacker-type active species. Fig. 4 shows the results of TPR profiles of the supported catalysts as well as the references monometallic catalysts of $CuCl_2$/AC and $PdCl_2$/AC in a temperature range from 30 to 700 °C. For the sake of comparison, the TPR profiles of pure $PdCl_2$, $CuCl_2$ and CuCl are also concluded.

Parent activated carbon has a broad reduction peak at 630 °C, which associated with the reduction of surface oxygen groups on the carbon support. The TPR of pure $PdCl_2$ powder reference compound shows a negative peak around 20 °C. It is a known fact that bulk $PdCl_2$ can be reduced by H_2 at room temperature to form β-PdHx species, which gives a negative signal upon decomposition in the TPR run [19]. H_2 consumption in the form of a positive peak centered at a T_{max} of 186 °C can be seen in the TPR pattern of $PdCl_2$/AC catalyst.

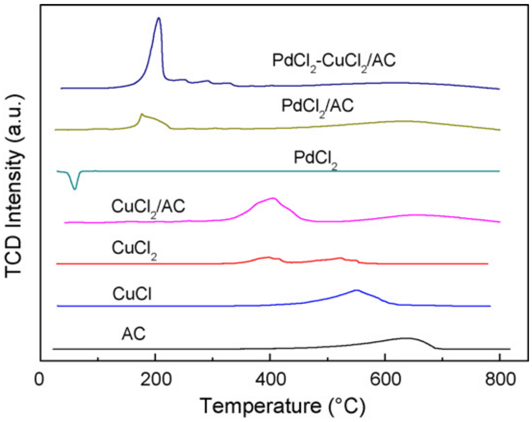

Fig. 4. TPR profiles of pure $PdCl_2$, $CuCl_2$, CuCl, $CuCl_2$/AC, $PdCl_2$/AC and $PdCl_2$–$CuCl_2$/AC.

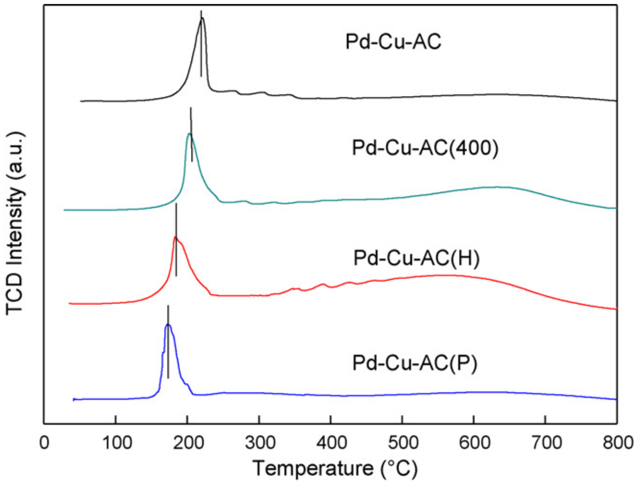

Fig. 5. TPR profiles of supported Wacker catalyst prepared by different activated carbons.

The TPR profiles of pure $CuCl_2$ powder have two-step reduction peaks at 400 and 530 °C, while pure CuCl powder has one peak at 550 °C. As compared with TPR profiles of pure $CuCl_2$ and CuCl powder, only one reduction peak was observed on $CuCl_2$/AC and shifted to the lower temperature around 390 °C for $CuCl_2$/AC. The reduction peak located at about 205 °C in the TPR profiles of $PdCl_2$–$CuCl_2$/AC catalyst can be ascribed to the reduction of Pd^{2+} into metallic palladium and Cu^{2+} to metallic copper. The reduction peaks for the Cu species on $PdCl_2$–$CuCl_2$/AC catalyst are further shifted to the lower temperatures about 205 °C as compared to $CuCl_2$/AC and $PdCl_2$/AC reference catalysts, which was suggested to be due to the strong chemical interactions among $PdCl_2$, $CuCl_2$ species and the carbon support.

TPR of four kinds of catalysts made of original and modified activated carbons as support is shown in Fig. 5. The presence of strong chemical interactions among $PdCl_2$, $CuCl_2$ species and the carbon support was already confirmed in the related reference [20]. It was known that the surface acidic groups can arouse the partial reduction of $PdCl_2$, but the presence of $CuCl_2$ inhibited the partial reduction of $PdCl_2$. The palladium species in the catalysts can significantly accelerate the reduction of the copper phase in all catalysts. The strong chemical interactions among $PdCl_2$, $CuCl_2$ species and the carbon support cause the combination of reduction peaks of Pd^{2+} and Cu^{2+} into one peak which is shown on all catalysts.

The reduction peaks presenting Cu^{2+} species reduction on $PdCl_2$–$CuCl_2$/AC, $PdCl_2$–$CuCl_2$/AC(400), $PdCl_2$–$CuCl_2$/AC(H) and $PdCl_2$–$CuCl_2$/AC(P) catalyst were 205 °C, 198 °C, 185 °C and 175 °C respectively. The shift of the Pd^{2+} and Cu^{2+} species to the lower temperature suggested the effect of the function of activated carbon supports. The lower temperature reduction peak of Cu^{2+} species presents the easier reducibility of Cu^{2+} species, which means the higher activity for CO oxidation. This correlation could be understood by taking into account the fact that the catalytic performance for the supported Wacker-type catalyst is closely related to the redox nature of the active phase.

4. Conclusion

The surface chemistry of AC can be modified by air oxidation or wet oxidation with the H_2O_2 and H_3PO_4 aqueous solution, which would affect the catalytic activity of CO oxidation at ambient temperature and high relative humidity (100%). The oxidation treatment can increase effectively the surface oxygen acidic groups on AC. It was found that the activated carbon with enriched oxygen-containing groups and macropore structure played an important role in CO catalytic oxidation. Macropore structure of catalyst support is available for the catalyst to retain the activity at high water contents, because it can decrease the pore filling with liquid and increase the gas–liquid interfacial surface area. The more active oxygen groups in activated carbon, the higher surface concentration of active Pd(II) and Cu(II) phase could enhance the catalyst activity for CO oxidation. The lower temperature of the Cu^{2+} species reduction peak presents the easy reducibility of Cu^{2+} species, which indicates the higher reactivity for CO oxidation. The presence of high surface concentration of active Pd(II) and Cu(II) phase and easy reducibility of Cu^{2+} result in the best performance (76% CO conversion) in the catalytic oxidation of CO at ambient temperature and high relative humidity.

Acknowledgements

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