

TPO–TPD study of an activated carbon-supported copper catalyst–sorbent used for catalytic dry oxidation of phenol

Jianghong Zhao, Zhenyu Liu*, Dekui Sun

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Graduate School, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China

Received 20 May 2004; revised 10 July 2004; accepted 16 July 2004

Available online 26 August 2004

Abstract

Adsorption of organic pollutants in wastewater by carbon-based catalyst–sorbents followed by in situ catalytic dry oxidation of the adsorbed pollutants to regenerate the catalyst–sorbents at low temperatures is promising for the treatment of toxic and/or biorefractory wastewater streams. This paper investigates an activated carbon-supported copper catalyst–sorbent (CuO/AC) for catalytic dry oxidation of phenol at low temperatures in a TG/MS system through temperature-programmed oxidation (TPO) and temperature-programmed desorption (TPD). Phenol oxidation activities and ignition characteristics of the catalyst–sorbent were mainly discussed. The results indicate that the CuO/AC catalyst–sorbent has high catalytic activities for phenol oxidation and for AC ignition compared to the AC support itself; the initial oxidation temperature for phenol is about 190 °C, which is 130 °C lower than that for the AC. Consecutive adsorption–oxidation experiments show that the phenol adsorption capacity of the CuO/AC catalyst–sorbent decreases from an initial value of about 140 mg/g to a stable value of about 70 mg/g in 9 cycles, which is much better than the performance of activated carbon reported in the literature. TPD results indicate that phenol molecules adsorb on different types of active sites on AC and CuO/AC catalyst–sorbent. CuO plays an important role both in enhancing the affinity between phenol and CuO/AC catalyst–sorbent during phenol adsorption and in promoting catalytic activity for phenol oxidation.

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Keywords: Catalytic dry oxidation; Carbon-supported catalyst; Phenol; Wastewater; Carbon-based sorbent

1. Introduction

Phenol and phenolic compounds are a group of organic pollutants that often appear in wastewaters from many heavy chemical, petrochemical, and oil refining industries. Because of their toxicity and poor biodegradability [1], phenolic wastewaters must be specially treated before disposing off. However, conventional treatments cannot be carried out because these polluting agents in high concentrations are not appropriate for direct biological treatment, or in low concentrations are not economically feasible for recovery [2].

Wet air oxidation (WAO) is a well-established technique to decompose toxic and/or nonbiodegradable organic compounds in wastewaters, which requires high temperatures (125–320 °C) and pressures (0.5–2.0 MPa) conditions, and consequently carries a high cost [3–5]. Catalytic wet air oxidation (CWAO) is emerging as an alternative to WAO. It can reduce COD/TOC to the same degree as in the case of a WAO process but at milder pressure and temperature conditions due to the presence of a catalyst, and thus is more economical than WAO. However, CWAO has not been largely implemented for wastewater treatment for lack of suitable catalysts, which are active and durable under the operating conditions [5–9].

Catalytic dry oxidation of organic pollutants adsorbed on regenerable catalyst–sorbents has been reported to be promising for treatment of toxic and/or biorefractory waste-

* Corresponding author. Fax: +86 351 4050320.
E-mail address: zyliu@sxicc.ac.cn (Z. Liu).

water streams [10–12]. This is a discontinuous two-step process, including adsorption of organic pollutants in water for a long period of time and catalytic dry oxidation of the pollutants adsorbed on the catalyst–sorbents in a short period of time after discharging the water from the adsorption tower [13]. In this process, the pollutants adsorbed can be oxidized into CO₂ and H₂O by air under much milder conditions than those for CWAO, and at the mean time the catalyst–sorber is regenerated. Because of the integration of the adsorption and the catalytic dry oxidation in the same unit, this process has many advantages, such as [5,9,11]: the oxidation process is accelerated by the high concentrations of pollutants adsorbed on the catalyst–sorbents; a large number of adsorption–regeneration cycles can be realized under much mild operating conditions; the in situ oxidation avoids shipment of spent catalyst–sorbents to a special regeneration unit; heating of whole water body to the temperature of oxidation is not necessary; high operating pressure is not necessary due to high oxygen concentration in the gas phase (air, for example) compared to that in the liquid phase in wet oxidation; reduced leaching of catalyst components due to low adsorption temperature and pressure. These advantages largely improve the economy of the process.

Adsorption has been frequently applied in wastewater treatment for many years. Many types of adsorbents (such as polymeric resins and mixed oxides [12,14]) have been used; however, activated carbon (AC) is the common choice because of its superior adsorption capacity. Adsorption by activated carbons is widely used for removing phenol from aqueous solutions [15,16]. It is well known that activated carbon can be used as a support in the preparation of oxidation catalysts [17]. Hence, activated carbon-supported metal catalyst–sorber seems to be a good choice for the treatment of phenol wastewaters using a catalytic dry oxidation process. In such cases, suitable metal/AC catalyst–sorbents should have: (1) high adsorption capacities for phenol; (2) high activities for low-temperature oxidation of the adsorbed phenol; and (3) high resistance to self-burn off under oxidation conditions.

Since Cu-based catalysts show significant activities for the catalytic oxidation of phenol [18–24], this paper studies an AC-supported copper catalyst–sorber through temperature-programmed oxidation (TPO) and temperature-programmed desorption (TPD) in a TG/MS system. Phenol oxidation activities are mainly discussed. As Cu has catalytic activity in carbon gasification [25–27], the ignition characteristics of the catalyst–sorber are also discussed. Adsorption–oxidation experiments are performed to investigate the catalytic activity and stability of CuO/AC catalyst–sorber. Finally, the role of CuO and the behavior of phenol desorption are investigated to understand the mechanism of catalytic dry oxidation of phenol better.

2. Experimental

2.1. Materials

The granular activated carbon used in this work is a commercial product from Xinhua Chemical Plant (Taiyuan, China), which was crushed into particles of 40–60 meshes (0.3–0.45 mm) before use. BET surface area and chemical constitution of the AC are shown in Table 1. The metal salts and phenol used in the study are analytical grade and were used without further purification.

2.2. Preparation of CuO/AC catalyst–sorber

Copper oxide was supported on the AC by pore volume impregnation using an aqueous copper(II) nitrate solution, followed by drying in air at 50 °C for 12 h, and then at 110 °C for 12 h, finally by calcinating in Ar at 250 °C for 2 h. Metal loadings in the catalyst–sorbents were determined by the concentration of the copper nitrate solution used in the impregnation. The prepared CuO/AC catalyst–sorber contains 5 wt% of Cu and is termed Cu5/AC.

2.3. Preparation of phenol-adsorbed catalyst–sorbents

The phenol-adsorbed catalyst–sorbents were obtained in batch adsorption experiments in an aqueous phase with a phenol concentration of 500 mg/L. The experiment was carried out in a thermostatic automatic shaker at 25 °C for 1 day. The phenol-adsorbed particles were separated out from the aqueous phase by filtration, and then dried in air at 25 °C to constant weight. Phenol loading on the samples was determined from the difference in phenol concentration of the aqueous solutions before and after the adsorption measured on a UV spectrometer ($\lambda_{\text{max}} = 270 \text{ nm}$).

The samples with phenol are termed AC-phe and Cu5/AC-phe, and the samples without phenol are termed AC-blank and Cu5/AC-blank, for AC and Cu5/AC, respectively.

2.4. Experimental procedures

The temperature-programmed oxidation and the temperature-programmed desorption experiments were carried out in a TG/MS coupling system. The TG apparatus is a Setaram TGA 92 analyzer and the MS is a Balzers QMG 422 quadrupole mass spectrometer. Samples of 15–25 mg were heated from room temperature to 600 °C at a rate of 10 °C/min under a flow of air/Ar (10% O₂, 12 ml/min).

Consecutive adsorption–oxidation cycles were also carried out. The adsorption process is the same as that shown

Table 1
BET surface area and chemical constitution of the AC

Activated carbon	BET (m ² /g)	Micropore volume (ml/g)	Ash (wt%)	C (%)	H (%)	N (%)	S (%)	O (%) (diff)
AC	936	0.300	8.32	88.47	0.50	0.43	0.46	1.82

in subsection 2.3 except that the phenol concentration of the solution is 1500 mg/L and the adsorption period is 3 days to ensure equilibrium [11]. The adsorption capacity, q , defined as the mass of adsorbate per gram of adsorbent (mg/g), is calculated using

$$q = \frac{(C_0 - C_e)V}{M}, \quad (1)$$

where V is the volume of solution used in liters, C_0 and C_e are the initial and equilibrium phenol concentrations in milligrams per liter, and M is the weight of Cu5/AC catalyst-sorbent in grams.

The catalytic dry oxidation in the consecutive adsorption-oxidation cycles was carried out in a fixed-bed quartz reactor (8 mm i.d.) coupled with a Balzers QMG 422 quadrupole mass spectrometer to investigate the evolved gases. The phenol-adsorbed Cu5/AC catalyst-sorbent (about 0.50 g) was oxidized in an oxidant gas stream (5% oxygen in helium, 70 ml/min) at 260 °C for 1 h.

2.5. Characterization of the catalyst-sorbents

BET surface area and micropore volume of the AC support were measured through nitrogen adsorption at 77 K using an ASAP2000 surface area analyzer. C, H, N, and S contents of the AC were measured on a Vario EL from Elemental Analysensysteme GmbH.

X-ray diffraction patterns (XRD) were obtained on a Rigaku computer-controlled D/max 2500X using Cu-K α as the radiation source. The applied current and voltage were 100 mA and 40 kV, respectively. During the analysis, the sample was scanned from 5 to 85° at a speed of 0.4° min⁻¹. X-ray photoelectron spectroscopy measurements (XPS) were carried out on a PHI-5300/ESCA system using Al-K α radiation (1486.6 eV). The vacuum in the analysis chamber was 2.9×10^{-7} Pa.

3. Results and discussion

3.1. Characterization of surface copper species

XRD was carried out to examine the crystalline structure of the catalyst. Fig. 1 shows the XRD pattern of Cu5/AC catalyst-sorbent. The low signal to noise ratio reveals low crystallinity of the sample. The presence of CuO diffraction peaks indicates that CuO is the main component of the copper species in the catalyst-sorbent.

XPS was conducted to provide information on the oxidation state of copper species. Fig. 2 shows Cu 2p spectrum of Cu5/AC catalyst-sorbent, where the peak at 933.53 eV is assigned to 2p_{3/2} of Cu²⁺ in the form of CuO. The well-defined shake-up satellites observed at ca. 7.5 and 9.8 eV on the high binding energy side of the copper core line 2p_{3/2} (centered at 933.53 eV) are typical of Cu²⁺ species and due to multiplet splitting. The existence of these strong satellite

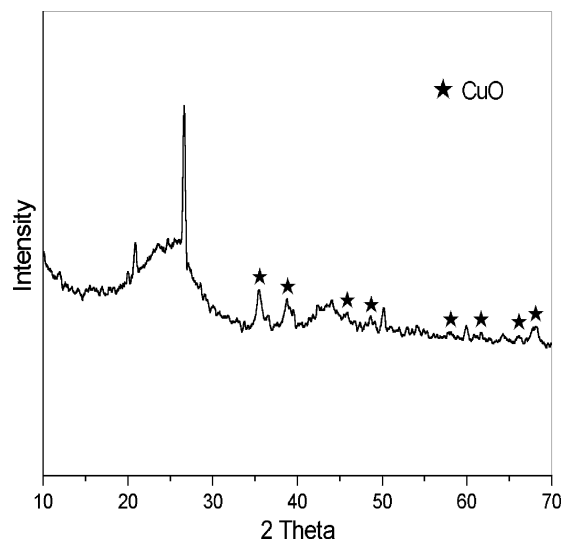


Fig. 1. XRD patterns of CuO/AC catalyst-sorbent.

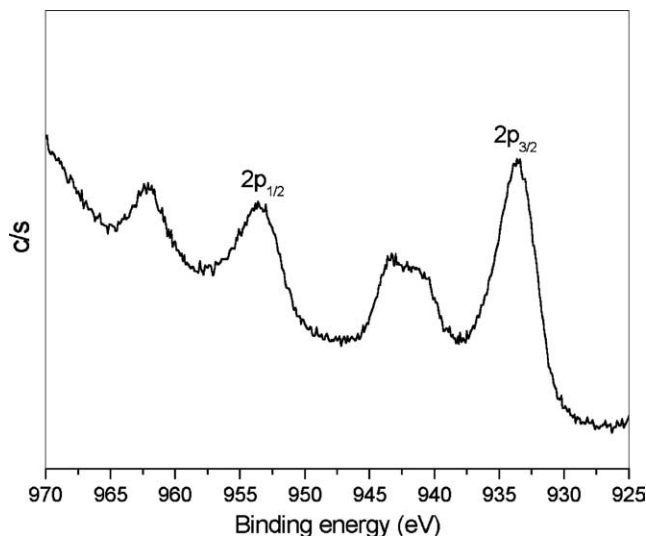


Fig. 2. XPS spectra of Cu 2p of the CuO/AC catalyst-sorbent.

features for Cu 2p rules out the possibility of the presence of Cu₂O phase [28]. The peaks at about 953.6 and 962.1 eV are attributed to Cu²⁺ 2p_{1/2} in CuO and its satellite peak, further confirming the existence of CuO species in the Cu5/AC catalyst-sorbent [29]. All this information shows that the copper species in the Cu5/AC catalyst-sorbent is mainly in the form of CuO.

3.2. Phenol oxidation activities and ignition characteristics of Cu5/AC catalyst-sorbent

To understand the phenol oxidation activities and ignition characteristics of Cu5/AC catalyst-sorbent better, it is important to introduce two characteristic temperatures, the initial oxidation temperature of the adsorbed phenol (T_{ip}) and the initial ignition temperature of the AC skeleton (T_{ic}) [30]. These two temperatures are defined based on

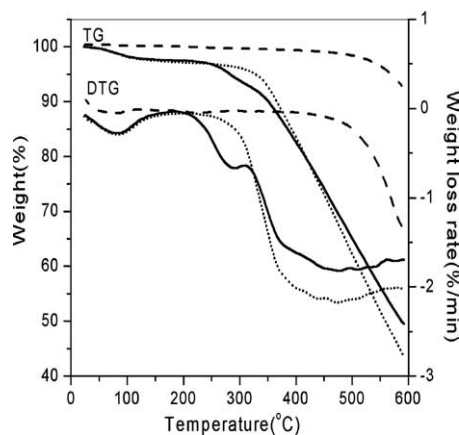


Fig. 3. TG/DTG curves for samples in TPO: (dash) AC-phe; (dot) Cu5/AC-blank; (solid) Cu5/AC-phe.

TG/DTG curves. T_{ip} is the temperature where the second DTG peak for Cu5/AC-phe begins to deviate from the DTG curve for Cu5/AC-blank. T_{ic} is the temperature of an inflection point in TG curves, which is accompanied by a sharp weight loss of carbon beyond this temperature.

Fig. 3 shows TG/DTG profiles obtained in the TPO experiments. The samples used are Cu5/AC-blank, Cu5/AC-phe, and AC-phe each adsorbed with about 5 wt% phenol. Fig. 4 shows MS signals of CO_2 (m/e 44), benzene (C_6H_6 , m/e 78), and phenol ($\text{C}_6\text{H}_6\text{O}$, m/e 94) corresponding to the data in Fig. 3. The sample AC-phe shows a weight loss of less than 2 wt% at temperatures below 500 °C and no significant peaks in the corresponding DTG curve, but the corresponding MS curves show evolution of $\text{C}_6\text{H}_6\text{O}$ and C_6H_6 starting at around 250–300 °C and peaks at about 390 and 440 °C, respectively. Significant evolution of CO_2 (m/e 44) starts at about 500 °C. These data indicate that the AC has no activity on oxidation of phenol and its ignition starts at about 500 °C, only a small fraction of the adsorbed phenol desorbs and/or dissociatively desorbs from the AC, and a large fraction of the adsorbed phenol remains on the AC before the AC ignition.

Compared to AC-phe, Cu5/AC-blank shows a low initial ignition temperature, at about 310–320 °C, suggesting a high catalytic effect of CuO on oxidation of AC. Meanwhile, the absence of MS signals for C_6H_6 and $\text{C}_6\text{H}_6\text{O}$ suggests that AC itself does not emit these compounds during the TPO.

TG/DTG profiles of Cu5/AC-phe show a significant weight loss starting at around 190 °C and a DTG peak at 280 °C. The weight loss recorded for this peak, from 190 to 320 °C, is about 5 wt%. After subtracting the weight loss of Cu5/AC-blank in the same temperature range, a weight loss of about 3.1 wt% is obtained, which corresponds to about 65–70% of the phenol adsorbed on the catalyst–sorber. Furthermore, in the corresponding MS curves, there is no phenol and benzene evolution in the temperature range of up to 600 °C, but a CO_2 peak starting at around 190 °C and peaking at 280 °C. These suggest that the adsorbed phenol is mostly oxidized into CO_2 and H_2O in the temperature range

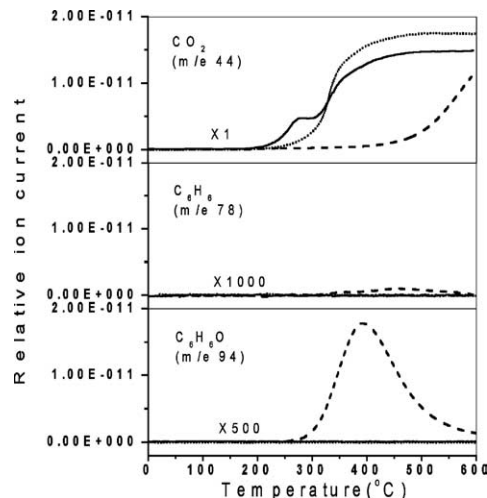


Fig. 4. MS curves for samples in TPO dash: AC-phe; dot: Cu5/AC-blank; solid: Cu5/AC-phe.

of 190 to 320 °C, and 30–35% of the adsorbed phenol or its decomposition residue remains on the catalyst–sorber before ignition of the AC support. The second DTG peak for Cu5/AC-phe, which starts at around 320 °C and is accompanied by a large amount of CO_2 release, suggests ignition of the AC support.

It is clear that the Cu species on the AC surface catalyze oxidation of the adsorbed phenol and the AC. The initial oxidation temperature for phenol is about 190 °C, which is 130 °C lower than the ignition temperature of the AC. Under the TPO conditions, about 65% phenol adsorbed on the Cu5/AC is oxidized prior to the ignition of AC. These imply that catalytic dry oxidation of the spent Cu5/AC catalyst–sorber is possible and can be achieved at temperatures below 300 °C.

3.3. Activity and stability of Cu5/AC catalyst–sorber during adsorption–oxidation cycles

To understand the catalytic activity and stability of Cu5/AC catalyst–sorber, adsorption–oxidation experiments were carried out consecutively for 12 cycles. The oxidation was performed at 260 °C for 1 h. Cycle 0 is the fresh state of Cu5/AC catalyst–sorber.

The results, in Fig. 5, show that the adsorption capacity decreases with increasing number of adsorption–oxidation cycles, but reaches to a steady state value of ca. 70 mg/g after 9 cycles, which corresponds to about 50% of the initial adsorption capacity. This behavior is not ideal, but is much better than those reported for thermal regeneration [31,33]. It is important to note that the oxidation results presented in Fig. 5 are much more effective than those determined in Fig. 3. In the first cycle in Fig. 5, about 82% of the adsorbed phenol is oxidized, while 65–70% oxidation efficiency is determined from Fig. 3. These data suggest that the oxidation efficiency of the phenol is related to the oxidation temperature and time. The longer oxidation time (1 h) at 260 °C for

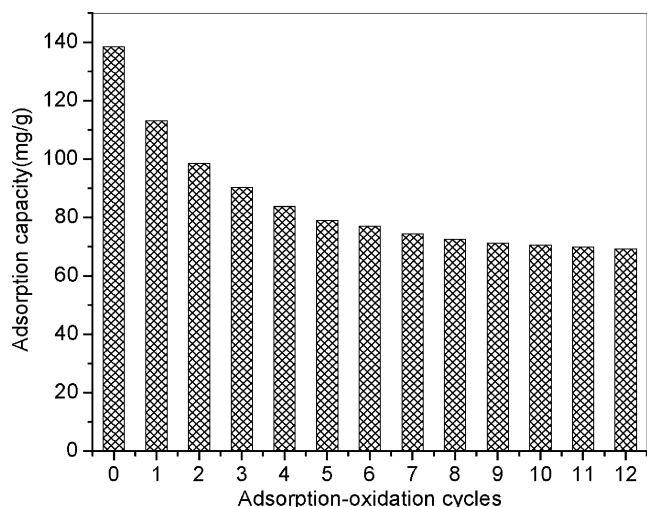


Fig. 5. Adsorption capacity for CuO/AC catalyst-sorbent during twelve adsorption-oxidation cycles.

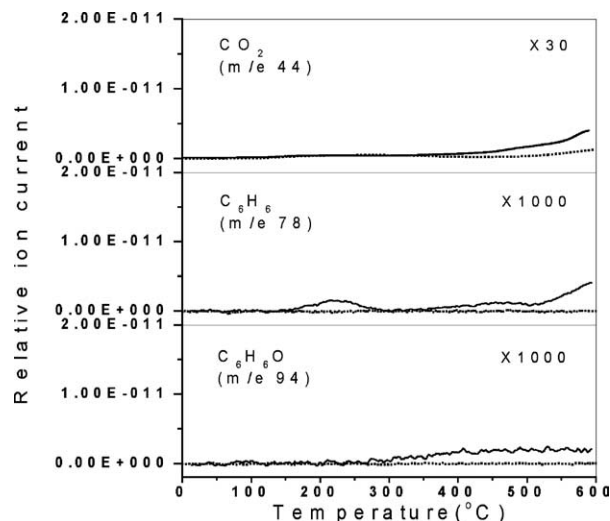


Fig. 7. MS curves for samples in TPD dot: AC-blank; solid: AC-phe.

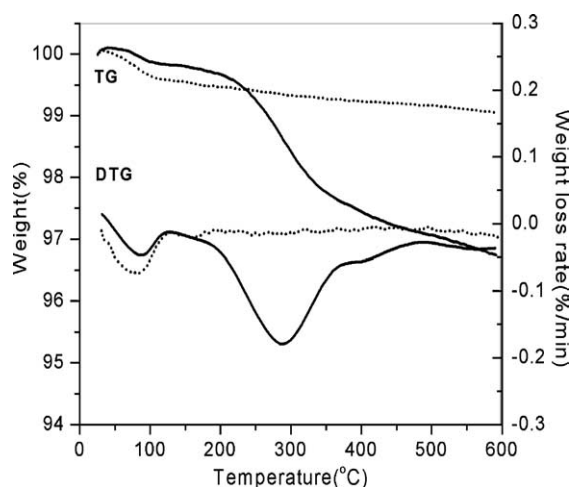


Fig. 6. TG/DTG curves for samples in TPD (dot) AC-blank; (solid) AC-phe.

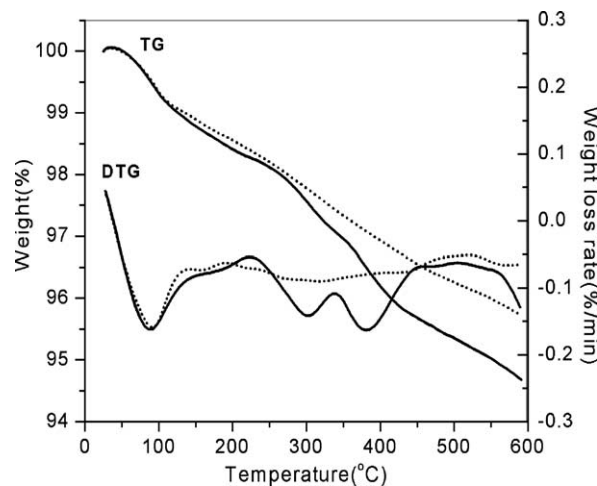


Fig. 8. TG/DTG curves for samples in TPD (dot) Cu5/AC-blank; (solid) Cu5/AC-phe.

the data in Fig. 5 is the main reason for the increase in phenol oxidation efficiency. The gas analysis performed in the oxidation step during the 12 cycles confirms that the adsorbed phenol removed from the catalyst-sorbent in the oxidation is decomposed to CO₂ and H₂O.

3.4. Role of CuO in phenol adsorption and oxidation

TPO results presented in Figs. 3 and 4 show that Cu5/AC catalyst-sorbent has significant catalytic activity for phenol oxidation and the presence of CuO is very important. It is logical to believe that the presence of CuO also affects phenol adsorption. To understand the role of the CuO in phenol adsorption and oxidation, several TPD experiments were conducted.

Figs. 6–9 are TPD results of AC-blank, AC-phe, Cu5/AC-blank, and Cu5/AC-phe under Ar environment. Fig. 6 shows that, except for the first DTG peak at about 80°C corresponding to the desorption of H₂O, AC-blank undergoes

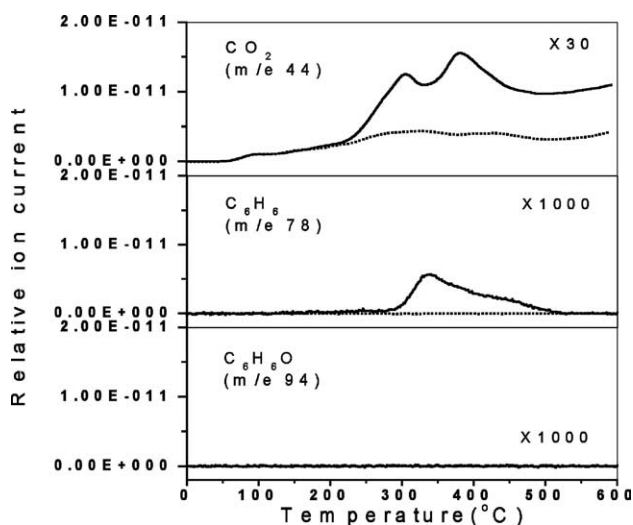


Fig. 9. MS curves for samples in TPD dot: Cu5/AC-blank; solid: Cu5/AC-phe.

only a slight weight loss (about 0.5 wt%) possibly due to destruction of some oxygen-containing surface functional groups [32], as suggested by the weak CO₂ release shown in Fig. 7. These results indicate that the employed AC is of low oxygen content, which is consistent with the data in Table 1. The absence of MS peaks of C₆H₆ and C₆H₆O suggests that the AC itself does not emit these compounds during the TPD.

The TG curve of AC-phe (Fig. 6) shows an additional weight loss of about 2.5 wt% compared to AC-blank, which is about 50% of the adsorbed phenol. This may indicate that about half of the adsorbed phenol may desorb and/or dissociatively desorbs from the AC during the heating up to 600 °C in Ar. Some other phenomena were observed during the TPD of AC-phe: The absence of C₆H₆O peaks (Fig. 7) at temperatures below 300 °C indicates that the interactions between phenol and AC is strong, and phenol molecules mainly chemisorbed on the surface; The TG/DTG curves (Fig. 6) show a comparably larger weight loss (about 2 wt%) between 170 and 380 °C and a DTG peak at about 290 °C, but the corresponding MS curves (Fig. 7) show very limited C₆H₆O, C₆H₆, and CO₂ evolutions and no peaks of C₆H₆O, C₆H₆, and CO₂ corresponding to the DTG peak. These seem to suggest that the phenol adsorbed on the AC undergoes transformation in TPD, which results in release of some other volatile compounds not detected by MS [33,34]. The CO₂ evolution beyond 320 °C suggests that some oxygen surface groups of the AC participate in the phenol degradation processes [33]. In addition, it is important to note that the TG/DTG, C₆H₆O, and C₆H₆ profiles of AC-phe in TPD (Figs. 6 and 7) are very different from those in TPO (Figs. 3 and 4). The TPD results show more weight loss but less C₆H₆O and C₆H₆ evolution. These differences indicate that oxygen plays important roles in phenol desorption and dissociative destruction.

The TG curve in Fig. 8 show that Cu5/AC-blank undergoes a weight loss of about 4.3 wt% and the phenol-adsorbed sample, Cu5/AC-phe, results in only an additional 1 wt% weight loss at temperatures greater than 225 °C. Compared to the weight loss of AC-phe (about 2.5 wt%), it suggests that CuO enhances the affinity between phenol and Cu5/AC catalyst-sorbent. The result is in agreement with the reports that metal species may act as active centers and/or alter the electronic nature of AC surface, possibly through anchoring to the π system of the carbon-supported basal planes [35], which plays an important role in phenol adsorption, implying “ π - π interactions” and a “donor-acceptor complex” mechanism [36], and therefore enhance the affinity between phenol and CuO/AC catalyst-sorbent. The MS curve of CO₂ for Cu5/AC-blank shows overlapping desorption peaks in the whole temperature range, and the peak intensities are stronger than those for AC-blank, indicating that more oxygen in the catalyst-sorbent participates in the TPD in the presence of CuO. For Cu5/AC-phe, the TG/DTG and MS curves of CO₂, with two DTG peaks and two CO₂ peaks at about 306 and 383 °C, respectively, show that about 0.8 wt% of the adsorbed phenol is oxidized to CO₂ possibly using

oxygen in CuO, and small amounts of the adsorbed phenol is decomposed to benzene. Meanwhile, C₆H₆O does not evolve in the whole temperature range. These results suggest again the role of oxygen in desorption and dissociative destruction of phenol, and also indicate that there are mainly two types of CuO containing active sites, which are likely to be responsible for the high activities of Cu5/AC catalyst-sorbent for phenol oxidation.

4. Conclusions

CuO/AC catalyst-sorbent is promising for catalytic dry oxidation of phenol. It is found in this work that: (1) the AC used has no phenol oxidation activity prior to its own combustion; (2) the CuO supported on AC has high catalytic activity on oxidation of both phenol and AC; (3) phenol adsorbed on Cu5/AC can be oxidized starting at about 190 °C, about 130 °C lower than AC ignition; (4) Cu5/AC catalyst-sorbent has high catalytic activity for phenol oxidation and is stable during adsorption-oxidation cycles; the steady-state adsorption capacity in consecutive adsorption-oxidation cycles is about 70 mg/g; (5) there are mainly two types of CuO-containing active sites, which are likely to be responsible for the high activities of Cu5/AC catalyst-sorbent for phenol oxidation; (6) CuO plays an important role both in enhancing the affinity between phenol and Cu5/AC catalyst-sorbent during phenol adsorption and in promoting catalytic activity for phenol oxidation.

Acknowledgments

The authors express their grateful appreciation for financial support from the Natural Science Foundation of China (20276078), and to Prof. Bijiang Zhang for his useful suggestions.

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