Catalytic dry oxidation of aniline, benzene, and pyridine adsorbed on a CuO doped activated carbon

Bingzheng Li*,**, Zhenyu Liu*,***,†, Zhiping Lei*,****, and Zhanggen Huang*

*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences,
Taiyuan 030001, P. R. China
**Graduate University of Chinese Academy of Sciences, Beijing 100049, P. R. China
***State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology,
Beijing 100029, P. R. China
****School of Chemical & Chemistry, Anhui university of Technology, Maanshan, 243002, P. R. China
(*Received 31 July 2008 • accepted 27 December 2008*)

Abstract−Adsorption of aniline, benzene and pyridine from water on a copper oxide doped activated carbon (CuO/AC) at 30 °C and oxidation behavior of the adsorbed pollutants over CuO/AC in a temperature range up to 500 °C are investigated in TG and tubular-reactor/MS systems. Results show that the AC has little activity towards oxidation of the pollutants and CuO is the active oxidation site. Oxidation of aniline occurs at 231-349 °C and yields mainly CO_2, H_2O and N_2. Oxidation of pyridine occurs at a narrower temperature range, 255-309 °C, after a significant amount of desorption starting at 150 °C. Benzene desorbs at temperatures as low as 105 °C and shows no sign of oxidation. The result suggests that adsorption-catalytic dry oxidation is suitable only for the strongly adsorbed pollutants. Oxidation temperatures of CuO/AC for organic pollutants are higher than 200 °C and pollutants desorbing easily at temperatures below 200 °C cannot be treated by the method.

Key words: Catalytic Dry Oxidation, CuO Doped Catalyst, Aniline, Benzene, Pyridine, Desorption

INTRODUCTION

There are usually many aromatic compounds in wastewater streams from chemical factories [1]. These compounds are toxic and/or carcinogenic [2] and should be effectively removed before discharging of the streams. Many techniques including adsorption [3], aerobic and anaerobic biodegradation [4], ion exchange [5], wet air oxidation [6] as well as supercritical wet oxidation [7] have been developed for such a purpose, but the widely used method is adsorption by activated carbons (ACs) [8]. Among various types of AC-based methods, a method for integrating adsorption of organic pollutants on an AC, followed by catalytic dry oxidation of the organic pollutants upon discharging of water (termed adsorption-catalytic dry oxidation, ACDO in short) was found to be promising especially for wastewaters of low pollutant concentrations [9-13]. The ACDO method has a number of advantages including low energy consumption, repeat use of the sorbent/catalyst, and reduced leaching of catalyst component from the sorbent. Our earlier studies [11,13] showed that a CuO doped activated carbon (CuO/AC) sorbent/catalyst is capable to adsorb a significant amount of phenol from wastewater at room temperature and to oxidize the adsorbed phenol into CO_2 and H_2O at temperatures below 300 °C. It is of interest, therefore, to see the CuO/AC's ability to adsorb and oxidize other organic pollutants.

In this work, three organic compounds, aniline, pyridine and benzene, are adsorbed and tested through temperature programmed oxidation (TPO) and temperature programmed desorption (TPD) with the aid of mass spectroscopy to understand their oxidation behaviors over CuO/AC.

EXPERIMENTAL

1. Materials

Analytical grade aniline, benzene, and pyridine were used. These compounds were dissolved separately into distilled water to yield aqueous solutions with a concentration of 1,000 mg/L for each pollutant.

The AC used was a commercial product from Xinhua Chemical Factory (Taiyuan, China), which was crushed into particles of 40-60 mesh (0.3-0.45 mm) and dried in air at 110 °C for 48 h.

2. Preparation of CuO/AC and Pollutant-adsorbed CuO/AC

CuO/AC were prepared by pore volume impregnation of the AC with an aqueous copper (II) nitrate solution, followed by aging at room temperature for 2 h, drying in air at 50 °C and at 110 °C for 6 h, respectively, and finally calcining in N_2 at 250 °C for 2 h. Cu loading of the prepared CuO/AC is 5 wt%, which was determined by the concentration of the copper (II) nitrate solution used in the impregnation.

The pollutant-adsorbed AC and CuO/AC were prepared in batch adsorption experiments in the aqueous solutions with an initial pollutant concentration of 1,000 mg/L. 0.500 g AC or CuO/AC was submerged in a 50 ml aqueous solution in a 50 ml flask, which was continuously agitated by a thermostatic automatic shaker at 30 °C and 150 rpm for 3 days. The pollutant-adsorbed sample was then separated out from the solution by filtration, and then subjected to

drying in air at 30 ℃ to a constant weight. The AC adsorbed with aniline, benzene and pyridine are termed AC-ani, AC-ben and AC-pyr, respectively, while the CuO/AC adsorbed with aniline, benzene and pyridine are termed CuO/AC-ani, CuO/AC-ben and CuO/AC-pyr, respectively. The AC and CuO/AC submerged in distilled water at conditions the same as these pollutant-adsorbed samples were prepared and termed AC-blank and CuO/AC-blank, respectively.

The amount of a pollutant adsorbed on a sample was determined from the difference in the pollutant concentration in the aqueous solution before and after the adsorption, which were measured on a UV-Vis spectrometer (Techcomp UV2300, China). The wave length for aniline, benzene and pyridine measurements was 230 nm, 200.4 nm and 252 nm, respectively. The adsorption capacity of a pollutant on AC or CuO/AC (q_e) is defined as the amount of a pollutant adsorbed on these solid samples in mg/g and calculated by using

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where C_i and C_e are initial and equilibrium concentrations of the solution in mg/L, respectively, and V is volume of the solution used in L and M mass of the sample in g.

3. Experimental

Temperature-programmed oxidation (TPO) experiments were carried out in a TG system to investigate weight loss behavior of samples. The TG apparatus is an STA 409 PC analyzer (NETZSCH). A sample of about 20 mg was loaded in the TG and was heated from room temperature to 500 ℃ at a rate of 10 ℃/min under a flow of O_2/Ar (5% O_2, 12 ml/min).

A tubular-reactor/MS system was used for the study under the same conditions as that of the TG system, which contains a tubular-quartz reactor of 6 mm in id and 370 mm in length, and a Balzers QMG 422 quadrupolar mass spectrometer. Temperature-programmed desorption (TPD) was also carried out in the system under an Ar stream (99.99%) at the same conditions.

Pore volume and Brunauer Emmett Teller (BET) surface area of the AC and CuO/AC were measured through nitrogen adsorption at 77 K by using an ASAP 2000 surface area analyzer (USA). The pore volume was calculated by density-function-theory (DFT).

X-ray diffraction (XRD) patterns of the samples were obtained on a Rigaku computer-controlled D/max 2500X using Cu-Kα as the radiation source. The applied current and voltage were 100 mA and 40 kV, respectively. The sample was scanned from 5 to 85 ℃ at a speed of 0.4°/min.

RESULTS AND DISCUSSION

### 1. Characterization of the AC and CuO/AC

Table 1 shows texture parameters of the AC and CuO/AC. Compared to the AC, pore volume and BET surface area of CuO/AC are significantly small, indicating filling of the AC's pores by CuO.

Table 1. BET surface area and texture parameters of adsorbents

Samples	S_{BET} m²/g	V_{mic} ml/g	V_{mes} ml/g
AC	936	0.304	0.113
CuO/AC	786	0.249	0.069
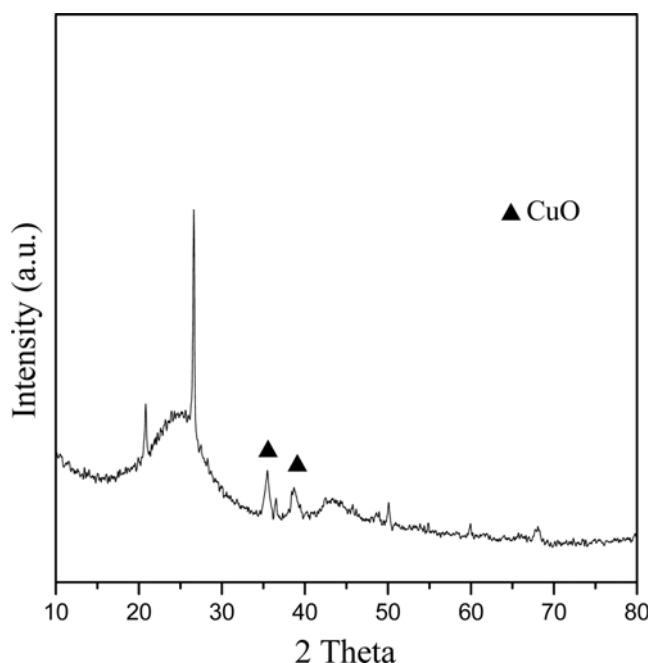
Fig. 1. XRD patterns of CuO/AC.
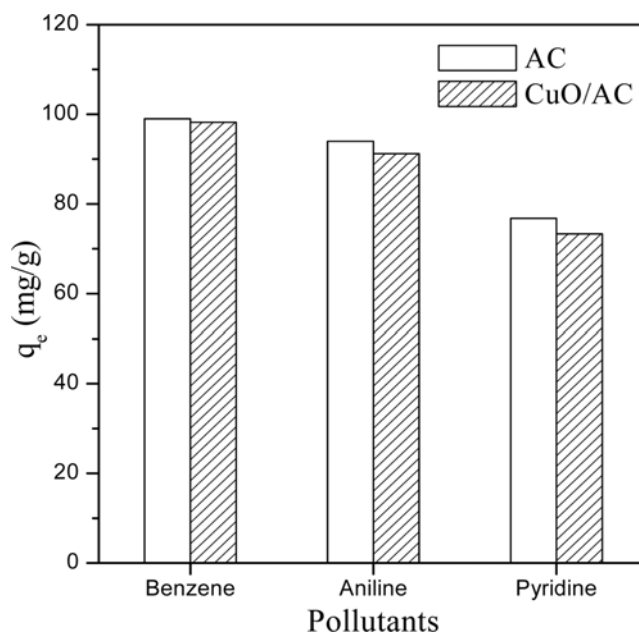
Fig. 2. Equilibrium adsorption of benzene, aniline and pyridine on AC and CuO/AC at 30 ℃ with an initial concentration of 1,000 mg/L.

Fig. 1 shows XRD pattern of CuO/AC. The presence of CuO diffraction peaks and the low signal to noise ratio indicates the CuO is finely dispersed on the AC.

2. Adsorption of Pollutants

Fig. 2 shows amounts of aniline, benzene and pyridine adsorbed on the AC and CuO/AC at equilibrium with an initial concentration of 1,000 mg/L. Apparently, supporting CuO on the AC affects adsorption of these compounds only a little, resulting in small adsorption reductions. The amount of benzene adsorption is the largest,

98.2 mg/g corresponding to a 98% removal from the solution, while that of pyridine is the lowest, 73.3 mg/g corresponding to a 73% removal from the solution.

3. Oxidation Behavior

3-1. Oxidation of Aniline

Fig. 3 shows TG/DTG-MS curves for TPO of CuO/AC-ani and CuO/AC-blank. It can be seen in Fig. 3(b) that compared to CuO/AC-blank, CO_2 release from CuO/AC-ani starts at about 231 °C, reaches a plateau at 305 °C and then speeds up at 349 °C, indicating an initial oxidation temperature of 231 °C for aniline and an initial
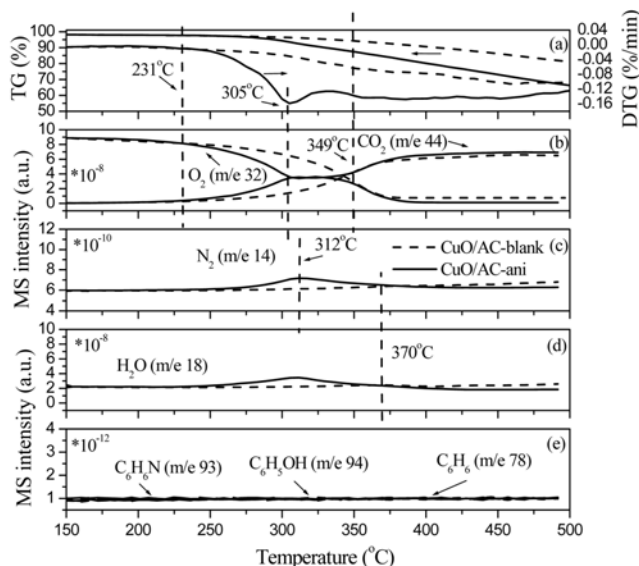
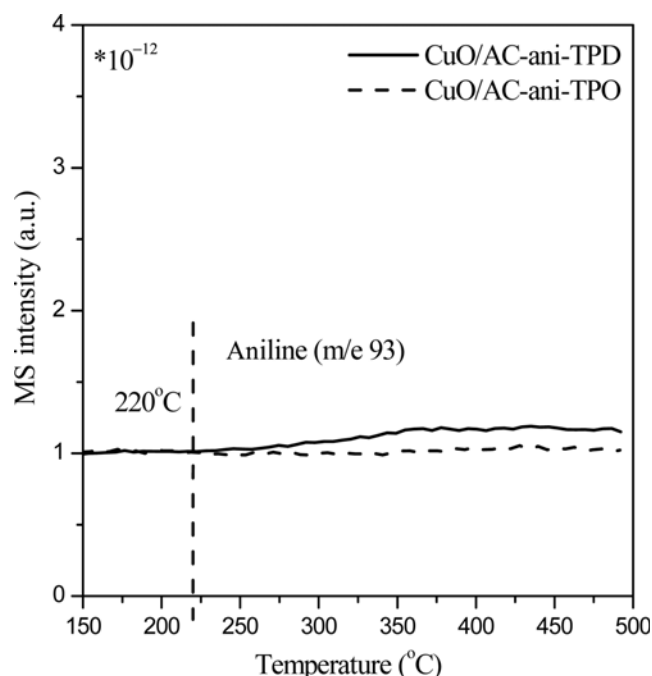**Fig. 3. TG/DTG-MS profiles for TPO of CuO/AC-blank (dot) and CuO/AC-ani (solid).**

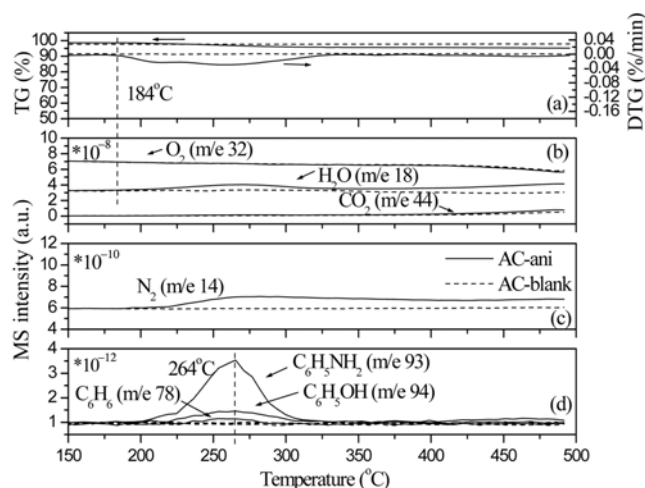**Fig. 4. MS profiles of aniline evolution for CuO/AC-ani in TPO and TPD.**

Fig. 5. TG/DTG-MS profiles for TPO of AC-blank (dot) and AC-ani (solid).

ignition temperature of 349 °C for AC. DTG profile (Fig. 3(a)) of CuO/AC-ani also starts to deviate from that of CuO/AC-blank at around 231 °C and shows a peak at 305 °C. The weight loss recorded for this peak, in a temperature range of 231-349 °C, is about 10.5 wt%. After subtracting weight loss of CuO/AC-blank in the same temperature range, a net weight loss of about 6.8 wt% for CuO/AC-ani is obtained, which corresponds to 74.7% aniline adsorbed on the CuO/AC. Fig. 3(c)-(e) shows similar N_2 and H_2O releases, starting at about 231 °C and peaking at 312 °C, and the absence of aniline, benzene, and phenol releases. TPD of aniline (Fig. 4) further shows that aniline desorbs from CuO/AC at temperatures higher than 220 °C. Clearly, these data indicate that desorption of aniline is inhibited by O_2, and the adsorbed aniline can be mainly oxidized into CO_2, N_2 and H_2O at a temperatures window of 231-349 °C. Compared to wet air oxidation of aniline (at 5 MPa, 200 °C) [14], the catalytic oxidation over CuO/AC can be effectively operated at an ambient pressure.

To understand the role of CuO, AC-ani and AC-blank were also subjected to TPO; the TG/DTG-MS profiles obtained are shown in Fig. 5. Similar O_2 and CO_2 release profiles for AC-ani and AC-blank in Fig. 5(b) indicate little oxidation for aniline. The DTG profile of AC-ani in Fig. 5(a) starts to deviate from that of AC-blank at around 184 °C and shows a DTG peak at about 264 °C. This trend is the same as that for evolutions of aniline, phenol and benzene in Fig. 5(d). The higher initial oxidation temperature of aniline on CuO/AC-ani (in Fig. 3) than the desorption temperature of aniline from AC-ani in (Fig. 5) suggests promotion of aniline adsorption strength by CuO. These data along with the small evolutions of H_2O and N_2 indicate that the AC has a very limited catalytic activity for aniline oxidation.

3-2. Oxidation of Benzene

MS profiles of CuO/AC-ben and CuO/AC-blank in TPO experiments are shown in Fig. 6. Compared to CuO/AC-blank, CuO/AC-ben shows significant benzene desorption in a temperature range of 105-275 °C with a peak at 196 °C. The similar O_2, CO_2 and H_2O curves at temperatures below about 196 °C and the slightly higher O_2 consumption and the slightly more CO_2 and H_2O releases at temperatures higher than 196 °C suggest that only a small amount of
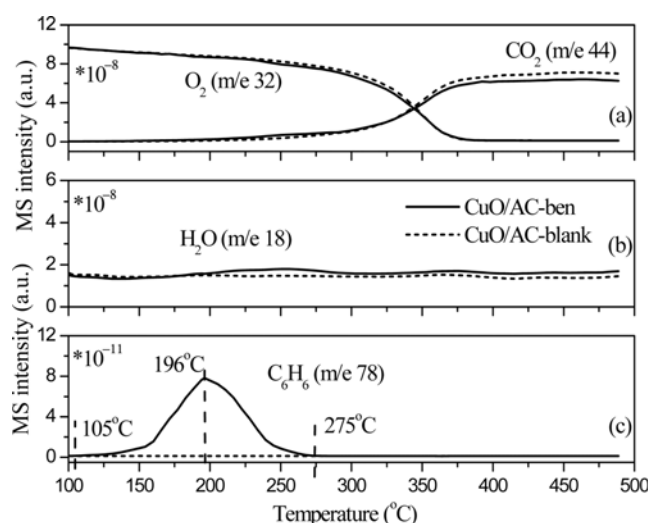
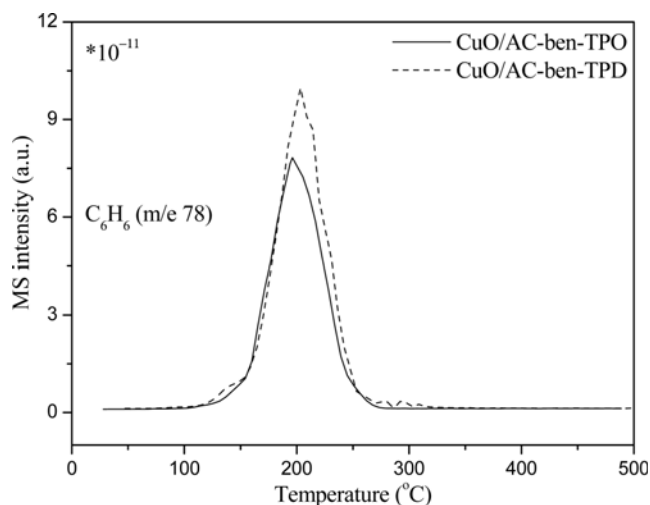Fig. 6. MS profiles for TPO of CuO/AC-blank (dot) and CuO/AC-ben (solid).

Fig. 7. MS profiles of benzene evolution for CuO/AC-ben in TPO and TPD.

residue benzene is oxidized.

To further understand oxidation behavior of benzene, TPD experiments of CuO/AC-ben were carried out. Fig. 7 compares MS profiles of benzene evolution during TPO and TPD of CuO/AC-ben. Apparently, the benzene desorption starts at 105 °C and yields a larger desorption peak in TPD than in TPO. If the TPD curve of CuO/AC-ben is chosen as a baseline, 83.5% benzene desorption and 16.5% benzene oxidation can be calculated for the TPO.

Although the benzene adsorbed on CuO/AC and benzene vapor that passes through other supports have similar oxidation temperatures at about 200 °C, the conversion of the adsorbed benzene (16.5%) is much smaller than that of the benzene vapor (about 100%) in the literature [15-17]. The difference may be derived from different processes (Table 2).

One reason that benzene conversion in ACDO is low may be resulting from benzene desorption. In contrast with thermostatic oxidation of benzene vapor at certain temperature higher than 200 °C,

Table 2. Comparison of benzene conversion for oxidation between ACDO and fixed bed flow reactor

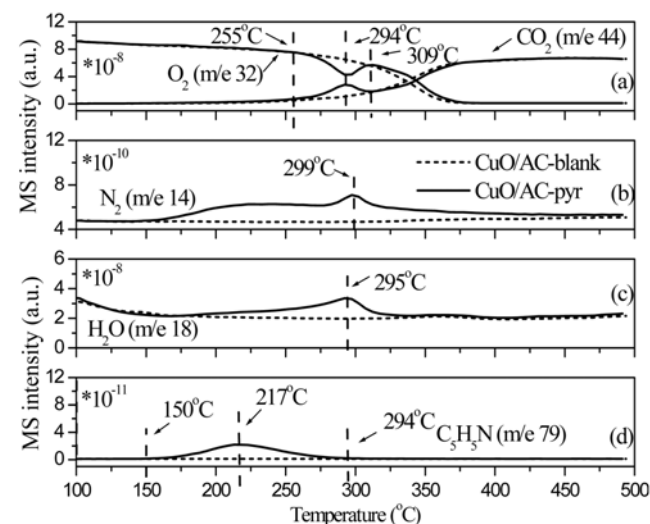|	Benzene vapor in flow reactor	Benzene adsorbed on CuO/AC in ACDO
Temperature Desorption	Thermostatic	Temperature programmed <196 °C
Retention time	Uniform	Different(function on the fixed bed)

Fig. 8. MS profiles for TPO of CuO/AC-blank (dot) and CuO/AC-pyr (solid).

benzene in ACDO is done in TPO. Benzene in ACDO oxidizes beyond 196 °C, initial temperature of benzene oxidation in TPO, which accords with the oxidation temperature of benzene vapor in the literature [15,16] and some of benzene adsorbed on CuO/AC inevitably desorbs below 196 °C and the desorption amount of benzene in TPO is 31.2% of total desorption one based on the integration of desorption curve of benzene in TPO (Figs. 6 and 7). It needs to be explained that the fact that the desorbed benzene can be oxidized over CuO/AC at a higher temperature has been verified in our previous experiment. As a result, benzene desorption in advance decreases the conversion.

Another one may be the effect of retention time on catalytic activity. It was reported that a longer retention time has an active influence on benzene vapor oxidation [16], so its retention time is expected to play an important role on benzene oxidation in ACDO. Compared to that of benzene vapor passing through the fixed bed, which is a constant, the retention time of benzene on different sites of CuO/AC is different because the distribution of the retention time of benzene is as follows: the nearer the benzene uniformly adsorbed on CuO/AC is to the end of the fixed bed along the direction of flow gas, the shorter the retention time. Beyond 196 °C, the benzene near to the bed end desorbs without oxidation, possibly due to shorter retention time.

3-3. Oxidation of Pyridine

Fig. 8 shows TPO-MS profiles of CuO/AC-pyr and CuO/AC-blank. It seems that some of the adsorbed pyridine desorbs from CuO/AC-pyr in the temperature range of 150-294 °C (Fig. 8(d)),
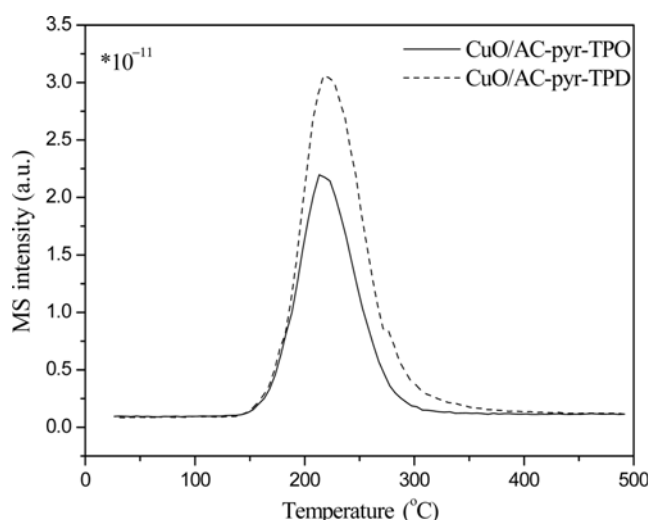
Fig. 9. MS profiles of pyridine evolution for CuO/AC-pyr in TPO and TPD.

Fig. 11. MS profiles for TPO of AC-blank (dot) and AC-pyr (solid).
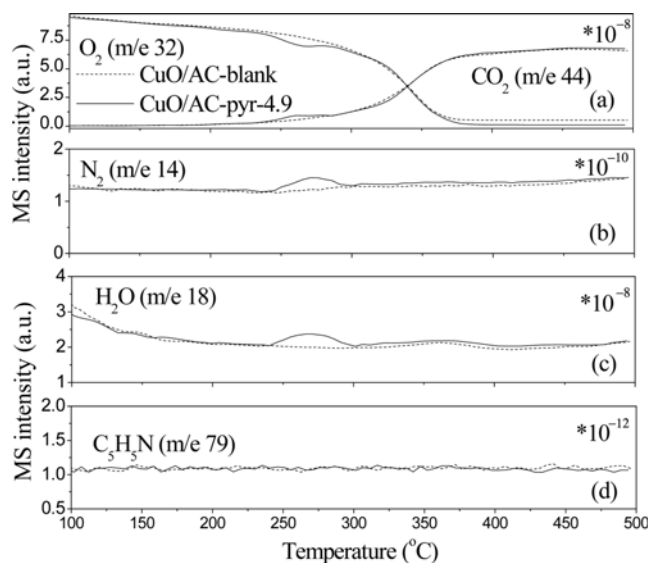

Fig. 10. MS curves for TPO of CuO/AC-blank (dot) and CuO/AC-pyr-4.9 (solid).

but some other pyridine is oxidized at a higher temperature range, 255-309 °C with a peak at 294 °C, as evidenced by the changes in O_2, CO_2, N_2 and H_2O profiles.

To evaluate the oxidation efficiency of pyridine in TPO, TPD experiments of the same samples were implemented. Fig. 9 compares MS profiles of pyridine evolution from CuO/AC-pyr during TPO and TPD. Apparently, TPD of pyridine starts at 150 °C and yields a larger evolution peak than TPO does; the TPO results in 63.7% desorption and 36.3% oxidation of pyridine.

To decouple oxidation and desorption of pyridine in TPO, CuO/AC adsorbed with a small amount of pyridine (4.9 wt%, about 1/15 of that in Fig. 9, termed CuO/AC-pyr-4.9) was subjected to TPO and compared with that of CuO/AC-blank. The results in Fig. 10 show only oxidation but no desorption of pyridine from CuO/AC-pyr-4.9. These data suggest that pyridine can be adsorbed at differ-
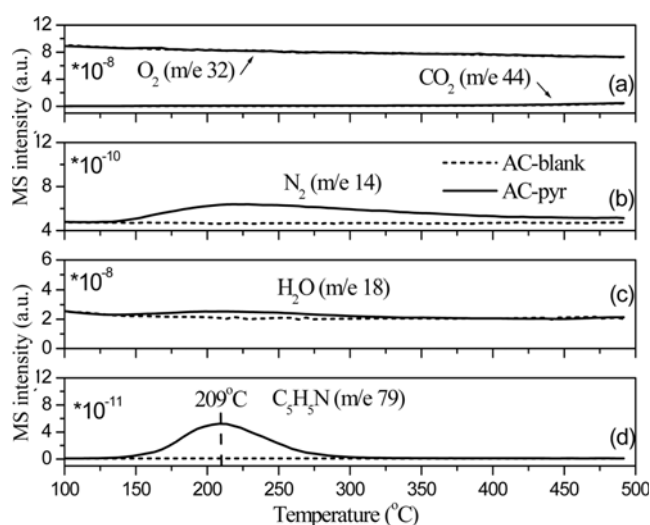
ent sites on CuO/AC. The sites with oxidation activity are stronger in adsorption than that without oxidation activity. Pyridine may preferentially be adsorbed on the stronger sites first and then on the weaker sites when the stronger sites are used up. The pyridine desorption shown in Fig. 8 can be attributed to the pyridine adsorbed on the weaker sites due to the high pyridine loading. It is likely that CuO provides the stronger sites and AC provides the weaker sites.

To verify the hypothesis discussed above, TPO of AC-pyr and AC-blank was performed and the results are shown in Fig. 11. The significant pyridine desorption from AC-pyr and similar O_2 and CO_2 curves between AC-pyr and AC-blank indicate the AC does not have strong sites for oxidation of pyridine. The small evolution of H_2O and N_2 from AC-pyr may be attributed to decomposition of pyridine.

It seems that CuO is active for oxidation of organic compounds only at temperatures higher than about 200 °C, as indicated also by other CuO-supported catalysts [18]. The different oxidation conversions of aniline (74.7%), pyridine (36.3%) and benzene (16.5%) over CuO/AC can be attributed to their adsorption strength over CuO/AC. As shown earlier, the desorption temperatures are 220 °C for aniline, 150 °C for pyridine and 105 °C for benzenes. Clearly, a lower desorption temperature of a pollutant corresponds to a lower oxidation activity over CuO/AC. It should be noted that desorption temperatures of these compound are proportional to their boiling points: 184.4 °C for aniline, 115.5 °C for pyridine and 80.1 °C for benzene.

CONCLUSIONS

AC has a poor catalytic activity for oxidation of aniline, benzene and pyridine. Doping of CuO results in significant increases in oxidation activity for aniline and pyridine. The initial oxidation temperature for these pollutants over CuO/AC is higher than 200 °C. Aniline oxidation occurs at 231-349 °C and yields mainly CO_2, H_2O and N_2. Pyridine oxidation occurs at a narrower temperature range, 255-309 °C after a significant desorption starting at 150°C. Benzene desorbs easily at 105 °C before it can participate in oxidation.

ACDO over CuO/AC is feasible for aniline in wastewater but not for benzene. Pyridine can be oxidized by CuO/AC, provided its adsorption on CuO/AC is low.

ACKNOWLEDGMENTS

NOMENCLATUTE

AC : activated carbons
AC-ani : the AC adsorbed with aniline
AC-ben : the AC adsorbed with benzene
AC-blank : the AC adsorbed with distilled water
AC-pyr : the AC adsorbed with pyridine
ACDO : adsorption-catalytic dry oxidation
BET : brunauer emmett teller
C_e : the equilibrium concentrations of adsorption solution [mg/L]
C_i : the initial concentrations of adsorption solution [mg/L]
CuO/AC : copper oxide doped activated carbon
CuO/AC-ani : the CuO/AC adsorbed with aniline
CuO/AC-ben : the CuO/AC adsorbed with benzene
CuO/AC-blank : the CuO/AC adsorbed with distilled water
CuO/AC-pyr : the CuO/AC adsorbed with pyridine
DFT : density-function-theory
M : the mass of the adsorbent [g]
MS : mass spectrometer
TG : thermogravimetric apparatus
TPD : temperature programmed desorption
TPO : temperature programmed oxidation
q_e : the amount of a pollutant adsorbed on an adsorbent [mg/g]
V : the volume of the solution [L]
XRD : X-ray diffraction

REFERENCES

1. B. Singh, S. Madhusudhanan, V. Dubey, R. Nath and N. Rao, *Carbon*, **34**, 327 (1996).
2. Agency for Toxic Substances and Disease Registry, *Toxicological profile for aniline, phenol, nitrobenzene*, U.S. Department of Health and Human Services (1999).
3. T. Karanfil and J. E. Kilduff, *Environmental science and technology*, Washington DC, **33**, 3217 (1999).
4. M. W. Reij, J. Kieboom, J. A. de Bont and S. Hartmans, *Appl. Environ. Microbiol.*, **61**, 2936 (1995).
5. H. Humbert, H. Gallard, V. Jacquemet and J. P. Croué, *Water Res.*, **41**, 3803 (2007).
6. V. S. Mishra, V. V. Mahajani and J. B. Joshi, *Ind. Eng. Chem. Res.*, **34**, 2 (1995).
7. K. S. Lin, H. P. Wang and M. C. Li, *Chemosphere*, **36**, 2075 (1998).
8. A. Dabrowski, P. Podkościelny, Z. Hubicki and M. Barczak, *Chemosphere*, **58**, 1049 (2005).
9. Y. I. Matatov-Meytal and M. Sheintuch, *Ind. Eng. Chem. Res.*, **36**, 4374 (1997).
10. G. Centi, M. Gotti, S. Perathoner and F. Pinna, *Catal. Today*, **55**, 51 (2000).
11. J. Zhao, Z. Liu and D. Sun, *J. Catal.*, **227**, 297 (2004).
12. G. E. Shter, Y. Shindler, Y. Matatov-Meytal, G. S. Grader and M. Sheintuch, *Carbon*, **40**, 2547 (2002).
13. Z. Lei and Z. Liu, *Fuel Process Technol.*, **88**, 607 (2007).
14. H. T. Gomes, B. F. Machado, A. Ribeiro, I. Moreira, M. Rosário, A. M. T. Silva, J. L. Figueiredo and J. L. Faria, *J. Hazard. Mater.*, **159**, 420 (2008).
15. S. S. Hong, G. H. Lee and G. D. Lee, *Korean J. Chem. Eng.*, **20**, 440 (2003).
16. C. Hu, Q. Zhu, Z. Jiang, Y. Zhang and Y. Wang, *Micropor. Mesopor. Mater.*, **113**, 427 (2007).
17. C.-H. Wang, S.-S. Lin, C.-L. Chen and H.-S. Weng, *Chemosphere*, **64**, 503 (2006).
18. J. Zhou, Q. H. Xia, S. C. Shen, S. Kawi and K. Hidajat, *J. Catal.*, **225**, 128 (2004).