Kinetics study on catalytic wet air oxidation of phenol by several metal oxide catalysts

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Abstract: Four metal oxide catalysts composed of copper (Cu), stannum (Sn), copper-stannum (Cu-Sn) and copper-cerium (Cu-Ce) respectively were prepared by the co-impregnation method, and γ-alumina (γ-Al$_2$O$_3$) is selected as support. A first-order kinetics model was established to study the catalytic wet air oxidation of phenol at different temperature when these catalysts were used. The model simulations are good agreement with present experimental data. Results showed that the reaction rate constants can be significantly increased when catalysts were used, and the catalyst of 6% Cu—10% Ce/γ-Al$_2$O$_3$ showed the best catalytic activity. This is consistent with the result of catalytic wet air oxidation of phenol and the COD removal can be arrived at 98.2% at temperature 210℃, oxygen partial pressure 3 MPa and reaction time 30 min. The activation energies of each reaction with different catalysts are nearly equal, which is found to be about 42 kJ/mol and the reaction in this study is proved to be kinetics control.

Keywords: catalytic wet air oxidation; catalyst; phenol

Introduction

Wastewaters originated from chemical, pharmaceutical and petrochemical industries are phenol-contaminated. Phenol is extremely toxic and imparts an unbearable odor and taste to water, even at concentration in the parts per billion range (Kulkarni, 1991). The phenol-contaminated wastewater therefore needs to be treated before its release. Due to the antibiotic properties of phenol, conventional biological treatments are inefficient in removing it.

Wet air oxidation (WAO) is a method of oxidizing dissolvable or suspended organic compounds as well as reducible inorganic compounds with oxygen or air under the circumstances of the high temperature and high pressure in liquid phase. WAO provides an efficient method for either partial or total destruction of organic pollutants such as phenol and substituted phenol, polyphenols and carboxylic acids (Joglekar, 1991). The application of traditional WAO is limited because of the high operation temperature, high operation pressure and long operation time (Mishra, 1995). Catalytic wet air oxidation (CWAO) was a new technology developed on the basis of WAO in the 1970s. It is a process that can speed the reaction, lower the reaction temperature and pressure with catalysts. Via the CWAO process, the organic compounds can be completely converted to CO$_2$ and H$_2$O or partly converted to less toxic intermediates (Hu, 2001). The presence of a catalyst in CWAO enables the process to be conducted at much less extreme operation conditions than the uncatalyzed process. Nevertheless, the reaction conditions of CWAO are still somewhat severe, and it is urgent for preparing the suitable catalysts with chemical and mechanical properties for performing in the severe reaction conditions. So investigation on catalysts with good activity and long life has become more important.

In this paper, four types of catalysts were prepared with the method of impregnation, and the catalytic wet air oxidation of phenol was evaluated. A kinetics model was also used to study the degradability of phenol by CWAO.

1 Experiments and methods

1.1 Experimental apparatus

The FYX-1 autoclave equipped with a stirrer and a heating device, which can keep the temperature, was employed in present study. There is a cooling coil and tow sampling outlets (liquid- and gas-phase outlet) in this device. The operation process is presented in Fig.1.
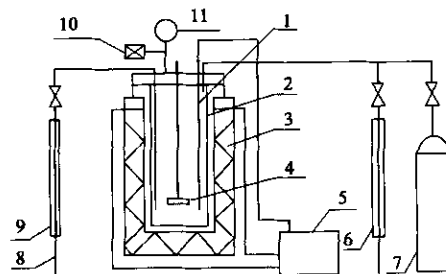

Fig.1 Schematic view of reactor

1. thermocouple; 2. reactor body; 3. heating jacket; 4. magnetic stirrer; 5. controller; 6. gas sampling valve; 7. oxygen cylinder; 8. liquid sampling valve; 9. cooling jacket; 10. relief valve; 11. pressure gauge

1.2 Catalyst preparation

Four metal oxide catalysts with different active

component were prepared by the impregnation method: (1) 6% Cu/γ-Al_2O_3 (wt%); (2) 6% Cu-10% Ce/γ-Al_2O_3; (3) 6% Sn/γ-Al_2O_3; (4) 6% Cu-6% Sn/γ-Al_2O_3.

Two different techniques can be used: adding each species by successive impregnation, or co-impregnation. At present study the latter technique was selected because it preferentially favors a homogeneous dispersion of the different metals added. The salt concentration of the impregnating solution is calculated to give the desired loading of metal oxides. γ-alumina, received as 3 mm diameter spheres, was selected as support because of its high surface area. The γ-Al_2O_3 was previously washed several times, and then was dried at 110℃ overnight, at last was calcined at 300℃ for 4 h. Afterwards the support was soaked at 30℃ for 5 h. The salts used in each case were $Cu(NO_3)_2 \cdot 2H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $SnCl_4 \cdot 5H_2O$ respectively. After impregnated, the alumina was washed several times and was successively dried 110℃ for 12 h and then was calcined at 400℃ for 5 h. The evaluation criteria of catalysts performance are COD removal of phenol.

1.3 Phenol degradation by CWAO

All experiments of phenol degradation were carried out by the following steps: (1) take 500 ml phenol solution in the autoclave; (2) add definite amount of catalyst; (3) turn on the heater; (4) when the temperature and pressure were up to the setting values, fill oxygen into the autoclave and it was the time zero. Outlets were taken every 5 min, and COD values of the samples were measured by the dichromate method.

1.4 Kinetic model

In this study, the chemical oxygen demand(COD) was used to represent the organic concentration of phenol solution. The mass transfer resistance was negligible because oxygen is in excess, as demonstrated by Mantzavinos et al. (Mantzavinos, 1996) and Lei et al. (Lei, 2000). By assuming that the CWAO follows the first-order reaction, we have

$$- \mathrm{d}c/\mathrm{d}t = kc, \qquad (1)$$

with the initial condition as: $t = 0$; $c = c_0$, where c and c_0 are the organic concentrations at reaction time t and zero, t is the reaction time and k is the rate constant, which follows the Arrhenius equation:

$$k = k_0 e^{-E/RT}, \qquad (2)$$

here k_0 is the pre-exponential factor, E represents the activation energy, R is the gas constant and T is the temperature.

The solution for Equation (1) is

$$c = c_0 e^{-kt}. \qquad (3)$$

So the COD value at any time is

$$COD = COD_0 e^{-kt}. \qquad (4)$$

Where the COD_0 is the COD value at reaction time zero.

The total removal of COD at any time can be calculated

by the Equation (4):

$$\eta = 1 - COD/COD'_0 = 1 - COD_0/COD'_0 \cdot e^{-kt}, \qquad (5)$$

where the initial COD value of the phenol, COD'_0 is larger than COD_0 because of the thermal decomposition of phenol during the heating up period.

2 Results and discussion

Fig.2—6 shows the COD removal of phenol solution by CWAO when the four types of catalysts prepared were used at: (△) 210℃; (◇) 180℃; (○) 150℃; (▽) 120℃ respectively.
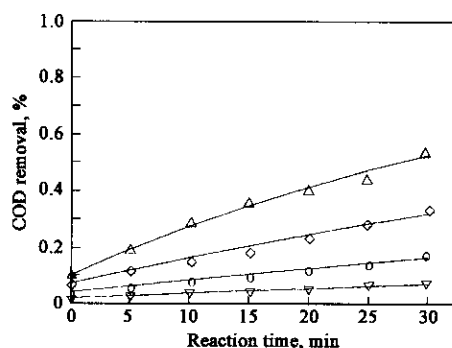

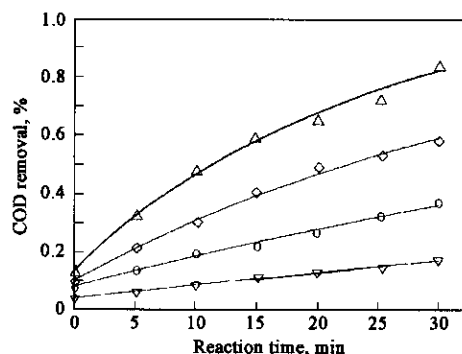Fig.2   COD removal of phenol solution by CWAO without catalyst

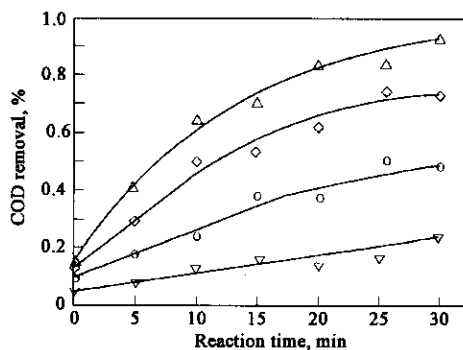Fig.3   COD removal of phenol solution by CWAO with 6% Sn/γ-Al_2O_3 catalyst

Fig.4   COD removal of phenol solution by CWAO with 6% Cu/γ-Al_2O_3 catalyst

The COD value of influent was kept at 10 g/L, and the oxygen partial pressure is 3 MPa, which is twice than that of
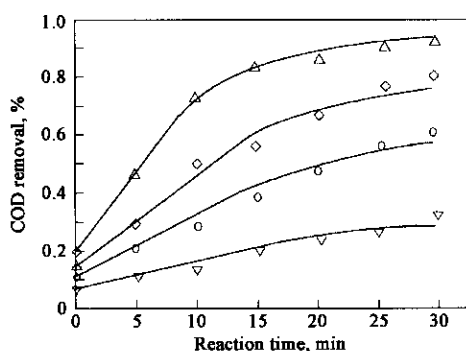
Fig.5   COD removal of phenol solution by CWAO with
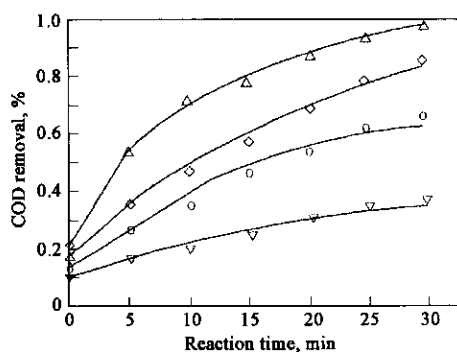6% Cu-6% Sn/γ-Al$_2$O$_3$ catalyst

Fig.6   COD removal of phenol solution by CWAO with
6% Cu-10% Ce/γ-Al$_2$O$_3$ catalyst

the theoretical amount of oxygen required to completely oxidize the organics in the solution. The experimental data are presented as symbols and the model fitting as solid lines. The COD removal has a non-zero value at $t = 0$. This is so because there is some thermal decomposition of organics during the heating up process. The thermal decomposition is more significant at a higher temperature. It can be seen in Fig. 2—6 that the model established fits the experimental data well. The extract parameters are listed in Table 1.

Table 1   Kinetic parameters of CWAO at different conditions

	T, ℃	120	150	180	210
K,	Non-catalyst	0.0017	0.0046	0.0104	0.0214
min^{-1}	6% Sn/γ-Al$_2$O$_3$	0.0048	0.0121	0.0263	0.0521
	6% Cu/γ-Al$_2$O$_3$	0.0064	0.0184	0.0401	0.0781
	6% Cu-6% Sn/γ-Al$_2$O$_3$	0.0092	0.0245	0.0437	0.0943
	6% Cu-10% Ce/γ-Al$_2$O$_3$	0.0116	0.0287	0.0536	0.1098

The results also showed that increasing the reaction temperature and the presence of catalysts can effectively accelerate the reaction rate. Both catalysts used in this study can significantly increase the reaction rate constants and among of them, the 6% Cu—10% Ce/γ-Al$_2$O$_3$ catalyst showed the best catalytic activity. This is accordant with the results of catalytic wet air oxidation of phenol. When temperature is 210℃, oxygen partial pressure is 3 MPa and reaction time is 30 min, the COD removal can be arrived at 98.2%.

The reaction rate constants at different conditions are

then used to obtain the activation energy of the oxidation reaction. Fig. 7 shows the dependence of rate constant on temperature. It can be seen from Fig. 7 that the activation energies of each oxidation reaction with different catalysts are nearly equal, which is found to be about 42 kJ/mol. The activation energy is much larger than 25 kJ/mol, a value where mass transfer resistance can be ignored (Satterfield, 1991; Shende, 1994). The results together with the excess oxygen supplied fully support the model assumption that the reaction in this study is under kinetics control.
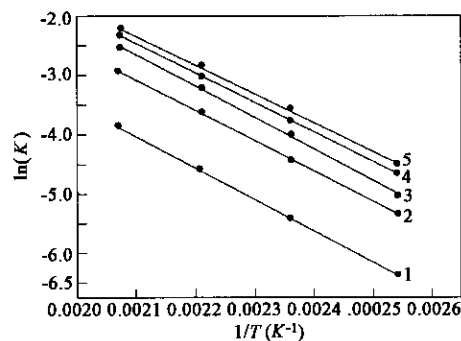

Fig. 7   Dependence of rate constant on temperature
1: non-catalyst; 2: 6% Sn/γ-Al$_2$O$_3$; 3: 6% Cu/γ-Al$_2$O$_3$; 4: 6%
Cu-6% Sn/γ-Al$_2$O$_3$; 5: 6% Cu-10% Ce/γ-Al$_2$O$_3$

3   Conclusions

Catalysts can effectively increase the removal of phenol at CWAO conditions, and the 6% Cu-10% Ce/γ-Al$_2$O$_3$ catalyst exhibited the best catalytic activity. The COD removal can be arrived at 98.2% at temperature 210℃, oxygen partial pressure 3 MPa and reaction time 30 min.

At present study, the catalytic wet air oxidation of phenol at different temperature fits the first-order kinetics model well. The activation energies of each reaction with different catalysts are nearly equal, which is found to be about 42 kJ/mol. It was proved that the reaction in this study is under kinetics control.

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