Catalytic wastewater treatment from chemical container cleansing

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The catalytic wet oxidation method was used for treatment of wastewater from chemical containers contaminated with various highly toxic pollutants. A heterogeneous catalyst containing Cu^{2+} ions on active carbon as an active component was proposed. The influence of the Cu^{2+} concentration, temperature, and calcination duration on the efficiency of the copper-containing catalyst was studied. The optimal results were obtained from the catalyst heated for 3 h at 573 K upon the impregnation with 6% Cu^{2+}. The study of the copper catalyst doped with cerium showed that the optimal content of the promoter was 6%. The copper and cerium catalysts were characterized by thermal analysis, scanning electron microscopy, and X-ray diffraction analysis. The catalyst lifetime and the resistance of cerium to removal were studied. The introduction of cerium increases the activity and life of the catalyst and decreases the concentration of Cu^{2+} ions removed from the surface to 15 mg L^{-1}. The treatment parameter estimated by a decrease in the chemical oxygen demand increased from 89.7 to 94.8%.

Key words: catalyst, catalytic wet oxidation process, wastewater treatment.

With the rapid development of logistic industry, a problem of cleansing of containers used from residues of transported chemicals arose. According to the International Transportation Regulation, the polluted containers can be reused only after being cleansed, dried, and deodorized.[1] Wastewater from the container cleansing contains highly toxic and poorly removable organic pollutants. The chemical oxygen demand (COD), *i.e.*, the amount of oxygen consumed by such a wastewater during the general chemical oxidation of organic components to harmless inorganic products, ranges from 5000 to 10 000 mg L^{-1}. If this wastewater would not be treated properly, they will pollute the environment dramatically. The COD value is determined by the oxygen concentration in mg L^{-1}, which is needed to oxidize organic or easily oxidizable compounds when treating a water sample with this or another oxidant under standard conditions.

Catalytic wet oxidation (CWO) is a new wastewater treatment technology by which hardly decomposed organics can be oxidized to harmless CO_2, N_2, and H_2O. This method also predicts deodorization, decoloration, sterilization, and disinfection of wastewater. No sludge is formed during the treatment, and only a small amount of the purified solution (raffinate) remains in the equipment and can easily be removed.[2,3] In the presence of a catalyst, the wastewater treatment process can occur at lower temperature and pressure, within a shorter time, and with smaller expenses.

When using[4] CWO, *p*-coumaric acid was used as a model pollutant, and the Fe—CeO_2 catalyst was prepared by the coprecipitation method. It was reported[4] that organic carbon (OC) can almost completely be removed by the treatment of the solution for 30 min at 403 K and 2 MPa, and the use of the catalyst decreases the reaction temperature and pressure. Other authors[5] used phenol as a model pollutant in the CWO process. The process was carried out at 423 K and a partial oxygen pressure of 7.3 bar, and the CuO—CeO_2 catalysts were prepared by the coprecipitation and sol—gel methods. The catalysts of both types are rather stable, if the reaction occurs under the hydrothermal conditions at low pH values. A comparison of the catalysts with the same copper amount under the same conditions showed that the samples prepared by the sol—gel method are 4 times more active and show ~25% improvement in selectivity to the formation of CO_2 than the samples obtained by coprecipitation. As compared to the homogeneous catalysts, the heterogeneous systems are more active and can more easily be separated from solutions. Another advantage of the heterogeneous catalysts is that it is not necessary to remove and isolate from water metal ions that are present in the catalyst. Nevertheless, a small loss of metals is also characteristic of the heterogeneous systems, which restricts the catalyst lifetime and stability.

In the present work, we focused on the choice of the method for preparation of a heterogeneous copper-con-

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taining catalyst capable of enhancing its activity and stability, which would result in a considerable acceleration of the treatment rate of wastewater from the chemical container cleansing.

Experimental

Preparation of the CuO/AC and CuO—CeO_2/AC catalysts (AC is active carbon). All catalysts were prepared by incipient wetness impregnation. Copper was used as the active component, and AC, which was washed with an appropriate amount of a $Cu(NO_3)_2$ solution, was the support. The catalyst was prepared by magnetic stirring and then dried and calcined.

The activity of the catalyst is significantly affected by such preparation conditions as the content of Cu^{2+} ions and the temperature and duration of calcination. Therefore, at the first stage, we searched for optimal conditions for the preparation of the CuO catalyst promoted by cerium additives and supported on the AC. For this purpose, the AC was first impregnated with $Ce(NO_3)_2$ solutions containing cerium in different concentrations (2, 4, 6, 8, and 10 wt.%), dried at 378 K, and calcined for 3 h at 573 K. Then the samples were impregnated with a $Cu(NO_3)_2$ solution containing 6 wt.% Cu. The optimal cerium content was determined by the results of studying the influence of the cerium content on the activity and stability of the catalyst.

Characterization of the catalysts. Thermogravimetric tests were carried out on a Q50 TGA, TTA Instruments. The flow water of the carrier gas (nitrogen) was 60 $cm^3\,min^{-1}$. A sample was heated from room temperature to 1173 K with a rate of 5 K min^{-1}. The dehydration and decomposition of the initial salts and the formation of the crystalline phase of the catalyst were studied during heating. Scanning electron microscopy (SEM) analyses were carried out with a Jeol JSM-6380LV microscope (at 20 kV). X-ray diffraction studies were carried out on a Rigaku D/max 2500 diffractometer in the range $2\theta = 10—90°$ at a scanning rate of 8.0 deg min^{-1}.

Evaluation of the catalytic activity. A wastewater sample obtained from the Huatai Container Service Limited Corporation was used for CWO experiments. In this sample, the main polluting component is dodecylphenol, and the COD value necessary for its decontamination is 5720 mg L^{-1}. Catalytic wet oxidation was carried out in a steel autoclave (Dialan Tongda Autoclave Company, China). A weighed sample (1 g) of the catalyst was placed in a vessel with a wastewater sample (1 L) containing 17.16 g of H_2O_2 (ratio H_2O_2 : COD = 3) and stored for 1 h in the autoclave at 100 °C. The catalyst activity was estimated by a decrease in the COD content in the sample of treated effluent. The removal of Cu from the catalyst was evaluated by measuring the Cu concentration in the reaction solution by atomic absorption spectrophotometry (WFX-120, Bejing Ruili Analysis Equipment Company, China).

Results and Discussion

The experimental results obtained by choosing the conditions of CuO/AC catalyst preparation are given in Table 1. According to these data, the most efficient catalyst is obtained, if the Cu concentration is 6%, the calcination temperature reaches 573 K, and the calcination duration is 3 h. The CuO/AC catalyst prepared under the optimal conditions was doped with different amounts of CeO_2, and the systems obtained were used for the treatment of water effluent contaminated with dodecylphenol. The quality of the wastewater entering treatment and the procedure of water treatment were the same as those when using the catalysts of the CuO/AC series. The results of experiments are shown in Fig. 1. The CuO—CeO_2/AC catalysts exhibited the higher activity than CuO/AC. As can be seen from Fig. 1, with an increase in the CeO_2 content, the catalytic activity of the sample at first increases, then (at the promoter content 6%) passes through a maximum, and then decreases slightly. The CuO(6%)—CeO_2(6%)/AC system turned out to be the best: in the presence of this catalytic system, the COD decrease reaches 94.8%. A possible explanation of the promoting effect of cerium can be the interaction of Cu^{2+} and CeO_2

Table 1. Experimental results obtained by choosing the conditions of CuO/AC catalyst preparation

Cu^{2+} (%)	T/°C	t^a/h	Content of COD in treated water/mg L^{-1}	Decrease in COD consumption[b] (%)
2	200	3	932	83.7
	300	4	899	84.3
	400	5	1173	79.5
4	200	4	967	83.1
	300	5	850	85.1
	400	3	722	87.4
6	200	5	699	87.8
	300	3	586	89.7
	400	4	767	86.6

[a] Duration of catalyst heating.
[b] COD = $(COD_1 - COD_2)/COD_1$, where COD_1 is the oxygen content in the water sample coming to treatment, and COD_2 is the oxygen content in the sample of treated water.

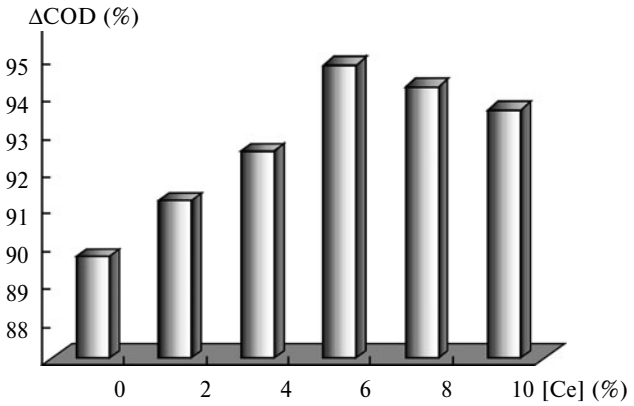

Fig. 1. Effect of the CeO_2 content on the catalytic activity of the CuO—CeO_2/AC system.

and the cation exchange between Cu^{2+} and Ce^{2+} in CeO_2 or between CuO and CeO_2. This exchange stabilizes Cu^{2+} in the catalyst and thus enhances its stability. The increase in the catalytic activity can also be due to the ability of CeO_2 to retain and then donate oxygen.[6] Although the activity of the samples containing more than 6% CeO_2 decreases slightly, it is still higher than the activity of the CuO/AC system. In these samples, the cerium ions, being in excess, displace the copper ions from carbon support surface, decreasing the fraction of the active sites, which are present on the surface due to Cu^{2+} or copper oxides. It is most likely that this decreases the activity.[7]

Investigation of the properties of the catalysts. *Thermal analysis*. The results of thermogravimetric analysis of the CuO/AC and CuO—CeO_2/AC catalysts are shown in Fig. 2. On heating to temperatures lower than 373 K, the weight loss is mainly caused by dehydration. When the temperature reaches 723 K, the weight loss of the both catalysts increases rapidly due to processes of AC metamorphization and CuO decomposition.[8] As can be seen from Fig. 2, *a*, at 723 K the weight loss by the CuO/AC catalyst was 3% and the maximum rate of weight loss reached 0.0291 % K^{-1}. At the same time, Fig. 2, *b* shows that at 723 K the weight of the CuO—CeO_2/AC catalyst decreased by 2.31% only, whereas the maximum weight loss rate did not exceed 0.01947 % K^{-1}. Thus, the presence of CeO_2 impedes CuO transformation and thus improves the stability of the catalyst.

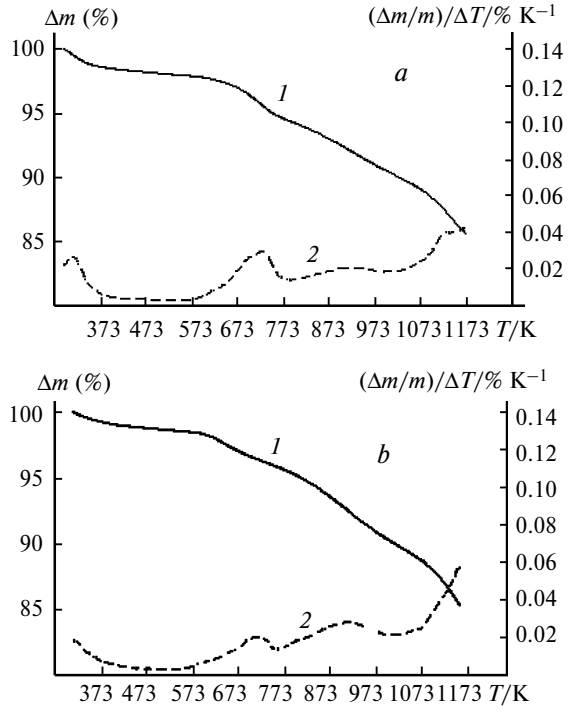

Fig. 2. TG (*1*) and DTG (*2*) curves of the CuO/AC (*a*) and CuO—CeO_2/AC (*b*) catalysts.

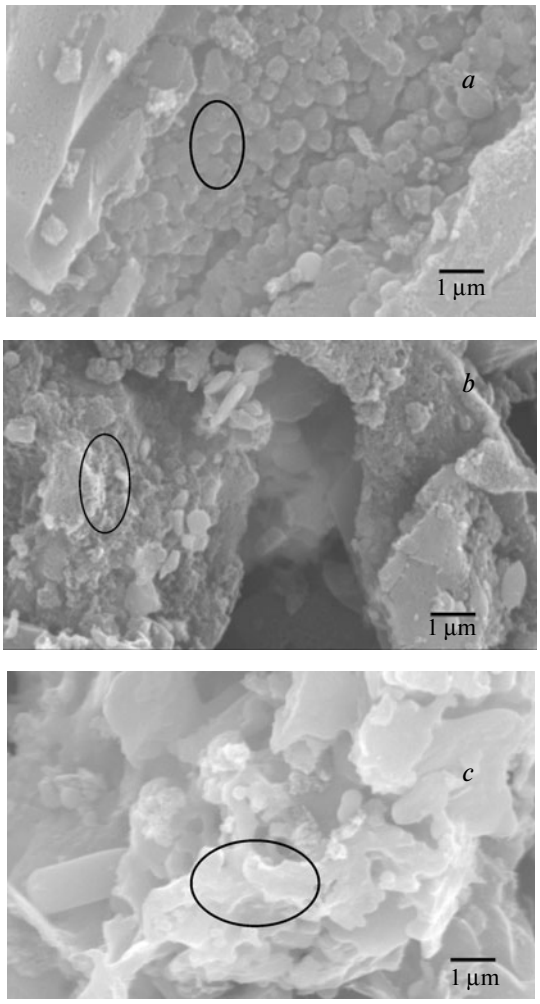

Fig. 3. SEM images of the AC (*a*), CuO/AC (*b*), and CuO—CeO_2/AC (*c*) catalysts.

Scanning electron microscopy. The AC powder and the CuO/AC and CuO—CeO_2/AC catalysts were studied by scanning electron microscopy (Fig. 3). A comparison of the areas identified in the images (see Fig. 3, *a*, *b*) by circles shows that the active phase of copper forms discrete particles distributed over the CuO/AC surface. The morphology of the CuO—CeO_2/AC catalyst (see Fig. 3, *c*) reflects the interaction between the active components, which can result in the formation of structures of the spinel type between the layers of the carbon support.[9] Possibly, these structures increase the oxygen flow rate, which increases the catalytic activity. It is not excluded that the improvement of activity is due to a promoter effect that includes the replacement of comparatively large cerium ions in CeO_2 by smaller copper ions. As a result, the CeO_2 structure becomes defect, and numerous vacancies are formed in it.[9]

X-ray diffraction studies. The X-ray patterns of the CuO/AC and CuO—CeO_2/AC catalysts are presented in

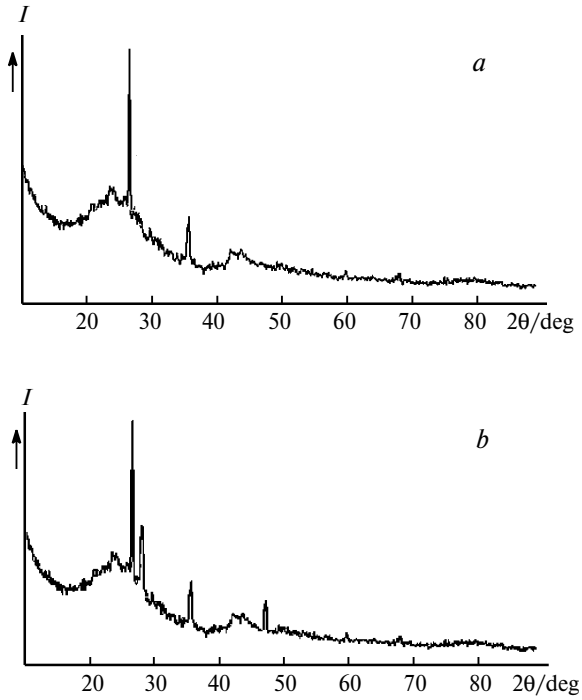

Fig. 4. X-ray patterns of the CuO/AC (*a*) and CuO—CeO_2/AC (*b*) catalysts.

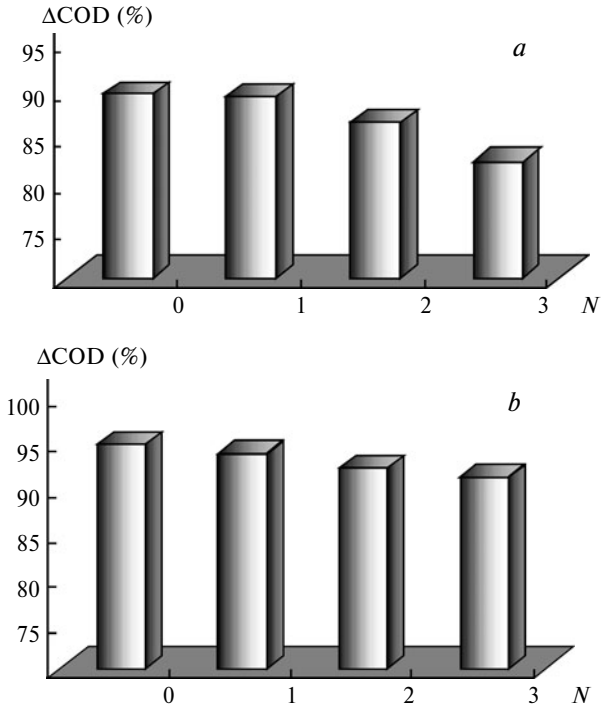

Fig. 5. Influence of the multiple use of the CuO/AC (*a*) and CuO—CeO_2/AC (*b*) catalysts on the decrease in the COD consumption; *N* is the number of catalytic cycles.

Fig. 4. The X-ray diffraction pattern of the CuO/AC catalyst exhibits a diffraction maximum of the crystalline phase of CuO ($2\theta = 35.499°$) and a small peak related to the presence of the AC support ($2\theta = 26.517°$). A maximum assigned to CeO_2 is observed along with the mentioned two signals in the X-ray diffraction pattern of CuO—CeO_2/AC. An analysis of the diffraction patterns suggests that the catalytic activity of the catalyst is associated with the CuO and CeO_2 phases.

Estimation of the catalytic activity. *Comparison of the lifetimes of the catalysts.* The results on the wastewater treatment obtained by the multiple use of the CuO/AC and CuO—CeO_2/AC catalysts, under the same conditions as those for the CWO process, are shown in Fig. 5. The catalytic activity of CuO/AC decreases after several treatment cycles. After three cycles, the COD consumption decreases from 89.7 to 82.5% (see Fig. 5, *a*). It is most likely that a reason for the decrease in the catalytic activity is the removal of Cu^{2+} from the catalyst. The COD consumption in experiments on the multiple use of CuO—CeO_2/AC also decreases gradually but not so rapidly than in the case of CuO/AC (see Fig. 5, *b*). After three cycles in the presence of this catalyst, the COD consumption decreases to 91.1% only. This indicates that the promoted catalyst CuO—CeO_2/AC retains rather high activity. Evidently, cerium oxide retards the removal of the Cu^{2+} ions and thus stabilizes the catalytic effect of copper.

Removal of active components of the catalysts. Since the removal of a considerable amount of Cu^{2+} ions from the catalyst decreases the catalytic activity, it seemed interesting to estimate the stability of the catalyst operation by the determination of the Cu^{2+} catalysts in water treated in the presence of the CuO/AC and CuO—CeO_2/AC catalysts. The corresponding results obtained by atomic adsorption spectrophotometry are given in Table 2. In the first cycle (using CuO/AC) the Cu^{2+} concentration in the reaction solution was 0.2209 mg L^{-1}, while in the presence of CuO—CeO_2/AC it decreased to 0.1351 mg L^{-1}. The multiple tests showed that the removal of Cu^{2+} from the CuO—CeO_2/AC system is also less intensive than that from the CuO/AC catalyst (see Table 2). These data along

Table 2. Concentration of Cu^{2+} in water after the catalytic treatment

Catalyst	*N**	$[Cu^{2+}]$/mg L^{-1}
CuO/AC	—	0.2209
CuO/AC	2	0.1304
CuO/AC	3	0.1645
CuO/AC	4	0.1633
CuO—CeO_2/AC	—	0.1351
CuO—CeO_2/AC	2	0.1246
CuO—CeO_2/AC	3	0.1175
CuO—CeO_2/AC	3	0.1152

* Number of treatment cycles.

with the results of studies of the catalyst structure indicate that CeO_2 prevents copper removal from the surface of the catalyst and stabilizes its catalytic activity.

The experiments performed revealed that in the CuO/AC system the catalyst containing 6% Cu^{2+} ions and heated for 3 h at 573 K has the optimal catalytic properties. In the promoted catalyst CuO—CeO_2/AC, the optimal cerium content is 6%. In the presence of this catalyst, COD removal increased up to 94.8%. The CuO(6%)/AC and CuO(6%)—CeO_2/AC catalysts were studied by differential thermal analysis, scanning electron microscopy, and X-ray diffractometry. An analysis of the TG—DTG curves shows that with cerium as a promoter the weight loss decreases from 3.0 to 2.31% and the weight loss rate decreases from 0.02971 to 0.01947 % K^{-1} on heating to 723 K. This indicates that the addition of CeO_2 to the catalyst suppresses the reduction of CuO to Cu_2O and increases the catalyst stability. According to the data of electron microscopy, the active components of the promoted catalyst CuO—CeO_2/AC interact with the support to form structures of the spinel type on the sample surface. The X-ray patterns of the samples revealed that catalytically active CuO and CeO_2 exist on the surface of the promoted catalyst. The promotion of the CuO/AC catalyst with cerium enhances the stability of operation and increases the activity in COD absorption. The introduction of CeO_2 decreases the intensity of Cu^{2+} removal from the catalyst surface.

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References

1. P. Jinzhao, Z. Xiufeng, Y. Zongzheng, L. Yao, *J. Tianjin University Sci. Technol.*, 2007, **22**, 31.
2. B. Miranda, E. Diaz, S. Ordonez, A. Vega, F. V. Diez, *Chemosphere*, 2007, **66**, 1706.
3. M. E. Suarez-Ojeda, A. Guisasola, J. A. Baeza, A. Fabregat, F. Stuber, A. Fortuny, J. Font, J. Carrera, *Chemosphere*, 2007, **66**, 2096.
4. G. Neri, A. Pistone, C. Milone, S. Galvagno, *Appl. Catal. B: Environmental*, 2002, **38**, 321.
5. S. Hocevar, U. Opara, B. Orel, A. S. Arico, H. Kim, *Appl. Catal. B: Environmental*, 2000, **28**, 113.
6. Y. Min, Eng. D. diss., Chinese Academy of Sciences, 2007.
7. T. Haiyan, Eng. M. Diss., Harbin University of Sciences and Technology, 2005.
8. E. Lecheng, W. Dahui, *Advanced Oxidation Technology of Water Treatment*, Chemical Industry Press, Beijing, 2001, p. 150.
9. S. Wenjuan, F. Zhaochi, L. Zhonglai, Z. Jing, S. Wenjie, L. Can, *J. Catal.*, 2004, **228**, 206.

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