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Study on Catalyst of Catalytic Wet Oxidation of High-concentration Industrial Organic Wastewater

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Abstract：A kind of compound catalyst containing the main activate component CuO, the second activate component ZrO_2 and electronic promoter La_2O_3 was prepared. It was applicable to treat with high-concentration dimethyl acetylsuccinate (DMAS) production wastewater with catalytic wet air oxidation technology which was used in continuous bubble columns reactor. In this article the influences of concentration of soaked liquid of every component and the second activate component were studied, and the best preparation condition has been determined. The experimental results indicated that the catalyst of $CuO-ZrO_2-La_2O_3/ZSM-5$ had a higher activity when handling high-concentration DMAS production wastewater. With this catalyst the COD_{cr} removal rate could get 98.7% while non-catalyst only 35.8％ at the reaction conditions as follows: reaction temperature 240℃, reaction pressure 3.5MPa, liquor space velocity＝2.0 h^{-1}, V（oxygen）：V（wastewater）＝250:1 and influent wastewater pH=7.

With the rapid development of industrial technology and the expanding scale of production, all kinds of industrial wastewater containing high concentrations of refractory organic chemical and biological pollutants, nitrogen compounds, suspended solids increases by gradually. Because the conventional biological purification methods can not meet the purification's technical and economic requirements, such a kind of high concentration of industrial wastewater purification in recent years has gradually become one of the hot research topics of an international environmental protection technology[1-3] .

Dimethyl Acetylsuccinate, DMAS is a kind of important organic chemical intermediates. It is applied to some fields such as pesticide, medicine, dyestuff, food additives broadly. With the rapid development of the pharmaceutical and dye industry in recent years, DMAS' research and applications continue to expand, whose market demand is growing. At present, many inland enterprises have successfully developed a DMAS production process, but the problems encountered in a large number of wastewater, characterized by high concentrations, complex components, high chemical oxygen demand, so the traditional approach is more difficult.

Catalytic wet air oxidation is an effective means dealing with high concentrations, toxic and harmful and persistent organic wastewater[4-7].But because of demanding high temperature pressure, it is limited in practical applications. If we can develop efficient and economical catalyst, lower reaction temperature and pressure, while there is a satisfactory treatment effect, its application will be of great significance to the promotion[8-9].In view of this, this study aim at the high concentration organic wastewater as experimental subjects from a chemical company in the production of DMAS

actually , ZSM-5 as a carrier, Cu and Zr as an active component, La as an electronic promoter, We prepare a syndromous load catalyst $CuO\text{-}ZrO_2\text{-}La_2O_3/ZSM\text{-}5$ and use O_2 as oxidant to CWAO test in order to better treatment effect.

Experiment

1.1 Methods

According to GB(11914-89) COD was determined COD_{cr} in this experiment. According to GB(7474－87) Cu^{2+} concentration was determined by sodium diethyl dithiocarbamate extraction spectrophotometry amino. Catalyst's specific surface area was determined by BET, determining by CHEMBET-3000. The pH value of Inlet and outlet water was determined by PHS-3 pH-electrode.

1.2 Catalyst's preparation

Catalyst's preparation uses immersion method. Nitrate solution including active component of the metal mixed configured impregnation, impregnating the carrier in the dipping solution, while adding a certain amount of complexing agent, and immersed in water bath after a certain time, filtered, and then dried at a certain temperature, claimed compound catalyst.

1.3 Experimental method

The experiment wastewater was high concentration organic producting DMAS including, aldehyde, carbinol and DMAS and so on. And COD_{cr} was 16542mg/L, pH value was 4.6. The experiment equipment used a continuous fixed-bed bubble reactor, whose flow was shown as Figure 1.The pressure was 15Mpa and reaction temperature <400℃,its inner diameter D＝15mm and length＝600mm.The wastewater was layed aside rabbet (1), packed off by high-pressure metering pump. High-pressure metering pump high-pressure oxygen from the oxygen bottles(4) after dive through a mass flow meter(6) and high pressure metering pump a mixture of high-pressure liquid mixture; gas-liquid mixture into the preheater(10) by a common pipeline, after preheating to enter from the bottom fixed-bed reactor(12). Reactor placed in electric furnace (11) within a unified instrument control by the heating process, the reactor were heated by three to achieve the controllability of heating; Reactor, the bottom filled with quartz sand, the middle of loading the catalyst bed height of about 8cm; High temperature reaction material from the top of the reactor, the condenser by the cooling water, and finally into the gas-liquid separation tank; where some exhaust back pressure valve by venting, back pressure valve to stabilize the system pressure through the role; liquid product from the bottom of gas-liquid separation tank sampling valve.

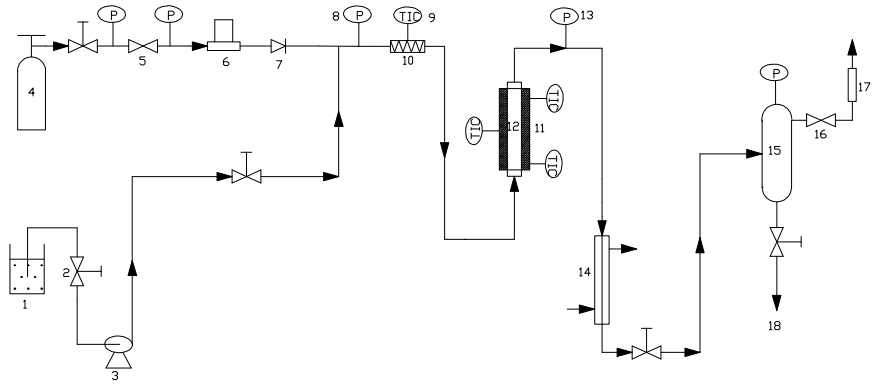

Fig 1 Experimental apparatus of catalytic wet oxidation rector

1－metering rabbet；2－ball valve；3－High-pressure metering pump；4－oxygen bottle；5－decompression valve；6－gas mass flowmeter；7－check valve；8－import pressure gage；9－thermoelectric couple；10－gas-liquid mixture forewarmer；11－heating furnace；12－reactor capacity；13－exit pressure gage；14－condenser；15－gas-liquid separator；16－foot valve；17－gas flow meter；18－liquid sampling

Results and Discussion

2.1 Confirming carrier

CuO was chosed as primary active component，and used γ-Al_2O_3, TiO_2, ZSM-5 as carrier respectively to prepare catalyst by steep method, the mass fraction of Cu was 3％.The reaction temperature 240℃, reaction pressure 3.5MPa, liquor space velocity＝2.0 h^{-1}, V（oxygen）：V（wastewater）＝250:1 and influent wastewater pH=7, initial COD_{cr}16542mg/L.The result was shown as Table 1.

Table 1 influence from different carriers on catalyst activity

catalyst	initial COD_{cr}（mg/L）	effluent COD_{cr}（mg/L）	COD_{cr} dislodge rate（％）
CuO/ZSM-5	16542	6666	59.7
CuO/γ-Al_2O_3	16542	9462	42.8
CuO/ TiO_2	16542	10223	38.2
WAO（nothing）	16542	12456	24.7

Different carriers on the catalytic activity can be seen from Table 1, in the same reaction conditions, the load carrier in any active component CuO effluent CODcr removal are significantly increased while the use of ZSM-5 as a catalyst deal better, so the main experimental use CuO as a catalyst active component, the choice of ZSM-5 as a catalyst of high concentration of dimethyl acetyl Succinic wastewater.

2.2 Cu loading's effection on the catalyst surface area, the loss of copper ions and the removal of CODcr. Experiment, ZSM-5 as the carrier, CuO as the main active component, selected the Cu concentration of impregnating solution were 0%, 2%, 3%, 4%, 5%, 7% and 9%, using different impregnation Cu catalyst loadings, the catalyst activity evaluation. The results were shown in Table 2.

Table 2 Cu loading's effection on catalyst surface area, Cu^{2+} loss and CODcr removal

Cu mass fraction（％）	COD_{cr} dislodge rate（％）	specific surface area（m^2/g）	Cu^{2+}concentration（mg/L）
0	28.6	248.7	0
2	48.9	224.8	1.2
3	59.7	212.6	2.1
4	64.8	204.3	2.7
5	65.2	197.4	4.3
7	60.3	173.1	6.6
9	52.1	152.3	9.4

From Table 2, the active component is less than 4%, CODcr removal rate increased with the amount of active ingredient increased significantly, while the percentage of active component greater than 5% of the quality, CODcr removal began to decline. May be due to the increase of load capacity, easy to join the active component, particles become larger, blocking the catalyst pores, resulting in reduced surface area of active components, so not only does not increase the catalytic activity, but will reduce the catalytic properties; However, if the load is too small, the active component is still not completely cover the surface of the carrier, resulting in decreased utilization of carrier surface. At the same time can also be seen from the Table 2 with the Cu loading increases, the loss of copper ions was slowly increasing. Therefore, from the most efficient use of carrier surface area, economy, and the secondary pollution of copper ions into account, selects the Cu impregnation concentration of 4% loading obtained by impregnating the appropriate load.

2.3 Effection on catalysis effect by the second active component

The metallic oxide Fe, Ni, Zr, Mn, Zn, Co as the second active component, CuO as the main active component, According to a certain percentage we loaded of ZSM-5 carrier in the preparation of the CuO- Fe_2O_3/, CuO-NiO_2, CuO-ZrO_2, CuO-MnO_2, CuO-ZnO_2, CuO-CoO_2 composite catalyst and its catalytic activity evaluation. The results were shown in Table 3.

Table 3 the second active component addition on CODcr removal

catalyst	inflow（$mg \cdot L^{-1}$）	effluent（$mg \cdot L^{-1}$）	COD_{cr} removal rate %
CuO	16542	5823	64.8
CuO-Fe_2O_3/ZSM-5	16542	7212	56.4
CuO-NiO_2ZSM-5	16542	5426	67.2
CuO-ZrO_2ZSM-5	16542	3490	78.9
CuO-MnO_2/ZSM-5	16542	5062	69.4
CuO-ZnO_2ZSM-5	16542	7560	54.3
CuO-CoO_2/ZSM-5	16542	4748	71.3

From Table 3, CuO-ZrO_2 composite catalysts on the production of acetyl-Dimethyl Succinic wastewater, in the same reaction conditions CODcr removal rate 78.9%, while the Cu catalyst in the same reaction conditions CODcr removal only 64.8%, respectively. This showed that the compound ZrO_2 better improve the catalytic effect, so our study, ZrO_2 as a second active component.

2.4 Effection on catalysis effect and the loss of copper ions by the dosage of second active component

The second experiment as a catalyst active component Zr, Cu-based active components, loading of ZSM-5 vector in the Cu-Zr composite prepared catalyst. Figure 2 The effects of Zr concentration of impregnating solution on the catalytic activity of the catalyst.

From Figure 2, the second active component Zr content increases the loss for the Cu^{2+} had no effect, and the effluent concentration of Cu^{2+} in waste water was always in 2.5mg / L or so, but with the increasement of Zr content in catalytic activity is increased. Not to join the active component in the second when dealing with the production of dimethyl acetyl butyric CODcr removal rate was 64.8% water, with the Zr content increases, the water CODcr removal rate gradually increased to 3 when the Zr content % time, CODcr removal rate of 83.5%, then with the increase of Zr content, CODcr removal rate increases began to become obvious. Therefore, this experiment selected the second active component Zr content of 3%.

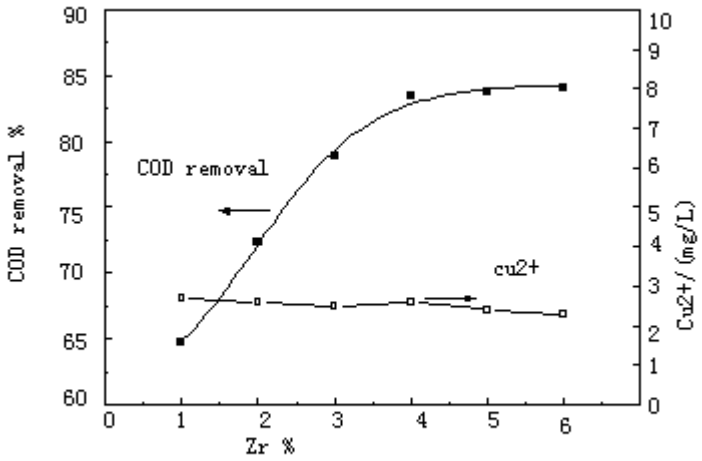

Fig 2 Effect of Zr addition on COD removal and Cu^{2+} loss

2.5 Effection on catalysis effect and the loss of copper ions by electronic auxiliary

Better in the previous experiment based on the ratio of catalytic effect, the use of lanthanum as an electronic agent added, effects of different La addition on catalytic activity and the impact of the loss of copper ions, the experimental results shown in Figure 3.

Figure 3 showed that, with the La content increases, the water CODcr removal rate increased, when the La content increased to 2%, CODcr not added La removal from the 83.5% to 92.3%, then with the La content increase, CODcr removal rate increase becomes obvious. This indicates that a small amount of lanthanum rare earth composition on the activity of Cu and Zr are two components to promote the role of catalytic ability, which may possess from cerium oxygen storage and the ability to transfer oxygen and transition metal oxides form a cooperative role, change their electronic state.

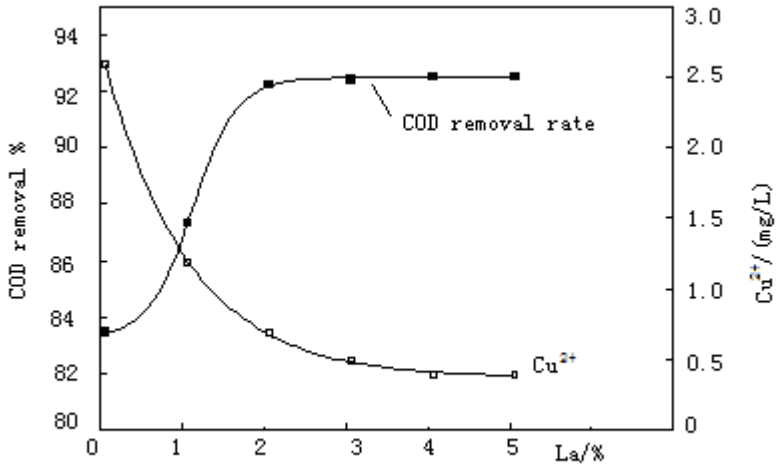

Fig.3 Effect of La addition on COD removal and Cu^{2+} loss

Experiment also investigated the added content on the catalytic activity of different components of La Cu^{2+} Loss. The results from Figure 3 can be seen that the addition of La on electronic aids the stability of the catalyst has significant influence. With the increase of La content, the loss of the catalyst in the smaller Cu^{2+} in the absence of added La circumstances, the loss of copper ions is 2.6mg / L, when added to 5% of La content, the loss of copper ions only 0.4mg / L that adds electronic stability increased additives lanthanum, cost considerations from the catalyst, 2% was chosen for the electronic aids, this time the loss of copper ions is 0.7mg / L.

To sum up: the present study, catalytic wet oxidation process chlorophenyl isocyanate selected wastewater main active component Cu, Zr is the second active component, La electronic aids, in the impregnating solution in the mass fraction of 4 %, 3%, 2%

Conclusion

（1）When the impregnating solution in Cu, Zr, La contents was 4%, 3%, 2%, calcination temperature was 550 ℃ for 10 h, the prepared catalyst in the treatment received CuO-ZrO2-La2O3/ZSM-5 Dimethyl acetyl butyrate production wastewater has higher activity.

（2）Composite catalyst used in the load temperature T = 240 ℃, reaction pressure P = 3.5MPa, space velocity = 2.0 h-1, V (gas): V (water) = 250:1, water under the conditions of pH = 7 CODcr concentration of the initial treatment 16542mg / L dimethyl acetyl Succinic wastewater, CODcr removal rate reached 98.7%, compared with no catalyst and the wet air oxidation increased by 62.9%.

References

[1]Zhao Xunzhi; Liu Zan; Cheng Zhilin. Research progress on wet catalytic oxidation technology for treating highly concentrated polluted wastewater and its application [J]. Industrial Water Treatment 2007,27(7):12-15

[2]Centi G. Catalytic wet oxidation with H2O2 of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts［J］. Catal. Today，2000，55：61- 69.

[3]Akolekar D B，Bhargava S K，Shirqoankar I，et al. An environmental solution for organic pollutant removal from paper and pulp industrial waste liquor ［J］. Applied Catalysis A：General，2002，236：255 -262.
[4]Yan Haisheng; Liu Bo; Yu Weifu; Xuan Yongmei;Liu Dongxue. Progresses in Research of Heterogeneous Non-noble Metal Catalysts Used in Catalytic Wet Air Oxidation Process[J]. Environmental Protection of Chemical Industry.2006,26(3):213-217
[5]Luck F. Wet Air Oxidation ：Past，Present and Future. Catalysis Today，1999，53（1）：81-91.
[6] Bin Yuejing, Zhu Wanpeng, Jiang Zhanpeng, Yin Tong, Yang Zhihua Research on Catalysts for Catalytic Wet Air Oxidation Process and Treatment Technologies[J]. Environmental Science,1999,20(2):42-44
[7]Zhu Wang-peng，Bin Yue-jing，Li Zhong-he et al. Application of Catalytic Wet Oxidation for the Treatment of H-acid Manufacturing Process Wastewater [J]. Water Research，2002 ，36 （8）：1947-1954.