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Trimetallic catalysts for continuous catalytic oxidation of aqueous phenol

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Abstract—The continuous catalytic oxidation of aqueous phenol solutions has been investigated using a series of trimetallic catalysts, called Mn-Sn-Sb/ γ -Al₂O₃ catalysts in a packed bed reactor. The influence of the co-impregnation and successive impregnation were studied for the preparation of the catalysts. Descriptive statistics for different catalysts indicated that the catalyst which was loaded by the manganese oxides first and then by the stannum oxides and stibium oxides had a better activity and stability. Using this catalyst, phenol conversion and TOC reduction could get 90.6% and 83.1% respectively at 150°C, 1MPa of oxygen partial pressure and space time of 27min. The leaching of metal ions was computed to negative correlation with the effluent pH for 100h operating at 120°C using pure oxygen as oxidant.

Keywords—phenol oxidation; trimetallic catalyst; wastewater treatment

I. INTRODUCTION

Catalytic wet oxidation (CWO) of aqueous solutions of organics has largely demonstrated its effectiveness [1] when these polluting agents are often in such small concentrations that economic recovery is not feasible. It is desirable to use a heterogeneous catalyst since a homogeneous catalyst requires an additional separation step. Different heterogeneous catalysts based in noble metals [2, 3] and transition metal oxides over different supports [4, 5] have been investigated. Obtaining suitable and durable catalysts and determining the optimal process conditions are the key to successfully implementing this treatment.

In the pore-filling method to prepare the heterogeneous catalysts, the support is impregnated with the volume of salt solution. Two different techniques, adding each species by successive impregnation or co-impregnation, can be used if several species are to be supported [6].

This study deals with the possibility of various trimetallic catalysts on the catalytic oxidation of phenol in aqueous phase. The performances of three different trimetallic oxidation catalysts is compared with that of manganese oxide supported over γ -alumina prepared by the techniques

of successive impregnation and co-impregnation. Besides manganese, the metals tested were stannum and stibium. The oxidation was continuously conducted in a packed bed reactor. Phenol conversion and TOC reduction was thus to experimentally obtain in 100h tests. The correlation between the concentration of leaching metal ions and effluent pH was analyzed using the statistical product and service solutions (SPSS), version 13.0.

II. EXPERIMENTAL

A. Catalyst preparation

Trimetallic catalysts were prepared by impregnating γ -Al₂O₃ with manganese nitrate, stannum chloride and stibium chloride aqueous solutions using the dry soaking method. All reagents used in experimentation were analytical grade and obtained from Sinopharm Chemical reagent Co., Ltd (Shanghai, China). Deionized water was used to prepare the different aqueous solutions. Each process was conducted under air atmosphere. The granule of γ -Al₂O₃ (Tianjin Research & Design Institute of Chemical Industry, Tianjin, China), 10-14mesh (1.43-2mm) was used as support.

Three kinds of catalysts were made by the techniques of co-impregnation and successive impregnation. The support was washed several times to remove all fines and dried for 24 h in an oven at 105°C. The first one is in use of co-impregnation, the aqueous solution of manganese nitrate (0.57mol•L⁻¹), stannum chloride (0.285mol•L⁻¹), stibium chloride (4.38mmol•L⁻¹), hydrochloric acid (0.5mol•L⁻¹) and ethanol was used for impregnating the support. Later, the catalyst precursors were dried at 90°C for 2 h, followed by calcining at 550°C for 4 h. This was called Mn-Sn-Sb-1. During the course of the successive impregnation, two kinds of catalysts were obtained according to the different impregnating sequences. The supports were impregnated in an aqueous solution of stannum chloride (0.285mol•L⁻¹), stibium chloride (4.38mmol•L⁻¹), hydrochloric acid (0.5mol•L⁻¹) and ethanol at first for 4h, and dried at 90°C for 2 h, followed by calcining at 550°C for 4 h. Later, the catalyst precursors were impregnated in the solution of manganese nitrate (0.57mol•L⁻¹) for 4 h again and dried at

This work was supported by Chinese National Natural Science Foundation, Project 50378066.

105°C for 12 h, followed by calcining at 550°C for 4 h. This was called Mn-Sn-Sb-2. The same procedure was followed to prepare Mn-Sn-Sb-3 except that it was impregnated by the solution of manganese nitrate at first and then by the aqueous solution of stannum chloride, stibium chloride, hydrochloric acid and ethanol. The three different catalysts all had a molar ratio of Mn to Sn of 2:1 and 0.1 wt% Sb.

B. Experimental apparatus and Procedure

Oxidation experiments were performed in a high-pressure up-flow co-current packed bed reactor, self-made of SUS 316 stainless steel tubing. The experimental setup has been described in detail elsewhere [7].

The experiments were carried out in a temperature range of 120-150°C, oxygen partial pressure of 1.0MPa, space time of 3-27min, and the aqueous phenol solution of 2500mg•L⁻¹. The Ph of feed solution was 6.47 and no adjustment of pH value was made in all the experiment. About the height of 30mm of nonporous glass pellets (diameter, 2mm), 300mm of catalyst particles and again 30mm of nonporous glass pellets (diameter, 2mm) were placed into the reactor from inlet to outlet in turn. During CWO runs, there was no electrode in the reactor. The liquid and gas phase were introduced upwards into the reactor through the glass pellet bed so that the flux of both phases was approximately uniform over the bed cross-sectional area. Initially, the reactor was charged with an amount of oxygen supplied by the bottled compressed oxygen to the experimental reaction pressure and heated at the same time. Once the desired temperature had been attained, the liquid was fed to the reactor by a reciprocating piston metering pump, which supplied the phenol solution at different flow rates. The gas flow rate was kept constant at 250ml•min⁻¹ in standard temperature and pressure (STP) conditions, which is well beyond the stoichiometric oxygen uptake needed.

C. Product Analysis

Liquid samples were withdrawn from the gas-liquid separator after steady state was reached. The residual phenol concentration in the collected samples at different time intervals was determined by UV-Visible spectrophotometer (Shimadzu, UV-1700) at wavelength 510nm, and the total organic carbon value was measured by a Shimadzu TOC-V_{CPN} analyzer. The concentrations of leached metal ions in the outlet samples were determined by inductively coupled plasma-optical emission spectrometer (Perkin Elmer, USA). The pH of the effluent was examined by means of a pH meter (Shanghai precision & scientific instrument Co., Ltd, China).

III. RESULTS AND DISCUSSION

A. Catalytic activity of different catalysts

The results for the catalytic efficiency evaluation of the different Mn-Sn-Sb/ γ -Al₂O₃ catalysts in the process of phenol catalytic wet oxidation are shown in Fig.1, and compared with results obtained for the reaction carried out on γ -Al₂O₃ support. In the absence of any active metals,

Fig. 1. Phenol conversion profiles for the different catalysts at 150°C, 1MPa of oxygen partial pressure.

phenol conversion is only 12.9% on the support of γ -Al₂O₃ at the space time of 27min. It is obvious that the trimetallic catalysts significantly increase the phenol conversion. Phenol conversion of Mn-Sn-Sb-1 catalysts is 62.7% higher than that of the support of γ -Al₂O₃ at the space time of 27min.

It is also clear that the activity of these catalysts depends strongly on the type of the impregnation techniques. Phenol conversions of the Mn-Sn-Sb-2 and Mn-Sn-Sb-3 catalysts, which were prepared by the technique of successive impregnation, are higher than that of the Mn-Sn-Sb-1 catalyst, which was prepared by the technique of co-impregnation. The Mn-Sn-Sb-2 catalyst is the most active one of all the three kinds of the Mn-Sn-Sb/ γ -Al₂O₃ catalysts. At the space time of 27min, phenol conversion of it could get 97.2% at the given condition.

B. Comparison of chemical stability

To analyze the catalyst deactivation several consecutive runs were performed under the condition of 120°C and 1MPa of oxygen pressure in 100h tests. Results are shown in Fig. 2.

As can be seen, the main trend common to all the catalysts is the severe deactivation observed during the operation. During the first 15h of the test, phenol conversion stabilizes in a relative higher level, which is almost similar for all the catalysts. After this point, the phenol conversion begins to decrease and the catalysts still lose activities until the end of the test. It should be noted that the initial behavior of Mn-Sn-Sb-2 catalyst was notably different since its activity increased for the first 4h until it reached its highest phenol conversion (over 85%). Later, this phenol conversion has a sudden drop. As noted above, the Mn-Sn-Sb-2 catalyst finally gives the lowest phenol conversion.

Fig. 2. Phenol conversion of different trimetallic catalysts in 100h tests at 120°C, 1MPa of oxygen partial pressure.

TABLE I. SUMMARY STATISTICS FOR DIFFERENT CATALYSTS

Catalyst		N	Min.	Max.	Mean	Standard deviation
Mn-Sn-Sb-1	Phenol Conversion, %	25	9.1	54.4	27.2	14.8
	TOC Reduction, %	25	5.3	49.9	22.6	15.2
	Valid N (listwise)	25				
Mn-Sn-Sb-2	Phenol Conversion, %	25	6.4	85.8	41.8	28.1
	TOC Reduction, %	25	3.2	77.3	35.2	26.6
	Valid N (listwise)	25				
Mn-Sn-Sb-3	Phenol Conversion, %	25	19.8	73.4	42.9	17.5
	TOC Reduction, %	25	12.8	67.0	36.4	17.6
	Valid N (listwise)	25				

For comparing the chemical stability of the catalysts further, descriptive statistics on phenol conversion and TOC reduction for different catalysts were computed in virtue of the statistical software SPSS and provided in Table I.

The mean phenol conversion for the catalysts ranges from 27.2% for Mn-Sn-Sb-1 catalyst to 42.9% for Mn-Sn-Sb-3 catalyst. There is substantial variation in phenol conversion. The standard deviation ranges from 14.8% for Mn-Sn-Sb-1 catalyst to 28.1% for Mn-Sn-Sb-2 catalyst.

The mean TOC reduction ranges from 22.6% for Mn-Sn-Sb-1 catalyst to 36.4% for Mn-Sn-Sb-3 catalyst. The standard deviation ranges from 15.2% for Mn-Sn-Sb-1 catalyst to 26.6% for Mn-Sn-Sb-2 catalyst. From these results, the mean phenol conversion and TOC reduction for Mn-Sn-Sb-3 catalyst is the highest and the variation is narrower, so the Mn-Sn-Sb-3 catalyst may be the best one among the three kinds of Mn-Sn-Sb/ γ - Al_2O_3 catalysts.

C. Relationships between pH and the leaching of metal ions

Based on the above results, it was further studied that the relationships between the effluent pH and the concentrations of leaching metal ions. Fig.3 shows the reactor outlet pH, the concentrations of the leaching Mn^{2+} and Al^{3+} evolutions during the 100h activity tests at 120°C, 1MPa of oxygen partial pressure.

As can be seen, the Al^{3+} concentration increases throughout the test. But at the same time, it must be noted that the amount of the Al^{3+} that dissolves during the reaction time is very small for the three catalysts. Later it stabilizes more or less at $0.65\text{mg}\cdot\text{L}^{-1}$, as also found by other authors [8]. So, the granule of γ - Al_2O_3 has been shown to be stable under this relatively mild condition and suitable to be selected as catalyst support.

Fig. 3. Aluminum concentration, manganese concentration and pH profiles in the reactor effluent for 100h operating at 120°C, 1MPa of oxygen partial pressure.

The loss in catalytic activity can be attributed to the leaching of manganese from the catalysts during the process. This speculation is proved by Fig.3, especially for the Mn-Sn-Sb-2 catalyst. At first, the rate of dissolution of Mn^{2+} rapidly increases until giving a maximum concentration around $9\text{mg}\cdot\text{L}^{-1}$. This behavior indicates that the activity of Mn-Sn-Sb-2 catalyst is lower than that of the Mn-Sn-Sb-3 catalyst; this is in good agreement with the present investigation.

At the same time, the relationship between the effluent pH and the concentration of leaching Mn^{2+} and Al^{3+} were assessed using Person correlation coefficient matrix by SPSS, as shown in Table II.

TABLE II. CORRELATIONS AMONG THE pH, THE CONCENTRATION OF LEACHING Mn^{2+} AND Al^{3+}

Catalyst		Pearson correlation coefficient		
		pH	$\text{Al}^{3+}, \text{mg}\cdot\text{L}^{-1}$	$\text{Mn}^{2+}, \text{mg}\cdot\text{L}^{-1}$
Mn-Sn-Sb-1	pH	1	-0.919(**)	0.275
	$\text{Al}^{3+}, \text{mg}\cdot\text{L}^{-1}$	-0.919(**)	1	-0.236
	$\text{Mn}^{2+}, \text{mg}\cdot\text{L}^{-1}$	0.275	-0.236	1
Mn-Sn-Sb-2	pH	1	-0.827(**)	-0.965(**)
	$\text{Al}^{3+}, \text{mg}\cdot\text{L}^{-1}$	-0.827(**)	1	0.738(**)
	$\text{Mn}^{2+}, \text{mg}\cdot\text{L}^{-1}$	-0.965(**)	0.738(**)	1
Mn-Sn-Sb-3	pH	1	-0.880(**)	-0.810(**)
	$\text{Al}^{3+}, \text{mg}\cdot\text{L}^{-1}$	-0.880(**)	1	0.539(**)
	$\text{Mn}^{2+}, \text{mg}\cdot\text{L}^{-1}$	-0.810(**)	0.539(**)	1

In all experimental runs, the effluent pH was in good correlation with the concentration of leaching Mn^{2+} . In addition, the concentration of leaching Mn^{2+} and the concentration of leaching Al^{3+} were negative correlation with the effluent pH to Mn-Sn-Sb-2 and Mn-Sn-Sb-3 catalysts, respectively. That is to say, the loss of the catalyst surface metal oxides will increase while the pH decreases. The intermediates in the phenol oxidation have been found to be mainly mono and di-carboxylic acids such as oxalic, acetic or formic acid [6], so the dissolution of metal ions is related to the attack on the catalyst by the extremely hot acidic medium where the oxidation takes place [9], which is evident from Pearson correlation coefficient matrix.

D. Influence of the temperature on Mn-Sn-Sb-3 catalyst

Because a significant activity of Mn-Sn-Sb-3 was observed, phenol conversion and TOC reduction of Mn-Sn-Sb-3 catalyst were carried out at different temperatures and 1MPa of oxygen partial pressure. Results obtained are shown in Fig. 4.

As can be seen, the increasing temperature has as a result increased phenol conversion (Fig. 4a), followed the same trend as TOC reduction (Fig. 4b). As the temperature rises from 130 to 150°C, phenol conversion increases from 44.3% to 90.6%, and TOC reduction from 39.4% to 83.1% at the space time of 27min. Hence, the supports exhibit a better catalytic activity at higher temperatures and this agrees well with results reported for CWAO of phenol on platinum and ruthenium catalysts [10].

IV. CONCLUSIONS

The oxidation of aqueous phenol was conducted in mild conditions of temperature (120-150°C), oxygen partial pressure (1.0MPa) and space time (3-27min) in a packed bed

Fig. 4. Phenol conversion (a) and TOC reduction (b) of Mn-Sn-Sb-3 catalysts at different temperatures and 1MPa of oxygen partial pressure.

reactor. Three kinds of Mn-Sn-Sb/ γ - Al_2O_3 were successfully prepared by using successive impregnation and co-impregnation separately. Descriptive statistics of different catalysts indicated that the catalyst which was loaded by the manganese oxides first and then by the stannum oxides and stibium oxides has good activity and stability. Using this catalyst, phenol conversion and TOC reduction could get 90.6% and 83.1% at 150°C, 1MPa of oxygen partial pressure and space time of 27min. Trimetallic catalysts including manganese, stannum and stibium oxides supported over γ - Al_2O_3 were demonstrated to have catalytic effect on the wet oxidation of phenol. The correlation analysis indicated that the dissolution of metal ions was negative correlation with the effluent pH, although the different impregnating sequences varied the results.

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