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Deactivation of zeolite catalysts for benzene oxidation to phenol

Pimu Zhai, Liqiu Wang, Changhou Liu*, Shouchen Zhang

School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, 43 Postbox, Dalian 116012, PR China

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Abstract

Coking and deactivating experiments were carried out in a fixed-bed reactor for benzene oxidation to phenol (BTOP). The catalyst used in this study was HZSM-5 ($SiO_2/Al_2O_3 = 20$) treated by high temperature steam at 700 °C. Then the catalysts undergoing different reaction time were analyzed and characterized. The amount of coke was measured by TG. The coke components were detected by infrared. At the same time, the main physics properties of the catalyst with coke deposition were characterized. The pores of the catalyst before and after coking were measured by N_2 adsorption at −196 °C. The amount of hexane and cyclohexane adsorption was measured by weight continuous flow. The acid sites of Bronsted and Lewis were characterized by pyridine adsorption-infrared measurements. Our results show that the deactivation of ZSM-5 in the BTOP reaction system is caused by the coke deposition in the mouth of pores and blocking the pores of the catalyst. It can also be found that the present process agrees with most coking processes over ZSM-5 caused by organic compounds, the Bronsted acid sites are the active sites of the coking.

Keywords: Nitrous oxide; Phenol; Deactivation; Coking; Benzene oxidation

1. Introduction

The partial oxidation of benzene to phenol by nitrous oxide in a single step is a challenge in industrial practice. Though the reaction process has been studied for over 10 years and many catalysts have been developed, the fast deactivation of catalyst is the main obstacle for its industrial application. Some reports show that the main reason to the deactivation of catalyst in BTOP is the coke deposits on the catalyst surface.

In many studies of coking caused by some organic substance reactions over ZSM-5, it was found that carbonaceous material was formed from lower alkene [1–3], undergoing polymerization, hydrogen migration, etc. to form long chain alkene and lower aromatic hydrocarbon, and then hydrogen migration and alkylation.

Dejaifve et al. [4] reported that coke precursors can be formed in different locations of channel networks over ZSM-5, offretite and mordenite. For H-offretite and H-mordenite, the channels are large enough to accommodate carbonaceous residues. But ZSM-5 has good shape-selective properties and the carbonaceous residues are primarily formed on the outer surface of the crystallites. Blackmond and Goodwin [1] and Dejaifve et al. [4] also reported that the acid sites of Bronsted are the active sites of carbonaceous formation.

Anderson et al. [5,6] have shown that, at 593–673 K, benzene reacts over ZSM-5 in the presence of oxygen to give a carbonaceous residue. It is claimed that channel intersections within ZSM-5 are the main locations for the formation of carbonaceous residues. This statement is consistent with the widely accepted idea that the Bronsted acid sites in ZSM-5 lie at the intersections of the two channels.

In BTOP reaction system, N_2O is introduced and phenol is formed. So the mechanisms of carbonaceous formation become very complicated. Some studies on carbonaceous formation in BTOP system were reported recently. Burch and Howitt [7] and Ivanov et al. [8] have shown more detailed studies on carbonaceous formation in BTOP reaction system. These two reports employed different samples and investigation methods for the coke deposition of catalyst in their respective experiments, moreover, the BTOP reaction process

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* Corresponding author. Tel.: +86 411 88993956.
E-mail addresses: liuch@chem.dlut.edu.cn, liuchanghou@163.com (C. Liu).

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is very complicated, and the conclusions are different. Burch and Howitt [7] claimed that the deactivation of catalyst was due to the carbonaceous deposition blocking the zeolite structure. Ivanov et al. [8] claimed that the deactivating effect of coke is caused by poisoning of active sites of catalyst.

In the study of kinetics of the hydroxylation of benzene with nitrous oxide, Reitzmann et al. [9] pointed out that the coke formed in BTOP was caused by further oxidation, dehydrogenation and oligomerisation of phenol formed in the active sites of catalyst. BTOP over the modified ZSM-5 was studied by us [10] recently. The coke components were detected by infrared and ^{13}C NMR in the study. Our results [10] show that the main components of coke on the catalysts consist of aromatic with alkyl and multiring hydrocarbon. In addition, the coke also consists of some aromatic with hydroxy groups which may be caused by further oxidation, dehydrogenation and polymerization of phenol formed on Lewis acid sites. In this paper we continue to study the relationship between the coke and deactivation for BTOP catalyst in order to find the reason and corresponding factors of coking and to develop a new catalyst to inhibit coke well.

2. Experimental

2.1. Deactivation tests for the catalyst

The $SiO_2/Al_2O_3 = 20$ (mole ratio) HZSM-5 powder was first treated by high temperature steam at 700 °C and then extruded and cut to be 0.8 mm diameter and 1 mm long particle used to test activity, analysis and characterization. The deactivation tests were carried out in a fixed-bed reactor. The reaction conditions were as follows: 1 g catalyst loaded in the fixed-bed reactor, 115 ml/min of gas (mol N_2O/mol $N_2 = 9.7/90.3$) flow rate, 6 g/h of benzene flow rate and 400 °C of reaction temperature. Analyzing gas and liquid composition regularly, calculating the conversion, selectivity and productivity.

2.2. Coke analysis and catalyst characterization

2.2.1. Collection of coke samples and coke analysis

When the reaction time of deactivation of catalyst was reached, shut off the materials (benzene and N_2O) fed to the reactor, and switched the flow rate of 30 ml/min of high purity N_2 (99.99%). Swept the catalyst for 40 min at 400 °C of reaction temperature. When the temperature dropped to room temperature, analyzed the catalyst and the amount of coke by TGA/SDTA851.

2.2.2. Characterization of the catalyst with the deposition of coke

The catalyst surface area and pore volume was measured with American Quantachrome Company AS-1-MP physical adsorption instrument by using nitrogen at 77 K.

The amount of hexane and cyclohexane adsorption was measured by weight continuous flow at 25 °C, standard pressure and 20 mmHg of partial pressure.

The acid sites of Bronsted and Lewis on the catalyst samples before and after coking were characterized by pyridine adsorption-infrared measurements.

3. Experimental results and discussion

3.1. Catalyst deactivation

Fig. 1 shows the relationship between the phenol productivity, the amount of coke and the total volume of the catalyst pores with reaction time.

3.2. Characterization of the catalyst with the deposition of coke

3.2.1. Characterization of the amount of coke deposition and pore structure

Table 1 shows the obtained results of the amount of coke deposit on the catalyst and the pore structure varying with the reaction time. In addition, Table 1 also gives the value of pore volume drop ΔV_B. Take 1.22 g/ml as the density of coke deposit, calculate the volume of coke deposition V_C and ratio of $\Delta V_B/V_C$.

3.2.2. The experimental results of cyclohexane and hexane adsorption on the catalyst

Table 2 shows the experimental results of cyclohexane and hexane adsorption on the catalyst before and after coke deposition.

3.2.3. IR analysis results of acidity on the catalyst samples

The acid sites of Bronsted and Lewis on the catalyst samples before and after coking were characterized by pyridine

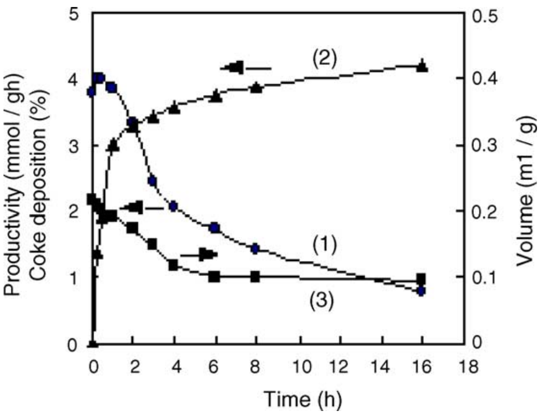

Fig. 1. The phenol productivity, amount of coke deposition and total volume of the catalyst pores at different reaction time: (1) (●) phenol productivity, (2) (▲) coke deposition (%) and (3) (■) the total volume of all pores.

Table 1
The amount of coke deposition and pore structure of the catalyst vary with the reaction time

	Reaction time (h)							
	0	0.5	1.0	2.0	3.0	4.0	8.0	16
Specific area (m^2/g)	306	285	270	250	241	229	210	188
Pore volume, V_B (cm^3/g)	0.216	0.202	0.193	0.171	0.147	0.118	0.102	0.096
Coke amount (wt.%)	–	1.93	3.00	3.28	3.44	3.58	3.88	4.21
Coke volume, V_C (cm^3/g)	–	0.0158	0.0246	0.0264	0.0282	0.0293	0.0318	0.0345
ΔV_B (cm^3/g)	–	0.014	0.023	0.045	0.069	0.098	0.114	0.120
$\Delta V_B/V_C$	–	0.886	0.934	1.67	2.45	3.45	3.58	3.48

Table 2
The amount of cyclohexane and hexane adsorption on the catalyst before and after different coke deposition times

	Reaction time (h)							
	0	0.5	1.0	2.0	3.0	4.0	8.0	16
Cyclohexane (wt.%)	5.2	4.81	4.61	3.29	2.90	2.82	2.87	2.97
Hexane (wt.%)	10.3	9.42	9.16	8.21	8.00	7.51	7.01	6.42
Cyclohexane/hexane	0.505	0.511	0.504	0.401	0.362	0.375	0.410	0.420

adsorption-infrared measurements. Fig. 2 shows the IR spectrums of acidity on the different catalyst samples.

3.2.4. Discussion

Fig. 1 shows the deactivation process can be divided into three steps according to the phenol productivity of catalyst varying with reaction time.

During the first step (0–1 h), the coke formation rate is fast but the deactivation rate of the catalyst is very slow and this indicates that the deactivation of the catalyst is not caused by poisoning the active sites. At the same time, the acidity on the catalyst samples showed in Fig. 2 indicates that the number of the acid sites of Bronsted is decreased significantly but the number of the acid sites of Lewis on the catalyst samples change slightly. This phenomena can be explained by the acid sites of Lewis being the active sites in BTOP agreed by most of researchers, and the acid sites of Bronsted being easier to cause coking than those of Lewis [4,10]. This statement is consistent with the results of coke analysis, that is, the main components of coke on the catalysts consist of aromatic with alkyl and multiring hydrocarbon caused by benzene coking on the acid sites of Bronsted directly. In addition, the coke also consists of some little aromatics with hydroxy groups caused by further oxidation, dehydrogenation and polymerization of phenol adsorbed on Lewis acid sites [9]. It is clear that the amount of coke formed on Lewis acid sites is very little. In this step, the values of $\Delta V_B/V_C$ are 0.886 and 0.934. The amount of cyclohexane and hexane absorbed on the catalyst decreases but the ratio of cyclohexane/hexane changes slightly (varying from 50.5% to 50.4%). This indicates that coke formed in this step does not block the mouth of channels. The values of $\Delta V_B/V_C$ are less than 1.0 which means the amount of coke formed on the external surface of crystallites is very large in this step.

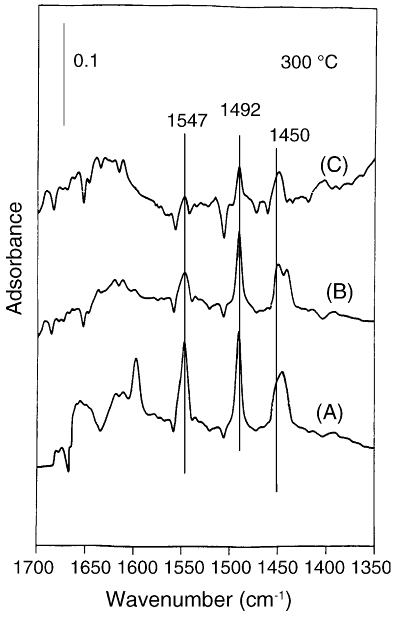

Fig. 2. IR spectrums of acidity on the different catalyst samples. (A) The fresh catalyst, (B) after reaction of 1 h and (C) after reaction of 8 h.

During the second step (1–3 h), the coke formation rate is not as fast as that in the first step, but the deactivation rate of the catalyst increases very fast. The micro-pore volume and the ratio of cyclohexane/hexane also decrease significantly. The values of $\Delta V_B/V_C$ increase to 1.67–2.45 (to 3.45 after 4 h reaction time). The ratio of cyclohexane/hexane decreases from 50.4% to 40.1–36.2%. This indicates that coke formation has blocked the mouth of channels of crystallite which is consistent with the conclusion claimed by Anderson et al. [5,6].

The last step is the reaction time is greater than 3 h. The values of $\Delta V_B/V_C$ decrease gradually from 3.58 to 3.48 during the reaction time from 8 to 16 h. This indicates that the amount of coke formed on internal surface of channels only increases slightly and the coke formed is located on external surface of crystallites mainly. The deactivation rate of the catalyst slows down and the catalyst has still high activity. Fig. 2 shows the results of acidity of catalyst samples. From Fig. 2 we can find that there are still many acid sites of Lewis on the catalyst samples after 8 h of reaction time. This indicates that some amount of N_2O and benzene can enter into the micro-pore which can be explained by two-dimension channel networks of ZSM-5, so that the coke cannot block all the mouths of channels of ZSM-5 together.

4. Conclusions

The main reason for deactivation of catalyst in BTOP is the coke deposition in the mouth of pores and blocking the pores of the catalyst. Similar to most coking processes over ZSM-5 caused by organic compounds, the Bronsted acid sites are also the active sites of the coking in this reaction system. The coke consists of some aromatics with hydroxy groups which may be caused by further oxidation, dehydrogenation and polymerization of phenol formed on Lewis acid sites.

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