

THE CARBON DEPOSITING BEHAVIOR AND ITS KINETIC RESEARCH IN BENZENE ALKYLATION PROCESS OVER HIGH SILICATE ZSM-5 ZEOLITE

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Abstract

In our invention, FCC (fluid catalytic cracking) dry gas could be used to react with benzene without any special purification, and more than 90% ethylene was converted to ethylbenzene. The phenomenon of carbon deposition over catalyst surface was obvious and leads to a deactivation of catalyst, so it is important to study the behavior of carbon deposition of catalyst during alkylation of benzene. The influence of several factors such as temperature, reaction time, reactant concentration of the amount and the kinetics of carbon deposition were investigated, during which carbon depositing rate equations were obtained for different reactant.

Keywords: benzene alkylation, carbon deposition, TG

Introduction

FCC (fluid catalytic cracking) dry gas consists of useful ethylene and propylene besides methane, nitrogen and carbon dioxide. In order to make full use of ethylene in FCC dry gas, Mobil and Badger Company developed the gas phase technology of ethylbenzene production by using ZSM-5 zeolite catalyst in 1970s. In 1980s, we explored another method for the ethylbenzene production from ethylene in FCC dry gas by using pentasil high silicate zeolite. According to our invention, FCC dry gas could be used to react with benzene without any special purification, and more than 90% ethylene was converted to ethylbenzene, otherwise, the phenomenon of carbon deposition over catalyst surface was obvious, leading the catalyst deactivate. That is to say, the carbon deposition was unfavorable to the life of catalyst. In order to improve the catalytic steady of catalyst in reaction, thermal analysis technology was employed to study the behavior of carbon deposition of catalyst during alkylation of benzene [1-5]. The influence of several factors such as temperature, reaction time, reactant concentration on the amount of carbon deposition and the kinetics of carbon deposition has also been investigated.

Experimental

Catalyst

The catalyst used for alkylation of benzene was high silicate zeolite ZSM-5 catalyst prepared by hydrothermal method. Before reaction the catalyst was treated by steaming and heating, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molecular ratio is 50.

Reactant

The reaction reactant used was ethylene, propylene, benzene, ethylbenzene and cumene, dilute gas used was N_2 .

Carbon depositing experimental

All experiments were performed on the Shimadzu DT-30 type thermal analyzer with range: 2–5 mg, heating rate: $10^\circ\text{C min}^{-1}$ or isothermally and chart speed: 1.25 mm min^{-1} .

The zeolite catalyst was put in a small basket made of quartz and suspended at the center of reaction tube and then balanced with weights.

First the zeolite catalyst was heated in a temperature programmed mode up to 500°C . This temperature was maintained for 30 min in order to eliminate physically adsorbed water, then the catalyst was cooled to reaction temperature. After this, reactant was brought to the reactor by the carrying gas at a speed of $30\text{--}40 \text{ ml min}^{-1}$. The temperature and the amount of carbon deposition were recorded.

Results and discussion

The effect of reaction time on the carbon deposition

Figure 1 shows the effect of reaction time on the carbon deposition of reactants such as benzene, ethylbenzene, propylbenzene (with concentration of 10 v%), ben-

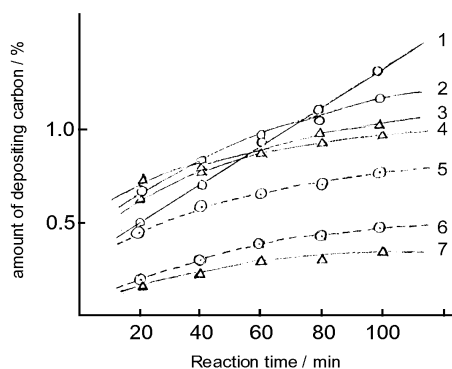


Fig. 1 The relationship between the amount depositing carbon and the reaction time. 1 – benzene/ethylene, 2 – benzene/propylene, 3 – propylene, 4 – ethylene, 5 – ethylbenzene, 6 – cumene, 7 – benzene

zene/ethylene, benzene/propylbenzene (with concentration of 30/70.5 v% and 20/5 v% respectively) and products as ethylbenzene cumene (with concentration of 7.5 v%) at 400°C.

It is clear from Fig. 1 that the amount of carbon deposition on catalyst increases with the reaction time whether using single reaction component or double component, and the increment of carbon depositing is decreased for other chemical components except benzene/ethylene. The carbon depositing profiles can be expressed as Voorleies equation:

$$C = Kct^m \quad (1)$$

where C – the amount of carbon deposition (%) Kc – constant, m – constant, t – reaction time (min).

From Eq. (1) we can get Eq. (2) in form of

$$\log C = \log Kc - m \log t \quad (2)$$

From Eq. (2), constants Kc and m can be obtained easily according to the linear relationship between $\log C$ and $\log t$.

Table 1 lists the results of m and Kc .

Figure 2 shows the relationships between carbon depositing ratio and reaction time for benzene/ethylene and ethylbenzene.

Table 1 The relationship between the amount of carbon deposition and reaction time

Reactant	$C=Kct^m$
Benzene	$5.610^{-4} \cdot t^{0.375}$
Ethylene	$3.9 \cdot 10^{-3} \cdot t^{0.195}$
Propylene	$2.88 \cdot 10^{-3} \cdot t^{0.275}$
Benzene/ethylene	$8.2 \cdot 10^{-4} \cdot t^{0.596}$
Benzene/propylene	$2.0 \cdot 10^{-3} \cdot t^{0.375}$
Ethylbenzene	$1.9 \cdot 10^{-3} \cdot t^{0.298}$
Cumene	$0.26 \cdot 10^{-3} \cdot t^{0.651}$

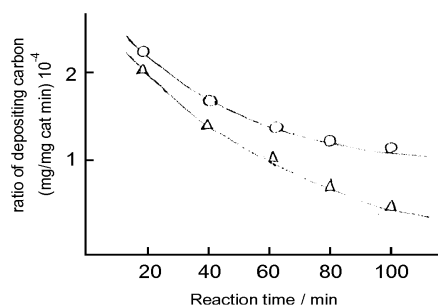


Fig. 2 The relationship between carbon depositing rate of benzene/ethylene or ethylbenzene and reaction time; o – benzene/ethylbenzene, Δ – ethylbenzene

It can be found that the carbon deposition rate is higher at preliminary time and then decreases with reaction time, which may be due to the asymmetricity of acidity of zeolite catalyst, because the depositing carbon would fill in entrance of pore-channel of zeolite, balking the diffusing of reactants and products, so the carbon depositing rate becomes slower.

The effect of concentration of reactants on the carbon deposition

Figures 3 and 4 show the relationship between reactant concentration and depositing carbon amount

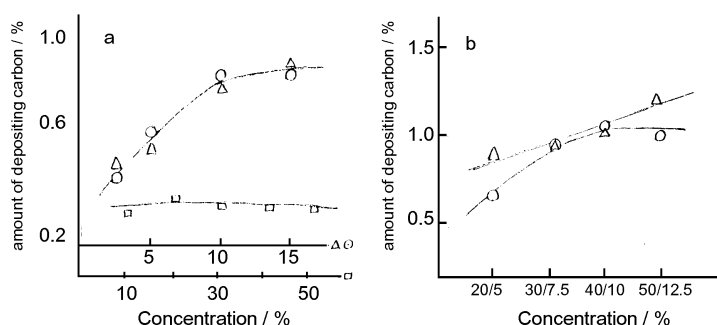


Fig. 3 The relationship between depositing carbon amount and reactant concentration; a: Δ – ethylbenzene, o – propylene, \square – benzene; b: Δ – benzene/ethylene, \bullet – benzene/propylene

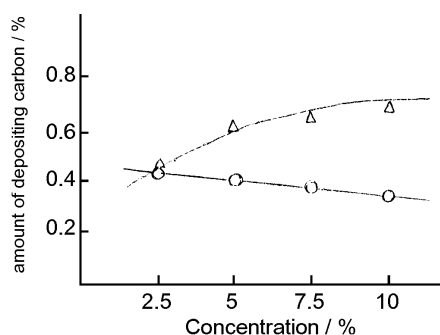


Fig. 4 The relationship between depositing carbon amount and product concentration
 Δ – ethylene, o – cumene

We can find that at 400°C the amount of depositing carbon is hardly influenced by the concentration of benzene, but is obviously enhanced with the increasing concentration of ethylene or propylene, the same as to benzene/ethylene and benzene/propylene. The amount of depositing carbon for ethylbenzene also increases when its concentration is not more than 5% (V), and then extends to the balance state with the increasing of ethylbenzene concentration, while cumene concentration has little effect on carbon deposition.

The kinetics research of carbon depositing in alkylation of benzene

The kinetics of carbon depositing in alkylation process is very complicated. In order to get the key point of its kinetics, we investigated the kinetics of benzene alkylation with ethylene, propylene, respectively and cracking of ethylbenzene.

Under the condition of constant reaction temperature, the carbon depositing equation is expressed as follows:

$$dc/dt = KPr^n \quad (3)$$

where dc/dt – rate of carbon depositing, K – rate constant, Pr – concentration of reactant, n – reaction order.

The constant of reaction rate can be expressed with Arrhenius equation:

$$K = Ae^{(-E/RT)} \quad (4)$$

Eq. (4) and Eq. (3) can be expressed as

$$dc/dt = Ae^{(-E/RT)}Pr^n \quad (5)$$

Table 2 Amount and rate of carbon depositing of benzene/ethylene reaction under different reactant concentration

Catalyst mass/mg	Concentration/%	Carbon deposition mass/		Carbon deposition rate/ mg min ⁻¹	ln(dc/dt)	lnPr
		mg	%			
30.96	20/5	0.271	0.875	1.06·10 ⁻⁴	-8.8319	-2.9957
31.49	30/7.5	0.290	0.917	1.53·10 ⁻⁴	-8.7851	-2.5903
30.83	40/10	0.330	1.070	1.78·10 ⁻⁴	-8.6337	-2.6026
30.91	50/12.5	0.446	1.310	2.40·10 ⁻⁴	-8.3349	-2.0794

Table 3 Amount and rate of carbon depositing of benzene/ethylene reaction under different reactant temperature (concentration of 30/7.5)

Catalyst mass/mg	T/°C	1000/T/ 1/K	Carbon deposition mass/		Carbon deposition rate/ mg min ⁻¹	ln(dc/dt)
			mg	%		
32.26	350	1.6053	0.385	1.190	1.93·10 ⁻⁴	-8.5272
32.07	375	1.5432	0.326	1.105	1.69·10 ⁻⁴	-8.6845
31.49	400	1.4859	0.290	0.917	1.53·10 ⁻⁴	-8.7851
32.07	425	1.4327	0.273	0.853	1.42·10 ⁻⁴	-8.8597
31.92	450	1.3831	0.244	0.760	1.27·10 ⁻⁴	-8.9605

From Eqs (3) and (4) we get

$$\ln(dc/dt) = \ln K + n \ln Pr \quad (6)$$

$$\ln(dc/dt) = \ln A + n \ln Pr - E/(RT) \quad (7)$$

We take benzene alkylation with ethylene as a typical example. Tables 2 and 3 list amounts and rate of carbon depositing of benzene/ethylene reaction under different reactant concentration and different reaction temperature.

Procedure of determination of reaction order and activation energy is illustrated in Figs 5 and 6, respectively.

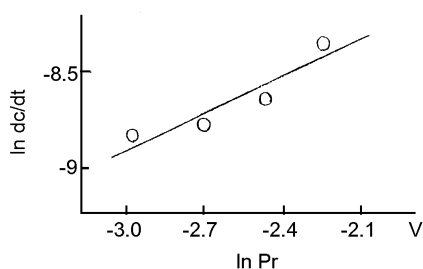


Fig. 5 Relationship between $\ln(dc/dt)$ and $\ln Pr$

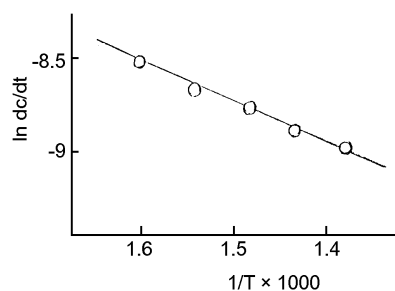


Fig. 6 Relationship between $\ln(dc/dt)$ and $1000/T$

Table 4 elucidates the reaction order and the activation energy of carbon depositing of benzene/ethylene, benzene/propylene and ethylbenzene, from which we can obtain carbon depositing rate equation (Table 5).

It can be seen from Fig. 5 that carbon depositing activation energy of benzene/ethylene or benzene/propylene is more than that of ethylbenzene. This explains that carbon depositing capacity of benzene/ethylene or benzene/propylene is lower than that of ethylbenzene. This is probable because conjugate effect of conjugate π band in the benzene ring make benzene ring stable, so it can be thought that carbon deposition during benzene alkylation comes from cracking of ethylbenzene product. Because ethylbenzene takes place cracking or disproportionation easily under reac-

Table 4 Results of reaction order and the activation energy results of carbon depositing for different reactants

Reactant	Kinetic parameter	
	N	$E/\text{kJ mol}^{-1}$
Benzene/ethylene	0.50	15.66
Benzene/propylene	0.40	31.51
Ethylbenzene	0.30	11.87

Table 5 Carbon depositing rate equation for different reactants

Reactant	Rate equation for carbon depositing
Benzene/ethylene	$dc/dt=3.45 \cdot 10^{-5} e^{(-3738.5/RT)} p_r^{0.5}$
Benzene/propylene	$dc/dt=1.52 \cdot 10^{-6} e^{(-7522.1/RT)} p_r^{0.4}$
Ethylbenzene	$dc/dt=1.91 \cdot 10^{-3} e^{(-2835.4/RT)} p_r^{0.3}$

tion temperature reproducing benzene and (C₂H₅) and poly-alkyl-benzene, which are easy to form long chain hydrocarbon and poly-circle-hydrocarbon, i.e. carbon depositing precursor.

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