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Influence of contaminants in catalyst stability and durability

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Introduction

The performance of the Fe/ZSM-5 catalyst in the hydroxylation of benzene by nitrous oxide is affected by the amount of Fe loaded into the catalyst, the nature and concentration of surface acid sites and steam pre-treatment [1]. The main reason for deactivation of catalyst is coke deposition, which may be caused from further oxidation of phenol on the mouth of pores, blocking them and followed by decrease in the number of active sites [2]. The catalyst can be regenerated using either O_2 or N_2O, which N_2O was found to be a more efficient reactivation reagent than O_2 [3]. The present work was conducted to examine the catalytic stability of Fe/ZSM-5 by adding H_2O, O_2, CO, and CO_2 to the feed reactants. It was concluded that H_2O exerts a promoting effect on prolonged activity of the catalyst and values for catalyst half-life improved by 3 days when concentrations of CO_x and H_2O were controlled at less than 3 wt% and 1 wt%, respectively.

Materials and Methods

Catalyst was prepared by steam treatment of H/ZSM-5 powder at 550-700°C for 1-4 hours (50 mol% water vapor in the gas phase), followed by treatment in an aqueous solution of iron chloride (0.1 M) at 80°C, and then by washing with demineral water and exposed to an atmosphere of reducing gas. Catalytic experiments were performed using a plug flow reactor. For each experiment, 100 mg of 0.1-1 mm diameter catalyst particles were placed into a stainless steel reactor with the inner diameter 3 mm. the feed gas components were controlled using mass flow controllers (AALBORG with the suitable range). Benzene feed rate was controlled using a (HARVARD APPARATUS, 0.00044-77 ml/min) syringe dosing system. The reactor exit gas mixture was sampled and analyzed online. Concentrations of products were determined via their separation at a capillary columns DB-1701 (J&W Scientific),Poraplot Q, and Molsieve 5A, by GC-MS (HEWLETT PACKARD G1800A).

Results and Discussion

The presence of iron in the ZSM-5 was reported to be essential for good catalyst activity in the hydroxylation reactions[4]. There is a considerable attention to oxidation of benzene in the gas phase from an economic point of view. However, the deactivation was observed mainly due to coke deposition on the surface of the catalyst. Thus, it is necessary not only regenerate the catalyst periodically but also improve catalyst stability. Table 1 shows the main characteristics for the catalyst. It was observed isolated and binuclear Fe sites are active centers for both decomposition of N_2O and hydroxylation of benzene. Though, the isolated Fe sites are more effective in the hydroxylation reaction, which dominates at low Fe concentration. Additionally, it was found that the benzene conversion decreased and the selectivity to phenol increased with increasing benzene concentration in the feed gas. In the present research, the influence of different contaminants and diluents was also investigated. The off-gas stream from the adipic acid or the ammonia oxidation plants must be treated to remove NO_x and oxygen. NO_x acts as a poison to the Fe/ZSM-5 and oxygen must also be limited in order to avoid the complete oxidation of benzene to CO_2 and H_2O. It was cocluded that NO_x and oxygen have to be removed to less than 50 ppm and 0.01 wt%, respectively. Moreover, It was observed that CO accelerates the removal of atomic oxygen from the catalyst surface, resulting in the decrease in the operation temperature to 100°C.

Table 1. Main characteristics of the catalyst

Catalyst	Fe (wt%)	BET Surface Area (m^2/g)	Pore Volume (m^2/g)	Pore size (Å)
Fe/ZSM-5	0.4	313	0.69	92.8

Figure 1 shows that catalytic stability was improved and the productivity was decreased when the catalyst was exposed to a wet feed in the presence of CO. It is assumed that water displaces phenol from the sites which resulted in 21 wt% decrease in the coke formation during 24 hours.

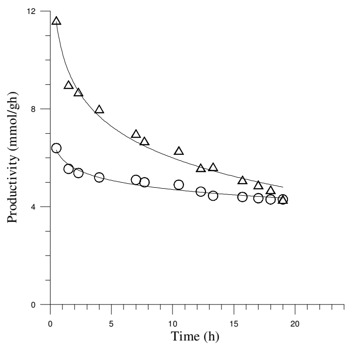

Figure 1. Influence of contaminants in the performance of the Fe/ZSM-5. Reaction temperature: 400°C, Feed composition: 40 mol% benzene, 5mol% N_2O, and He balance, Contact time 1 sec. (Δ) Dry feed, (O) Wet feed plus 0.5 wt% CO

Scienificance

The major advantages of this work include high yield conversion of N2O to phenol, and improve the catalyst stability. Nearly 98% of US phenol capacity is based on oxidation of cumene. As a result, the total fixed capital for the cumene process is about 17% higher than direct hydroxylation of benzene.

References

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