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Short communication

Coking and deactivation behavior of ZSM-5 during the isomerization of styrene oxide to phenylacetaldehyde

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ABSTRACT

Coking and deactivation behavior of ZSM-5 in the isomerization of styrene oxide to phenylacetaldehyde were investigated under gas-phase free of solvents. More soft coke was firstly formed on HZSM-5 and then partly converted to hard coke with the reaction carried through. The soft coke, which can be removed via desorption at 200–400 °C, had little effect on the catalyst activity and selectivity. While the hard coke, which had a certain degree of crystallization and must be completely removed via combustion with oxygen, would cause major catalyst deactivation. By confirmed, pore blocking was the predominant mode leading to deactivation of catalyst.

1. Introduction

Isomerization of styrene oxide and derivatives to aldehydes yields valuable compounds or intermediates used for production of fragrances, pharmaceuticals, insecticides, fungicides and herbicides, particularly the halogenated derivatives of aldehydes are more needed [1]. Various solid acid catalysts, including mixed-metal oxides [2], silica-alumina gels [3,4], natural silicates [5], Nafion-H [6], heteropoly acids [7] and zeolites [8–10], etc., have been tried to catalyze this process. Among them, zeolites of the mordenite, erionite, chabazite and pentasil types are all superior to others in view of suppressing side reactions by shape selectivity, particularly the pentasil zeolites have the best performance with phenylacetaldehyde yield of over 90% at 200 °C and WHSV = $3\,h^{-1}$, however the catalysts begin to show deactivation indicating by decrease of the styrene oxide conversion after running for 6 h time on stream [11].

Gou et al. [12] have investigated the effect of acidity of ZSM-5 (SiO_2/Al_2O_3 = 25–360) in the isomerization of styrene oxide to phenylacetaldehyde and find out that the catalyst lifetimes are affected by both acid strength and concentration. Increasing the acid concentration while decreasing their acid strength can prolong the catalyst lifetimes. A series of zeolites modified by different methods, such as dealumination [13], fluorine modification [14], phosphorus modification [15] and alkali treatment [16], have been applied for the reaction. However, the catalyst lifetimes have shown only limited improvement.

Although effects of acidity and structure of ZSM-5 on the isomerization of styrene oxide to phenylacetaldehyde have been widely studied, only a small quantity of reports focus on the coke species and deactivation behaviors of catalysts. The deactivation mechanisms of ZSM-5 are not yet clear. So in the present study, coke species and deactivation behavior of ZSM-5 were identified using N_2 adsorption, SEM, XRD, XPS, TG-DTA and NH_3-TPD/titration.

2. Experiment

Styrene oxide (> 98 wt%) was purchased from TCI (shanghai) development Co., Ltd. and used without further purification. HZSM-5 (SiO_2/Al_2O_3 = 135) were obtained from Catalyst Plant of Nankai University (Tianjin, People's Republic of China) and used as catalyst.

Isomerization of styrene oxide was carried out in a continuous flow fixed-bed reactor (stainless steel tube, i.d. = 9 mm) operated at 200 °C, WHSV = $3.0\,h^{-1}$ and flow rate of N_2 = 120 ml/min. The catalyst (0.5 g, 20–30 mesh) was loaded in the constant-temperature zone and pretreated at 500 °C for 2 h in nitrogen flow. Styrene oxide, free of any solvents, was introduced into the reactor with flowrate of 0.025 ml/min using a HPLC pump (model Series II, LabAlliance, USA). At end of each experiment, the used catalyst was unloaded after purging with nitrogen at 200 °C for 2 h to remove any possible residual reactants.

Scanning electron microscope (SEM) experiments were made on a Hitachi SU-8010 scanning electron microscope (FE-SEM, 5 kV). The powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert Pro diffractometer in 2θ range of 5–50° with Co Kα radiation source (λ = 0.1789 nm). N_2 adsorption was measured at 77 K on a Quantachrome Autosorb-1 instrument. The surface area was calculated according to the BET equation, and the pore volume and size were determined using the HK method.

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X-ray photoelectron spectra (XPS) were performed on a PHI-1600 ESCA spectrometer with Mg Kα radiation source (1253.6 eV). The binding energies were determined using C 1s peak of contaminant carbon (BE = 284.6 eV) as standard.

Thermogravimetry-differential thermal analysis (TG-DTA) measurements were conducted on a Perkin-Elmer Pyris 6 thermogravimetric analyzer at a heating rate of 10 °C/min from room temperature to 800 °C in air or nitrogen flow.

In order to investigate the acidity changes of the fresh and used catalysts, temperature programmed desorption of ammonia (NH_3-TPD) was performed on a conventional apparatus equipped with a thermal conductivity detector. The sample (100 mg, 20–30 mesh) was pretreated at 200 °C in nitrogen and then cooled down to ambient temperature. Sufficient NH_3 was supplied into the system followed by flushing with nitrogen at 150 °C for 1 h. The TPD profile was obtained by heating the sample from 150 to 500 °C at a rate of 15 °C/min. Simultaneously, the desorbed NH_3 was trapped in boric acid, followed by titration with a standard H_2SO_4 solution [17].

3. Results and discussion

As shown in Fig. 1, catalytic testing of HZSM-5 was carried out at 200 °C, WHSV = 3.0 h^{-1} and flow rate of N_2 = 120 ml/min. In a blank test without catalyst, the conversion of styrene oxide was below 1% all the time. While the initial conversion of styrene oxide (TOS = 1.0 h) over HZSM-5 was over 99%, suggesting that this reaction was a catalysis process. The styrene oxide conversion remained unchanged for the first 6 h, but thereafter the catalyst began to show deactivation as indicated by decreasing of the styrene oxide conversion. In order to compare the changes of the catalyst properties, the used catalysts before (used after 4 h time on stream) and after (used after 8 h time on stream) deactivation were unloaded from the reactor in two separate experiments. The phenylacetaldehyde selectivity kept > 96% from beginning to end of the reaction. The main by-product was the dimer (2,4-diphenyl-2-butenal) formed via aldol condensation of phenylacetaldehyde, maintained its selectivity of 1–3%. Some other by-products, such as phenylethanol, phenylethanediol, styrene and so on, were also detected by GC–MS with their total selectivity of < 1%. But the trimer (2,4,6-tribenzyl-*s*-trioxane) formed via trimerization of phenylacetaldehyde at external acid sites [12] could not be detected since the catalyst contained only a trace amount of external acid sites.

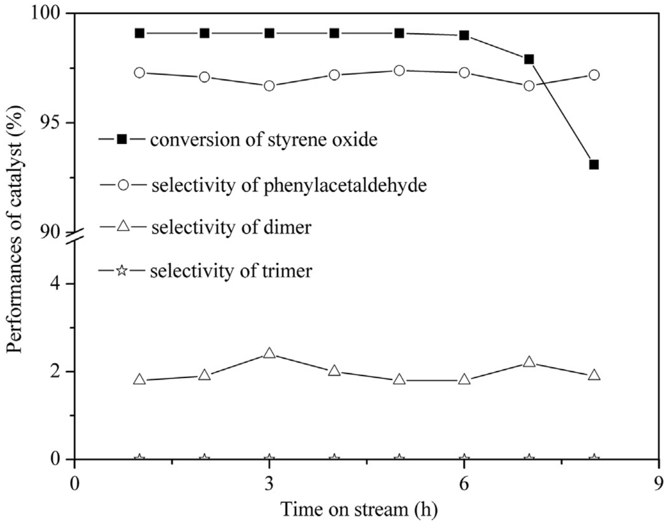

Fig. 1. Performances of HZSM-5 in the isomerization of styrene oxide to phenylacetaldehyde. Reaction conditions: T = 200 °C, P = 1 atm, catalyst loading = 0.5 g, flow-rate of N_2 = 120 ml/min, WHSV = 3.0 h^{-1}.

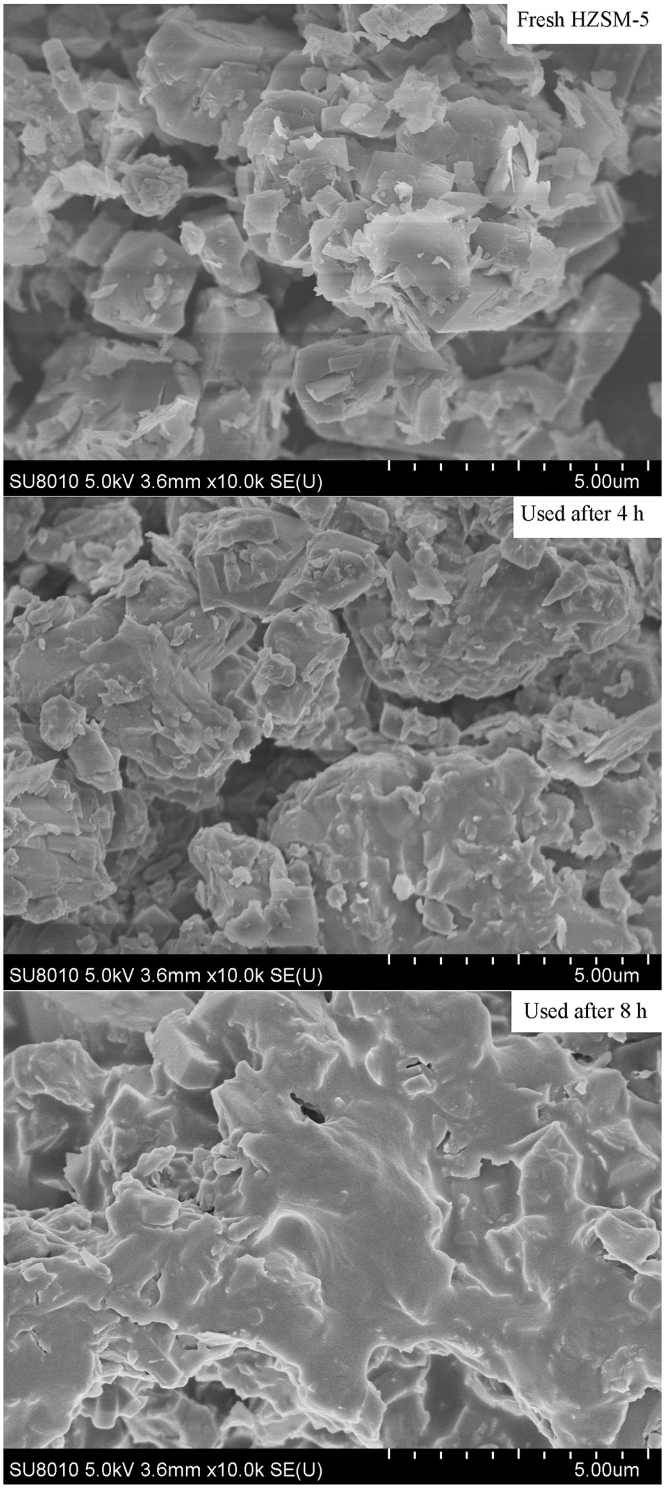

Fig. 2. SEM micrographs of the fresh and used HZSM-5.

For verification the deactivation behavior of HZSM-5 in the isomerization of styrene oxide to phenylacetaldehyde, several characterization techniques were implemented over the fresh and used catalysts. The SEM micrographs of the fresh and used catalysts are presented in Fig. 2. The borderline among the fresh catalyst granules was clear. While after reaction 4 h time on stream, the borderline among the catalyst particles became ambiguous. Increasing of the reaction time to 8 h, more and more catalyst particles were buried in the coke. Simultaneously, the activity of the catalyst gradually decreased with accumulation of the coke deposited on the catalyst surface. The filamentous carbon and other crystalline carbon were not observed on the used catalysts. But the structure of the coke can be