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Short Communication

Suitable acidity of ZSM-5 for the isomerization of styrene oxide to phenylacetaldehyde

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ABSTRACT

The effect of acidity of HZSM-5 ($SiO_2/Al_2O_3 = 25$–360) on isomerization of styrene oxide to phenylacetaldehyde was investigated under gas–phase free of solvents. The reaction was mainly catalyzed by the strong acid sites of HZSM-5 and catalyst lifetimes were affected by both acid strength and concentration. Trimerization of phenylacetaldehyde occurred at external acid sites, leading to a sharp decline in product selectivity. High Si/Al HZSM-5 (e.g., $SiO_2/Al_2O_3 = 360$), which contains weaker acid sites inside pores and trace amount of external acid sites, was found to be more effective with a higher stability and phenylacetaldehyde yield up to 95%.

1. Introduction

Phenylacetaldehyde, giving a narcissus-like smell, is an important fine chemical used for preparation of fragrances, pharmaceuticals, insecticides, fungicides and herbicides [1]. Hoelderich et al. [2,3] have previously reported that phenylacetaldehyde and its halogenated derivatives can be obtained via isomerization of styrene oxide and its halogenated styrene oxides over acid catalysts. However, the competitive aldol condensation or polymerization of aldehyde products and fast deactivation of catalysts by coke formation are still difficult problems at the industrial scale [1].

A series of heterogeneous catalysts, such as alkaline earth metal sulfonates [4], mixed-metal oxides [5], silica–alumina gels [6,7], natural silicates [8], Nafion-H [9], zeolites [10–12] and heteropoly acids [13], have all been applied as catalysts for the isomerization of epoxides to aldehydes. It can be seen that the active sites from weakly alkaline to strong acidic can catalyze this reaction, but the aldol condensation or polymerization can readily occur on alkaline [4,5] and strong acid sites [13–15], resulting in rapid deactivation of catalysts. Consequently, there is a need to find a suitable acid catalyst, which not only has high activity and stability, but also prohibits side reactions. However, detailed investigation on this topic has not yet been published.

It is reported that zeolites of the mordenite, erionite and chabazite types are all suitable to catalyze this reaction, particularly, zeolites of the MFI type have the best performance with phenylacetaldehyde yield up to 90% at 200 °C and WHSV $= 3\ h^{-1}$, but the catalysts deactivate within 6 h on stream [3]. The acidity of zeolites usually depends on the nature and amount of the framework aluminum atoms [16,17]. Therefore, a series of ZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 25–360 were chosen as catalysts to determine the effect of acidity on the reaction. Catalysts were characterized by XRF, nitrogen adsorption, XRD, NH_3-TPD/titration, FT-IR spectra of pyridine and 2,4,6-trimethyl pyridine adsorption.

2. Experimental

2.1. Materials

Styrene oxide (>98%) was purchased from TCI (Shanghai) Development Co., Ltd. and used without further purification. HZSM-5 ($SiO_2/Al_2O_3 = 25$–360) and NaZSM-5 ($SiO_2/Al_2O_3 = 25$) were all obtained from Catalyst Plant of Nankai University (Tianjin, PR China) and denoted as HZ-x and NaZ-x, where x referred to the SiO_2/Al_2O_3 ratio according to manufacturer's specifications.

2.2. Catalyst characterization

The chemical composition of the catalysts was determined by X-ray fluorescence (XRF) with a Bruker S4 Pioneer X-ray fluorescence spectrometer. Nitrogen adsorption was performed using a Quantachrome Autosorb-1 instrument at 77 K, after a vacuum pretreatment at 250 °C for 6 h. The surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation. The pore volume and size were estimated from the Horvath–Kawazoe (HK) method. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro diffractometer

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equipped with a Co Kα radiation (λ = 0.1789 nm). Data were collected in the range of 2θ = 5–50° with a step size of 0.02° at a scanning speed of 5°/min.

The acidic properties of the catalysts were studied by temperature-programmed desorption of ammonia (NH_3-TPD) and FT-IR spectra of adsorbed pyridine and 2,4,6-trimethylpyridine (collidine). 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 500 °C for 2 h with a N_2 flow (50 ml/min) and then cooled down to ambient temperature. Sufficient NH_3 was supplied to the system followed by flushing with N_2 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. The NH_3 desorbing between 150 and 500 °C was trapped in boric acid and then titrated with a standard H_2SO_4 solution [18]. According to the individual peak area, the amount of NH_3 can be calculated and then converted into the acid concentrations with the assumption of one NH_3 molecule per acid site.

FT-IR spectra of adsorbed pyridine and collidine were recorded on a Nicolet 380 spectrometer at 4 cm^{-1} resolution. The sample powder was pressed into a self-supporting wafer (diameter: 13 mm, weight: 15 mg) and activated at 500 °C for 2 h under vacuum (10^{-3} Pa). Probe molecule adsorption was taken place in situ at room temperature, followed by evacuation at 200 °C for 1 h. Afterwards, an IR spectrum was recorded at room temperature and a difference spectrum was obtained by subtracting the spectrum of the activated sample from the spectrum after probe adsorption.

2.3. Isomerization of styrene oxide

Isomerization was carried out in a vertical fixed-bed reactor (stainless steel tube, i.d. = 9 mm) operated at atmospheric pressure. Prior to each experiment, the sample (0.5 g, 20–30 mesh) located in the constant-temperature zone was treated in a N_2 flow at 500 °C for 2 h. After cooling to reaction temperature (200 °C), styrene oxide, free of any solvents, was fed with WHSV = 3.0 h^{-1} using a HPLC pump (model Series II, LabAlliance, USA). N_2 was used as the carrier gas, with a flow-rate of 120 ml/min, during the reaction. The reactor effluent was collected in an ice trap and analyzed by GC (Agilent 6820 FID) and GC–MS (Agilent 6890/5973 MSD) equipped with VF-5ms capillary column (30 m, 0.25 mm, 0.25 μm).

3. Results and discussion

3.1. Characterization results

The chemical composition and some physical properties of the catalysts are listed in Table 1. The bulk SiO_2/Al_2O_3 molar ratios determined by XRF were in good agreement with the values given by the manufacturer. All the samples showed typical type-I isotherms (figures not shown here), indicating uniform micropore structures according to IUPAC classification. The BET surface area, micropore volume and size were all similar to each other, suggesting that their textural properties did not lead to different catalytic performances.

Table 1
Chemical composition and physical properties of the catalysts.

Sample	SiO_2/Al_2O_3 (mol/mol)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)	Relative crystallinity (%)
NaZ-25	26.8	291.5	0.145	4.6	84
HZ-25	26.8	291.6	0.145	4.6	80
HZ-38	39.1	290.5	0.145	4.6	82
HZ-50	49.7	291.2	0.145	4.6	100
HZ-135	134.6	290.4	0.144	4.6	97
HZ-150	151.2	290.5	0.144	4.6	99
HZ-360	362.0	289.1	0.142	4.6	98

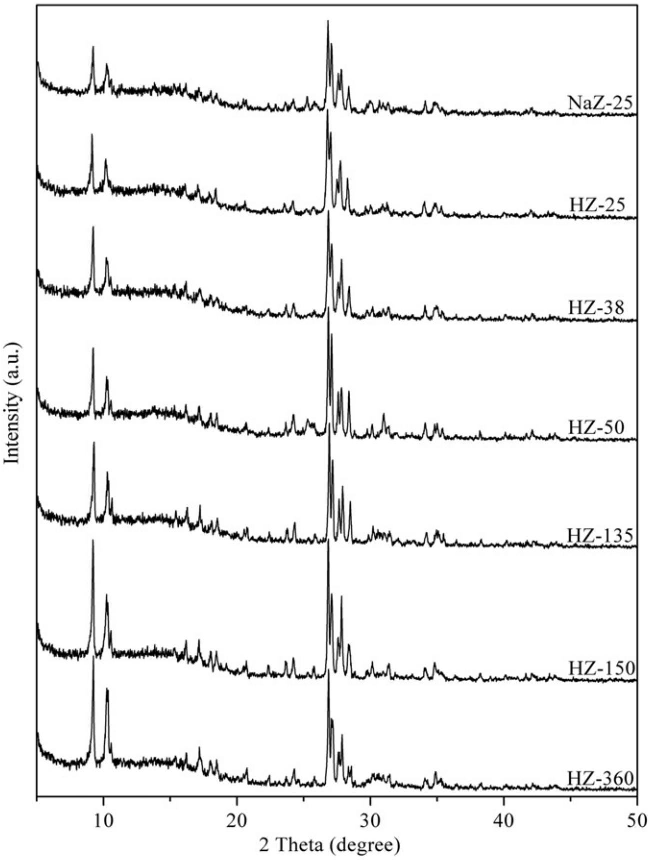

Fig. 1. XRD patterns of the catalysts.

The XRD patterns of the catalysts in Fig. 1 matched well with typical MFI-type structures and presented no additional phase. HZ-50 had the highest intensity and the relative crystallinity was obtained from the peaks' area of 2θ = 26–29° using HZ-50 as a reference for this study. As shown in Table 1, HZ-25 and HZ-38 had slightly lower relative crystallinity than other samples. This is probably due to more amorphous Si or Al species formed in either micropores or alongside the channels of ZSM-5 catalysts with lower Si/Al ratios during the ion-exchange with NH_4^+ and calcinations.

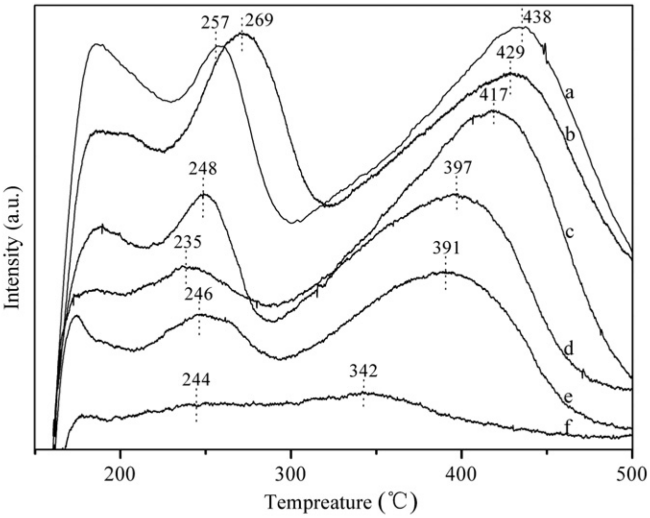

Fig. 2. NH_3-TPD profiles of the HZSM-5 zeolites. (a) HZ-25, (b) HZ-38, (c) HZ-50, (d) HZ-135, (e) HZ-150 and (f) HZ-360.