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Effect of acidic and red-ox sites over modified ZSM-5 surface on selectivity in oxidation of toluene

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ABSTRACT

The modified HZSM-5 zeolites via alkali-treated with various NaOH aqueous solution and supported iron oxide by impregnation technique was prepared, as proved by XRD, SEM, TEM, XPS, NH_3-TPD and ICP-OES to determine their phase structure, composition and surface character. These modified materials were tested for catalyzing solvent-free oxidation of toluene under mild conditions. The experimental results indicated that the alkali-treated HZSM-5 showed higher activity because of reduction of strong acidic sites on the surface. However, the alkali-treated HZSM-5 supported iron material exhibited high selectivity to benzaldehyde via promoting the oxidation of toluene or benzyl alcohol and limiting the further oxidation of benzaldehyde into phenol caused by lowing surface Brönsted acidity and introducing Fe red-ox sites.

1. Introduction

The selective oxidation of toluene to several organic chemicals, ranging from benzyl alcohol, benzaldehyde and benzoic acid has attracted more and more attentions during the past decades [1]. As a typical product of toluene oxidation, benzaldehyde (BzH) is known to be a very important starting material for preparation of organic intermediates in perfumery, pharmaceutical, dyestuff and agrochemical industries. It is traditionally produced by hydrolysis of benzal chloride in industry [2]. Traces of chlorine impurities and copious waste generated by this process were included in the product BzH. Thus, many attempts to circumventing this problem have prompted investigation on selective oxidation of toluene to BzH, including vapor- and liquid-phase reaction. The process of vapor-phase oxidation must be limited to avoid over-oxidation of the reactant into CO_2 and carbonaceous deposits (coke) at high reaction temperature [3]. As compared with the fix-bed system, the liquid-phase oxidation of toluene to BzH has some advantages such as high selectivity, mild reaction conditions etc [4].

H_2O_2 is widely used in liquid oxidation of organic compounds due to its clean and environmentally friendly nature. Many efforts have been dedicated to the liquid phase oxidation of toluene into BzH using H_2O_2 as an oxidant and a variety of catalysts such as mesoporous V-AlPO [5], VO_x/TiO_2-sepiolite [6], Ce(III) [7], MnO_x [8], VO_x [9], CrO_x [10]. and other transition metal or a noble metal catalysts [11–13] have been tested in these cases, thus yielding excellent catalytic performances. However, they are usually allowed to proceed in organic solvents like acetic acid and acetonitrile [14–16], inevitably causing the equipment corrosion and environmental pollution. In particular, separation of the oxidized products needs to be specified in these oxidation processes. Du et al. [17] found that alkali-treated zeolites could efficiently catalyze oxidation of toluene with H_2O_2 in aqueous media while the selectivity to BzH was lower. Brückner [18] described that Brönsted acidic sites on the catalyst surface could greatly promote benzaldehyde adsorbed on the surface, leading to its further oxidation to benzoic acid or CO_x. In our previous report [19], we had found that the surface acidity of zeolites had a great influence on the conversion of toluene and the selectivity to BzH. The selectivity to BzH had been enhanced when iron oxide was supported on HZSM-5 zeolite. The exploration for this observed result would provide an attractive alternative route for improving the selectivity to BzH in the oxidation of toluene via associating the relationship between the surface nature and catalysis characters of the catalyst. Herein, we wish to describe the catalytic process to achieve this goal, opening more environmentally acceptable and more economically attractive approach for selective synthesis of BzH from liquid-phase oxidation of toluene.

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2. Experimental section

2.1. Preparation of alkali-treated zeolites

The zeolite HZSM-5 (Si/Al = 38, purchased from Tianjin Chemist Scientific Ltd. Co.) was calcined at 550 °C for 6 h in an oven. After cooling down, 2.0 g of HZSM-5 was added to 40 mL of various concentrations (0.1, 0.2, 0.3 and 0.4 mol/L) of NaOH aqueous solution in a flask. The mixture was heated to 80 °C in a water bath and stirred at this temperature for 2 h. The alkali-treated zeolites were obtained by filtration, and then washed with distilled water until neutral washing water was achieved. The zeolites were dried at 110 °C for 12 h after washing and denoted as ZSM-5-x, respectively, where x represented the concentration of NaOH solution (x = 0.1, 0.2, 0.3, 0.4).

2.2. Preparation of Fe/ZSM-***5-x***

Preparation procedure of Fe_2O_3/ZSM-5-x was as follows: 2.0 g ZSM-5-x was impregnated with 0.5 mol/L $Fe(NO_3)_3$ solution in ethanol [4.04 g of $Fe(NO_3)_3 \cdot 9H_2O$ in 20 mL ethanol] and stirred at room temperature for 12 h. The resulting mixture was filtered to remove the filtrate. The obtained solid was washed with anhydrous ethanol, followed by drying at 100 °C for 4 h, and then calcined at 550 °C for 2 h in the muffle furnace to afford Fe_2O_3/ZSM-5-x after cooling to room temperature. The methods of preparing ZnO/ZSM-5-0.2, CeO_2/ZSM-5-0.2, CuO/ZSM-5-0.2, NiO/ZSM-5-0.2 were very similar with the above procedure; the only difference between them was that 0.5 mol/L $Fe(NO_3)_3$ solution in ethanol was substituted by $Zn(NO_3)_2$, $Ce(NO_3)_3$, $Cu(NO_3)_2$ and $Ni(NO_3)_2$ solutions in ethanol, respectively.

2.3. Characterization

X-ray diffraction (XRD) was performed on a Bruker AXS D8 advanced X-ray diffractometer (Cu K_α, $\lambda = 0.15406$ nm, 40 kV, 36 mA) in the step scanning mode (0.02 s per step) with the 2θ range between 10 and 80°. The morphology of the catalysts was observed by a Hitachi S-4800 scanning electron microscopy (SEM). The recording of transmission electron microscopy (TEM) was carried out using FEI Tecnai F20 equipment. X-ray photoelectron spectroscopy (XPS) was recorded on a Kratos-AXIS ULTRA DLDX X-ray photoelectron spectrometer. The N_2 adsorption/desorption isotherms were measured using a quantachrome Autosorb iQ instrument.

NH_3-TPD was performed on TP-5076 TPD dynamic adsorption apparatus. The catalyst sample (1 g) was pretreated in He flow (30 mL/min) at 500 °C for 1 h; and then it cooled down to room temperature. Thereafter, the sample was saturated with NH_3 (15 mL/min) for 30 min, followed by purging with He for 1 h to remove the physically adsorbed NH_3. After that, the sample was heated in He flow from ambient temperature to 600 °C at the rate of 6.4 °C/min. The amounts of NH_3 desorption were measured by the TCD. The Fe loadings, Na contents and ratios of Si to Al in the zeolites were determined by Optima 8000 ICP-OES (Perkin-Elmer Company).

2.4. Oxidation of toluene

5 mL (45.8 mmol) of toluene and 0.3 g of the catalyst (Fe_2O_3/ZSM-5-x) were added into a 50 mL three-necked flask fitted with a reflux condenser and a mechanical stirrer. The reactor was heated to 90 °C in a water bath with electric heater, and then 15 mL of 30% H_2O_2 (0.14 mol) was slowly dropped in. The resulting mixture was stirred at 90 °C for 4 h. At the end of the reaction, the mixture solution was filtered to remove the catalyst and the upper organic liquid of the reaction mixture was analyzed by GC (Agilent GC7820) and GC–MS (Agilent GC7890-MS5975C).

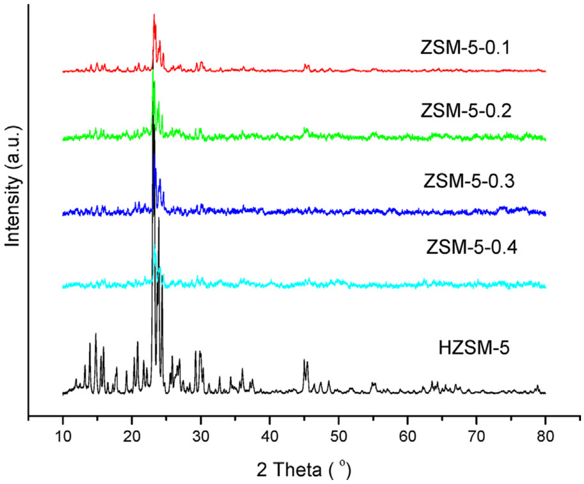

Fig. 1. XRD patterns of HZSM-5 and ZSM-5-x.

3. Results and discussions

3.1. Characterization of the alkali-treated zeolites

The X-ray diffraction patterns of HZSM-5 and alkali-treated zeolites ZSM-5-x recorded in the 2θ range of 10–80° were depicted in Fig. 1. All the alkali-treated zeolites ZSM-5-0.1, ZSM-5-0.2, ZSM-5-0.3 and ZSM-5-0.4 represented the typical diffraction peaks of parent HZSM-5 although obvious decrease in relative crystallinitty could be observed, implying that these alkali-treated samples basically preserved the specific MFI structure. The samples ZSM-5-0.3 and ZSM-5-0.4 exhibited too weak diffraction peak around 45° to be observed due to the NaOH solution severer dissolving Si or Al atoms from the zeolite framework. Moreover, significant changes were found in the Si/Al ratio, specific surface area and morphology for the alkali-treated zeolites as shown in Table 1 and Fig. 2. The Si/Al ratio was basically decreased as increasing in the NaOH concentrations, showing that the alkaline solution mainly dissolved Si from the framework [20]. The slight increase in Si/Al ratio of ZSM-5-0.3 was likely due to the stronger alkaline solution (0.3 mol/L) dissolving more aluminum than silica from the zeolite framework as compared with ZSM-5-0.2. The structure morphology of the materials was characterized by SEM analysis as depicted in Fig. 2. The SEM images clearly showed that the parent HZSM-5 displayed regular rectangular crystals (Fig. 2a) and the surface of the alkali-treated samples looks like rough, some irregular crystalline grains and defects on the surface were observed for ZSM-5-0.2 and ZSM-5-0.3 (Fig. 2c, 2d), which could lead to the increase in their external surface areas as compared with the parent HZSM-5 (Table 1). Further, the SEM image (Fig. 2e) suggested that more irregular crystalline grains were aggregated together after treatment with 0.4 mol/L NaOH solution, inevitably causing decrease in their specific surface areas (Table 1). At the same time, their pore volumes were increased after alkaline treatment, and mesopore diameters were also increased for ZSM-5-0.1, ZSM-5-0.2 and ZSM-5-0.3. The decrease in mesopore diameter for ZSM-5-0.4 was likely ascribed to collapse of the channels or the aggregate of the irregular crystalline grains.