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Wet milling of H-ZSM-5 zeolite and its effects on direct oxidation of benzene to phenol

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Abstract

The direct oxidation of benzene to phenol with N_2O over ZSM-5 catalysts suffers from the problem of rapid catalyst deactivation mainly due to the secondary transformation of phenol into heavier hydrocarbon compounds leading to the catalyst coking. In order to investigate the deactivation behavior of the ZSM-5 catalysts during this reaction, a comparative study was performed over ZSM-5 catalysts having different crystal sizes. The original catalyst was milled to two different periods of time to obtain catalysts having various crystal sizes. The original and the milled catalysts were tested for the benzene to phenol reaction to get an insight into the effect of crystal size on the catalyst deactivation. There was a decrease in catalyst deactivation with a decrease in crystal size. An indirect dependence of catalyst deactivation with total acidity was observed.

Keywords: Benzene oxidation; Nitrous oxide; Phenol; ZSM-5; Crystal size; Microreactor

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1. Introduction

Phenol is traditionally produced by the three-step cumene process. The main problems of this process are: (i) formation of hazardous intermediate cumene hydroperoxide; and (ii) formation of undesired co-product acetone, which is detrimental from the economic point of view. The most useful alternative method to the traditional three-step cumene process is the one step oxidation of benzene to phenol with nitrous oxide over zeolite catalysts, which is one of the demanding challenges in industrial bulk chemistry. Despite the advantages of this alternative process, it is associated with serious problems like rapid deactivation of the catalyst that results in lower yield and short lifespan of the catalyst [1–4]. In many studies concerning the oxidation of benzene to phenol over zeolite catalysts, it has been found that the activity of the catalyst gradually reduces with time due to coke formation, which is strongly dependent on catalyst pore structure, reaction conditions and nature of reactants [5]. The accumulation of phenol inside the pores of ZSM-5 crystals due to strong adsorption and slow diffusion of phenol is considered as the major causes for the rapid deactivation [6]. One of the possibilities to reduce the deactivation rate could be carrying out the reaction with catalyst (ZSM-5) having smaller crystal sizes, as the length of diffusion path for phenol molecule is considerably reduced. Thus, it is expected to increase the yield of phenol as well as the catalyst life time. The decrease in the zeolite crystal size has a positive effect in most of its catalytic applications as it enhances the intracrystalline diffusion steps [7].

There are two possible ways to obtain zeolite crystals having smaller crystal sizes. The first one is by modifying the conventional hydrothermal synthesis conditions. And the second one is through mechanical treatment (milling) of the commercially available zeolite catalysts. The milling of zeolite catalyst could either increase its external surface area or decrease its cyrstallinity due to amorphization, which would eventually increase the intercrystalline microporous space [8–11]. The partial collapse of the crystal structure may render different strength distributions of Brönsted and Lewis acid/base sites. The comparison of catalytic activity of the zeolite

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catalysts with the evolution of these factors is supposed to reveal their deactivation behavior. Kharitonov et al. [12] have studied the mechanism of Fe-ZSM-5 milling and its catalytic performance in the oxidation reaction of benzene to phenol. It has been found that the crystallinity of the Fe-ZSM-5 gradually decreased with increasing milling time and thereby reduction in the catalytic performance. This was attributed to the destruction of the zeolite crystals that caused the transition of active Fe-species into inactive Fe-species.

In the present work, the original ZSM-5 zeolite was milled for different periods of time using wet stirred media milling. The resultant ZSM-5 catalysts having different crystal sizes were characterized by XRD, FTIR, DLS, SEM, N_2 adsorption measurements and catalytic (oxidation of benzene to phenol) test reactions. Fe-ZSM-5 is known to exhibit high catalytic activity and selectivity in the oxidation of benzene to phenol [13]. Nevertheless, H-form of ZSM-5 catalyst was used in the present study in order to eliminate the coupled influence of crystal size and Fe content on the catalytic performance.

2. Experimental

2.1. Wet milling

The wet media milling of a commercially available zeolite NH_4-ZSM-5 (Si/Al = 21.4; ALSI-PENTA) was carried out in a laboratory stirred media mill (PE 075; Netzsch). The media mill consisted of a grinding chamber (0.6 l) and a stirrer with three perforated discs. Y_2O_3 stabilized ZrO_2 media ($\Phi = 0.5$–0.63 mm) were used for milling. About 1700 g of balls were charged into the grinding chamber which completely covers the three discs of the stirrer. A suspension (50 g of zeolite in 200 ml of distilled water) of the zeolite to be milled was added into the grinding chamber. Prior to milling, zeta potential (ζ) measurements (ZETA SIZER, Malvern Instruments) were done in order to know in which pH range the highest electrostatic stability exists for this particular zeolite.

2.2. Physico-chemical characterisation

The original and the milled zeolite catalysts were characterized by using various characterization techniques. X-ray powder diffraction (XRD) patterns were performed on an X'pert Pro diffractometer (Philips Analytical) using Cu Kα radiation. The relative crystallinity of the catalysts was determined from the sum of the areas of the peaks between $2\theta = 22.5^\circ$ and 25°. The original catalyst was considered as the standard (100% crystallinity) to calculate the relative crystallinity of the milled catalysts. N_2 adsorption/desorption analyses were measured at 77 K using an ASAP 2010 setup (Micromeritics). Before the measurement, catalysts were pre-heated at 300 °C for 2 h. Particle sizes of the original and the milled catalysts were measured using Dynamic Light Scattering (UPA Microtrac) instrument. FTIR spectra were recorded on a Perkin Elmer-72820 apparatus using KBr wafer technique. NH_3-TPD measurements were carried out in an Altamira 100 equipment. Prior to the experiment, catalyst was pre-heated at 550 °C for 2 h in helium atmosphere. After that NH_3 was adsorbed on the catalyst at 100 °C for 30 min. NH_3 desorption was carried out from 100 °C to 600 °C with a ramp of 10 °C/min. Helium was used as the carrier gas during the desorption process.

2.3. Catalytic reaction

The NH_4-form of the original and the milled catalysts were calcined at 550 °C for 3 h to obtain the H-form of the catalyst. The original and the milled catalysts were coated on microchannels of the microreactor using slurry coating technique. Coating procedure and the details of the microreactor are given elsewhere [15]. In the present study, 10 wt% of Al_2O_3 was used as binder.

The catalytic (benzene to phenol oxidation reaction) experiments were performed using a mircoreactor coated with zeolite (original and milled) catalysts in an automated laboratory setup. In the feed, the molar ratio of benzene to N_2O was 1:1. N_2 was used as the carrier gas. All the experiments were conducted at temperatures ranging from 400 °C to 480 °C with a fraction of benzene (8%), N_2O (8%) and N_2 (84%) at a modified residence time of 94 g min/mol (active mass of catalyst per molar flow rate). The conversion of benzene was measured as the ratio between the moles of converted benzene and the moles of benzene sent to the reactor. The yield of phenol is directly calculated from the obtained amount of phenol and the selectivity to phenol is defined as the molar ratio of the phenol obtained relative to benzene converted.

N_2O and other gases were dosed with thermal mass flow controllers (Bronkhorst HiTech). Benzene was fed into the reactor with a liquid flow controller through an evaporator. After each measurement the deactivated catalyst was regenerated with an oxygen/nitrogen mixture at 530 °C for 1 h to restore the initial activity. Analysis of the product stream was performed by on-line gas chromatograph (Hewlett Packard 5890 Series II Plus) equipped with a FID detector. Methane was used as an internal standard to calculate component concentrations from the peak areas.

3. Results and discussion

3.1. Wet milling of zeolites

Prior to milling, it was imperative to conduct the zeta potential (ζ) measurements on the desired zeolite sample in order to find out at which pH range a strong repulsive force between the zeolite particles exists in view to carry out milling at that particular pH condition. The point, where the surface charge is zero, is defined as the point of zero charge (pzc). The pzc is material dependent and can be determined experimentally by charge titration. It is important to distinguish the iso-electric point (IEP) from the pzc, where the measured ζ-potential is zero. At the IEP, the repulsive barrier vanishes and zeolites undergo aggregation as electrostatic repulsion between particles becomes zero. As a first step to measure the zeta potential of the catalyst, zeolite suspensions were made with different pH values ranging from 2 to 10 using