Phenol alkylation with methanol: effect of sodium content and ammonia selective poisoning of an HY zeolite

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Received 20 June 1995; accepted 25 October 1995

Sodium exchange and ammonia selective poisoning of the acid sites of an HY zeolite (Si/Al = 20) were carried out and their effects on the catalytic properties for the alkylation of phenol with methanol (200°C, 1 atm and N2/reactants molar ratio of 4) were evaluated. Results show that the reaction is highly sensitive to the number and strength of the acid sites of the catalyst. A decrease in the number of acid sites by sodium exchange of the protons or by ammonia selective poisoning produces important changes in the selectivity of the reaction. In fact, a high increase in the anisole/cresol ratio is observed as the percentage of exchanged sodium in the zeolite increases, while the ammonia selective poisoning shows that at low desorption temperatures (<250°C) only anisole is formed while at higher desorption temperatures both anisole and cresols were observed. These results show that anisole formation requires sites with lower acid strength compared to those necessary for cresol formation.

Keywords: phenol alkylation; HY zeolites; ammonia poisoning; effects of sodium content; anisole-cresols formation

1. Introduction

Substituted phenols are useful as organic intermediates for the production of dyestuffs, special polymeric components, pesticides, bisphenol A, adipic acid, caprolactam, etc. [1]. The use of zeolites in organic reactions has grown over the last several years because of the shape selectivity which the zeolites impose on a reaction together with lower environment pollution and high purity of the products [2,3]. Literature details examples of the alkylation of phenol with methanol over zeolites to produce both anisole (O-alkylation) and cresols (C-alkylation) [4-8]. However, the influence of the strength of acidic sites on the product distribution is not well established, one should expect that the distribution of products obtained from the reaction be dependent on the acid nature of the zeolite. In order to contribute to the understanding of the reaction scheme of phenol alkylation with methanol and to get some insight in the influence of the nature of acid sites of the zeolite, we have chosen to modify the acidity of the catalyst by cation exchange and by ammonia poisoning and to follow their influence on the activity and selectivity of the catalyst.

2. Experimental

HY zeolite (Na = 0.03%, Si/Al = 20) was a commercial sample provided by ZEOCAT. The characteristics of the commercial HY zeolite are: chemical analysis (weight% on dry basis): SiO2 = 95.87; Al2O3 = 4.07; Na2O = 0.06; Si/Al = 20. Unit cell parameter = 24.28 Å; relative crystallinity DRX = 93% (standard used: zeolite LZY52 from Union Carbide); surface area = 813 m2/g.

Prior to reaction, the zeolite was activated under N2 flow (4.3 ℓ/h) at 500°C for 12 h.

For the selective poisoning, a series of zeolite samples were treated with ammonia at room temperature and heated between 200°C and 500°C for 1 h in order to desorb the pre-adsorbed base.

In order to ascertain the effect of sodium loading, two samples were prepared by ion exchange, starting with the 0.03% NaHY zeolite. Samples were prepared using a 0.5 M NaNO3 solution at 25°C (ml solution/g zeolite equal to 20) to obtain sodium contents of 0.44% (0.44NaHY; Na/Al = 0.20) and 0.77% (0.77NaHY; Na/Al = 0.36) w/w.

A fixed-bed continuous flow reactor containing 0.5 g of catalyst was used for the catalytic measurements at equal pressures of phenol and methanol (0.1 bar) and of nitrogen equal to 0.8 bar, at 200°C with a N2/reactants molar ratio equal to 4. Different conversions were obtained during the deactivation of solids by coke formation or by changing the space velocities. The liquid reaction products were collected in an ice trap in sequences of 15 min and analyzed by gas chromatography using a WCOT fused silica coating with CP-SIL 5 CB 25 m capillary column.

3. Results and discussion

Both the surface area value and the relative crystalli-
Fig. 1. Activity evolution vs. time on stream for the original and sodium exchanged HY zeolites.

Fig. 2. Product distribution as a function of conversion, obtained during catalyst deactivation, for the original and sodium exchanged HY zeolites.

of the sample show that the commercial HY zeolite is a highly crystalline solid.

The evolution of activity as a function of time on stream for the alkylation of phenol with methanol for the 0.03% NaHY, 0.44% NaHY and 0.77% NaHY is shown in fig. 1. An increase in the sodium content produces a decrease in the initial activity of the zeolite accompanied by a better stability of the solids to deactivation by coke formation. This behavior is to be expected since the stronger acid sites of the initial zeolite, which catalyse secondary reactions to produce polyalkyl phenol, responsible for catalyst deactivation [9], are neutralized during the cation exchange.

Product distribution as a function of conversion obtained during catalyst deactivation is shown in fig. 2. It is observed that the selectivities on the three zeolites are quite similar. This similarity could be explained assuming different rates of deactivation for the solids. The initial zeolite with a 0.03% Na content deactivates faster than the 0.44% and 0.77% Na-zeolites (fig. 1). The higher rate of deactivation produces a more important change in the number of strong acid sites of the initial zeolite in comparison to that observed for the higher sodium content zeolites. The decrease in the anisole production and the constancy in the cresols formation for the initial experiments (fig. 2) can be explained by production of cresols via reaction of anisole with phenol as suggested in step 2 of scheme 1 [7]. However, the analysis of the anisole/cresol ratio (A/C) at isoconversion (10% of conversion, obtained at different space velocities) for fresh catalysts (15 min reaction) shows how the A/C ratio clearly increases with the sodium content on the zeolites (fig. 3), going from 3 for the 0.03% NaHY to 13 for 0.77% NaHY.

These results corroborate what we have previously observed for phenol alkylation over HZSM-5 zeolites [10,11]: that O-alkylation, being a less demanding reaction, can occur easily over the less acidic sites, while C-alkylation requires the presence of stronger acid sites. This observation is clearly established when we analyze the results for the selective poisoning of the initial zeolite (0.03% NaHY) with ammonia and desorption at different temperatures, prior to reaction at 200°C. As could be