

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

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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 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 ($\leq 250^\circ\text{C}$) 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-

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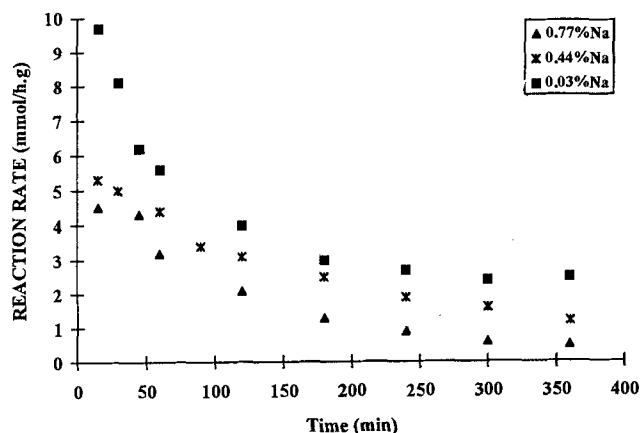


Fig. 1. Activity evolution vs. time on stream for the original and sodium exchanged HY zeolites.

nity 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 poly-alkyl 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

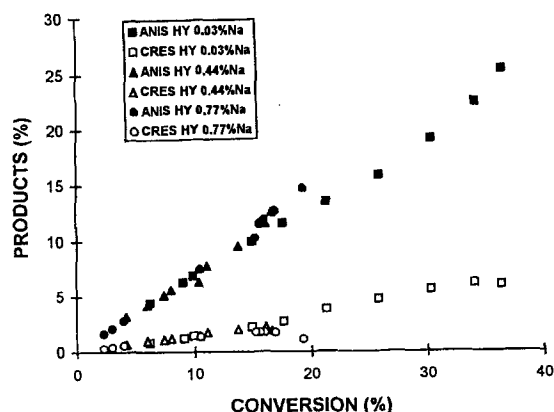
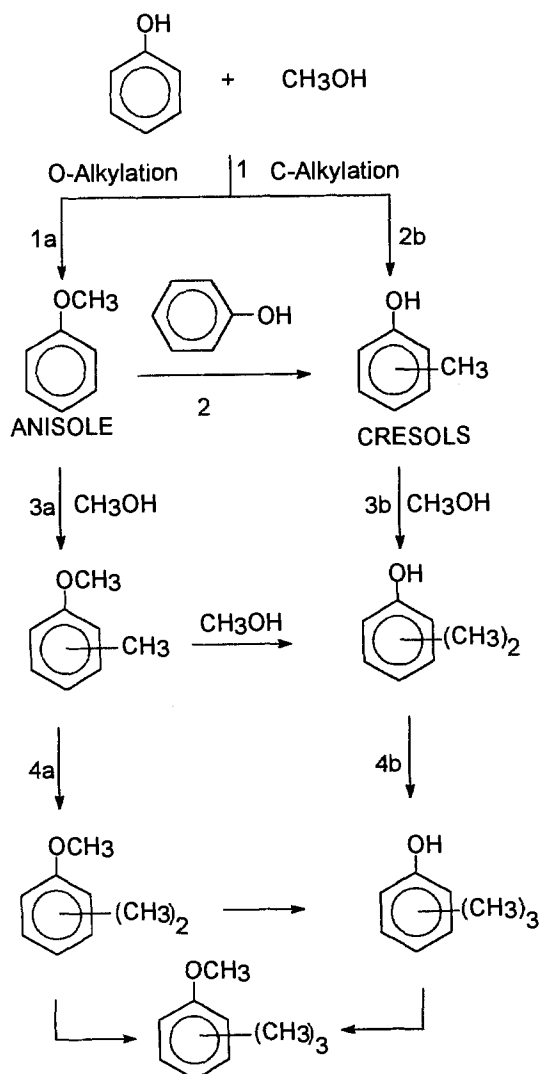


Fig. 2. Product distribution as a function of conversion, obtained during catalyst deactivation, for the original and sodium exchanged HY zeolites.

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



Scheme 1. Reaction scheme of phenol alkylation with methanol [7].

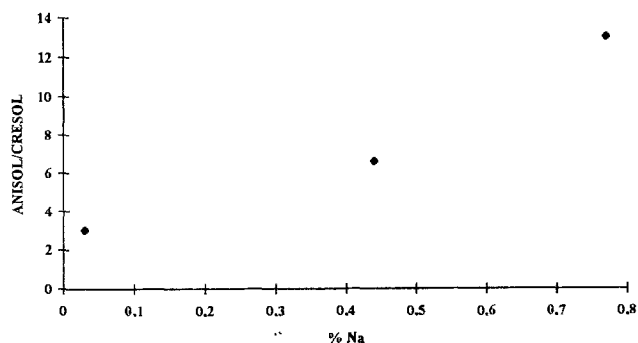


Fig. 3. Evolution of anisole/cresol ratio as a function of the sodium content for HY zeolites ($t = 15$ min; conversion = 10% obtained at different space velocities).

seen in fig. 4 for a temperature of ammonia desorption of 200°C (weak acid sites liberation) almost only anisole production is observed ($T = 200^\circ\text{C}$, $A/C \approx \infty$), while at higher temperatures of ammonia desorption (medium and strong acid sites liberation) both anisole and cresol are formed ($T = 250^\circ\text{C}$, $A/C = 10$; $T = 300^\circ\text{C}$, $A/C = 6.7$; $T = 350^\circ\text{C}$, $A/C = 5.9$; $T = 450^\circ\text{C}$, $A/C = 4.8$; $T = 510^\circ\text{C}$, $A/C = 3$). As a consequence the A/C ratio decreases as the temperature of ammonia desorption increases, going from almost infinite to a ratio of about 3 (fig. 4). This variation in the anisole/cresol ratio is not a consequence of differences in conversion, as was previously established when the A/C ratio was evaluated at isoconversion for zeolite with different Na contents (fig. 3). It is certainly due to differences in the acid strength of the acid sites capable of catalyzing the O- and C-alkylation [10].

As should be expected, the initial activity of the poisoned catalysts is strongly affected by the temperature of ammonia desorption (fig. 5). The activity increases as the temperature of ammonia desorption increases up to 500°C, at which it becomes equal to the activity of the unpoisoned solid (fig. 5) indicating that ammonia poisoning of the zeolite is completely reversible.

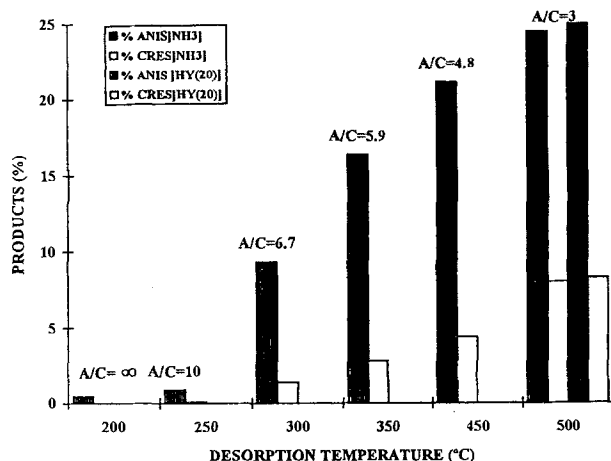


Fig. 4. Reaction product evolution as a function of ammonia desorption temperature.

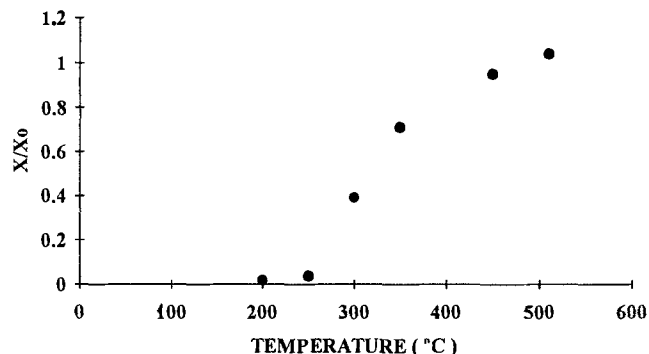


Fig. 5. Ratio of the conversion of poisoned to unpoisoned zeolite (X/X_0) vs. ammonia desorption temperature.

4. Conclusions

It has been shown that in the reaction of phenol alkylation with methanol O-alkylation and C-alkylation occurred at acid sites of different strength. While the O-alkylation requires weak acid sites ($T_{\text{desNH}_3} \leq 250^\circ\text{C}$) the C-alkylation needs the presence of stronger acid sites ($T_{\text{desNH}_3} \geq 250^\circ\text{C}$) to occur.

The observed product distribution after a considerable number of active sites have been poisoned by phenolic coking of the catalyst is similar to that obtained by poisoning of active acid sites by cationic exchange of protons or by ammonia adsorption, since the A/C ratio tends to infinite.

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