



Selective synthesis of cresols by regulation of nature, strength and density of acid sites in Na(Zn,H)Y zeolite

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Introduction

Zeolites are widely used as catalysts in many industrial processes due to their high acidity, thermal resistance, and characteristic porous structure. However there are many organic synthesis that still employs strong liquid acids, for example, p-cresol is commercially produced by toluene dehydration with sulfuric acid. The possibility of being able to modify and to control the acid superficial properties, according to the requirements of the reaction to catalyze, is an important challenge in solid catalyst development. The alkylation reactions require high density of strong acid sites, in particular the phenol alkylation with methanol leads to the formation of different product depending on the type of present catalytic sites in the catalyst. Solids containing only strong Brønsted acid sites favor the formation of anisole, whereas those containing both Lewis and Brønsted of strong strength form products of C-alkylation, mainly cresols [1].

The objective of this work was to find the conditions to modify the strength, nature and density of acid sites of in zeolitic materials to optimize the synthesis of cresols by phenol alkylation.

Materials and Methods

Samples with increasing content of Zn^{2+} (NaZnY) or H^+ (NaHY) were prepared by ion exchange of a commercial NaY (UOP-54, Si/Al=2.4) with $\text{Zn}(\text{NO}_3)_2$ and NH_4Cl solutions. Elemental compositions were determined by atomic absorption spectroscopy. The crystalline structure of the samples was confirmed by X-ray diffraction (XRD). BET surface areas were measured by N_2 physisorption. The strength, density and nature of surface acid sites were determined by TPD of ammonia and FTIR using pyridine as a probe molecule. The catalytic activity for the gas-phase methylation of phenol was evaluated at 473K and 101.3kPa, in a continuous fixed-bed reactor.

Results and Discussion

The superficial acidity of the NaY zeolite can be regulated by the incorporation of increasing amounts of Lewis (ZnNaY) and Brønsted (NaHY) acid sites. The incorporation of Zn to the NaY zeolite produced solely an increase of the amount and strength of Lewis acid sites, whereas the exchanges with NH_4^+ formed zeolites that contain acid sites of Brønsted and Lewis type. The NaY zeolite, that is inactive to alkylate phenol with methanol at 473 K, turned into an efficient catalyst when Zn^{2+} and H^+ sites are added; increasing its activity with the content of these cations, but also the deactivation increased. The deactivation was more pronounced on NaHY than on NaZnY samples. When the samples at equal level of initial conversion are compared, all presented similar selectivity towards the formation of cresols, independently of the distribution of the acid sites (Brønsted or Lewis). However, the p-/o-cresol ratio was higher on samples containing Zn^{2+} . This ratio increased

with the time on stream probably because the formation of carbon in the zeolite Y channel caused a shape selectivity effect

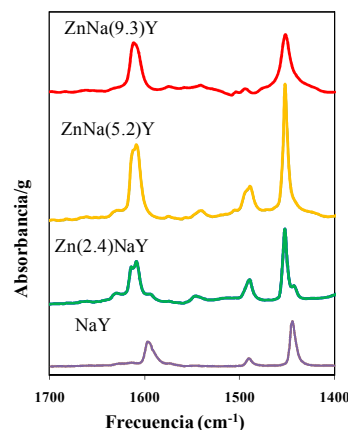


Figure 1. IR of Pyridine of ZnNaY samples ($T_{\text{desorption}} = 423\text{K}$).

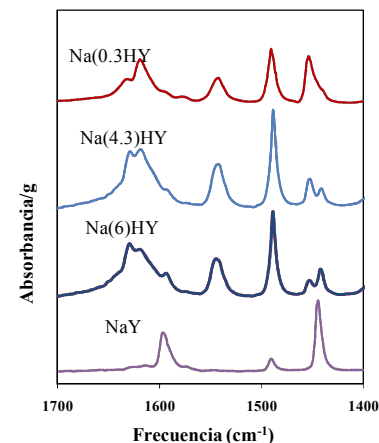


Figure 2. IR of Pyridine of NaHY samples ($T_{\text{desorption}} = 423\text{K}$).

References

1. M. E. Sad, C. L. Padró, C. R. Apesteguía, *Catal Today*, 720 2(008), 720, 133-135.
2. R. Ling; M. Yoshida; P. S. Mariano *J. Org. Chem.* 61 (1996) 4439.

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