

Theoretical study of the adsorption of acetic acid and methanol on H-BETA zeolite

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Introduction

The mechanism of the esterification of organic acids with alcohols catalyzed by acidic zeolites has many assumptions, with different models of adsorption of organic species being of great interest to the compression of the behavior of the solid acid catalyst in this process. In this work we studied the adsorption of acetic acid/methanol following the mechanisms proposed by Kirumakki *et al.*, 2006¹ and Bedard *et al.*, 2012². Different models of adsorption of acetic acid and methanol on the surface of H-BETA zeolite have been studied in order to provide information that could be helpful in the interpretation of the first step of the mechanism. The zeolite catalyst has been modeled by an extended cluster model 52T for H-BETA, with an overall composition $H_{63}O_{73}Si_{51}Al$. In this work, the adsorption of acetic acid and methanol in H-BETA has been systematically studied using ONIOM(M06-2X/6-31G(D):PM6) and M06-2X/6-31G(D) methods and the Gaussian 09 program. In the ONIOM scheme, the zeolite was represented by a 3T/52T model for the high and low layer, respectively. The high layer also includes the adsorbed molecules.

Results and discussion

The first mechanism (M_1) involves methanol (M-OH) adsorption on a Brønsted acid site (BAS) followed by activation and reaction with acetic acid (AA). The second mechanism (M_2) involves AA adsorption on a BAS followed by activation and reaction with M-OH. The third mechanism involves co-adsorption of AA and M-OH (M_3). We found that the most stable structure for the adsorption of AA (first step of M_2) correspond to a structure where the principal interaction is between the oxygen of the carboxylic group ($C=O_A$) and the proton of the Brønsted acid site of the zeolite (H_Z) with a $O_A \cdots H_Z$ distance of 1.41 Å. The adsorption energy is -18.23 kcal mol⁻¹. Other possible adsorbed complexes are found about 4-6 kcal mol⁻¹ higher in energy. For methanol adsorption (first step of M_1 and M_3) two different structures were found. The adsorption energy of the most stable complex is -21.57 kcal mol⁻¹ ($O_M \cdots H_Z = 1.42$ Å). The methanol adsorption is

more favorable energetically than AA adsorption showing that M_1 and M_3 are the preferred mechanism. For the co-adsorption of AA/M-OH (second step of M_3) the most stable complex involved the co-adsorption of M-OH over the AA adsorbed on the BAS (Fig.1). The methanol interacts with the AA mainly through the hydroxyl group of AA. The co-adsorption energy is -10.4 kcal mol⁻¹.

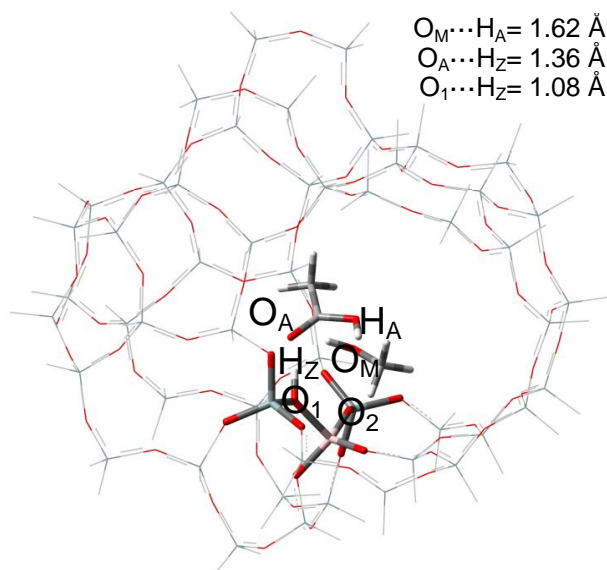


Figure 1: Adsorption of acetic acid and co-adsorption of methanol on the Brønsted acid site of H-BETA zeolite. O_1 , O_2 represent oxygen of the acid and basic site of the zeolite. Subscripts A refers to atoms of the acetic acid and M refers to methanol.

Conclusions

Our preliminary results provide information about the energetic parameters involved in adsorption of acetic acid and methanol, first elementary steps of the reaction of esterification of organic acids with alcohols catalyzed by acidic zeolites.

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¹ Kirumakki, S. R.; Nagaraju, N.; Chary K. V. R. *Appl. Catal. A: Gen.* **2006**, *299*, 185.

² Bedard, J.; Chiang, H.; Bhan, A. *J. Catal.* **2012**, *290*, 210.