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# On the mechanism of aromatic acylation over zeolites

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**Abstract**

Two possible mechanisms have been proposed for liquid phase acylation reactions using Brønsted acid zeolite catalysts such as H-Beta. For the acylation of anisole by acetic anhydride, Corma et al. [A. Corma, M.J. Climent, H. Garcia, J. Primo, Applied Catalysis 49 (1989) 109] have suggested that an acylium cation is formed by the protonation of an acyl species interacting with the proton of the zeolite, and that the acylium species attaches to the nucleophilic aromatic ring to form the acylated product. Based on desorption studies [M.L.M. Bonati, R.W. Joyner, M. Stockenhuber, Catalysis Today 81 (2003) 653; M.L.M. Bonati, R.W. Joyner, G.S. Paine, M. Stockenhuber, Studies in Surface Science and Catalysis 154C (2004) 2724], we have suggested that the acylating agent is ketene, which we have shown is formed in situ by the decomposition of acetic anhydride into acetic acid and ketene. The electrophilic ketene then reacts with the anisole in a rather similar manner to the acylium species proposed in the Corma mechanism. We show that these two mechanisms can be differentiated using deuterated reagents, and report on a series of experiments that show that the acylium cation mechanism is to be preferred in the liquid phase acylation at 333 K. We argue, however, that oligomerisation of ketene within the zeolite pores occurs in parallel to the acylation, and plays an important role in the deactivation (poisoning) of the H-Beta catalyst.

*Keywords:* Zeolite Beta; Acylation; Deactivation; Friedel Crafts; Mechanism; Isotopic exchange

## 1. Introduction

The acylation of aromatic compounds is an intermediate step in the synthesis of pharmaceuticals such as naproxen [4] and ibuprofen [5]. The conventional Friedel–Crafts acylation uses Lewis acid catalysts such as $AlCl_3$ [6], however these catalysts generate large amounts of environmentally toxic by-products; they are used in more than stoichiometric amounts, and furthermore the catalyst is non-regenerable. In this context, there is obviously a need for more environmentally friendly catalysts such as zeolites. These are a class of aluminosilicates that have gained attention for their ability to catalyse a number of organic reactions (e.g. [7,8]) and in particular the synthesis of aromatic ketones [9], without the drawbacks of conventional Friedel–Crafts catalysts. Spagnol et al. [10] were the first to report an industrial application for the acylation of anisole with acetic anhydride catalysed by zeolite Beta.

Considering the mechanism of acylation, Corma et al. [1] proposed that an acylium cation can be formed by protonation of an acyl chloride molecule interacting with a Brønsted acid site in the zeolite, and that this acylium ion would be the species attaching to the aromatic ring to form the acylated product. However Corma's conclusions were based solely on the catalytic activity of a series of partially Na+ exchanged zeolites Y. Additionally, Corma studied acyl chlorides as acylating agents, while the industrial process [10] employs other reagents because of environmental constraints on the use of chlorides. Bosacek et al. [11] investigated the adsorption of acetyl chloride on zeolites X, Y and ZSM-5 by $^{13}$C MAS NMR and found evidence of chemisorbed acylium ion. Gorte et al. [12] investigated the adsorption of acetic acid, acetic anhydride and acetyl chloride on H-ZSM-5 by TPD, FTIR and $^{13}$C MAS NMR. Upon adsorption of either acetyl chloride or acetic anhydride they report the presence of an acylium-like

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intermediate above 400 K, however this temperature is sensibly higher than the acylation temperature of 333 K that we used in our studies [2] although e.g. Rohan [13] used 333 K.

Previously we have reported on the reaction of anisole with acetic anhydride to give *para*-methoxyacetophenone (*p*-MAP) over a number of zeolite Beta (BEA) catalysts, and on their interaction of acetic anhydride, studied by temperature programmed desorption (TPD) [2]. We showed that ketene is an important product in the desorption of acetic anhydride and that there is an inverse relationship between initial rates of reaction and the amount of ketene desorbing. Further studies by FTIR [3] showed that acetic anhydride, upon adsorption on zeolite Beta, undergoes decomposition to acetic acid and a fragment identified as ketene. The interaction of the product, *p*-MAP, and zeolite Beta resulted in a species that had lost the aromatic ring vibrations and we detected again a band attributed to ketene. We interpreted the results by applying the concept of microscopic reversibility, i.e. at equilibrium the site that can form the bond between the acylating agent and anisole can also split this bond, and one of the products of this scission is ketene.

In this paper we report on isotopic labelling experiments that we have conducted with the aim of finding which of these two mechanisms dominates. Fig. 1 shows that, when

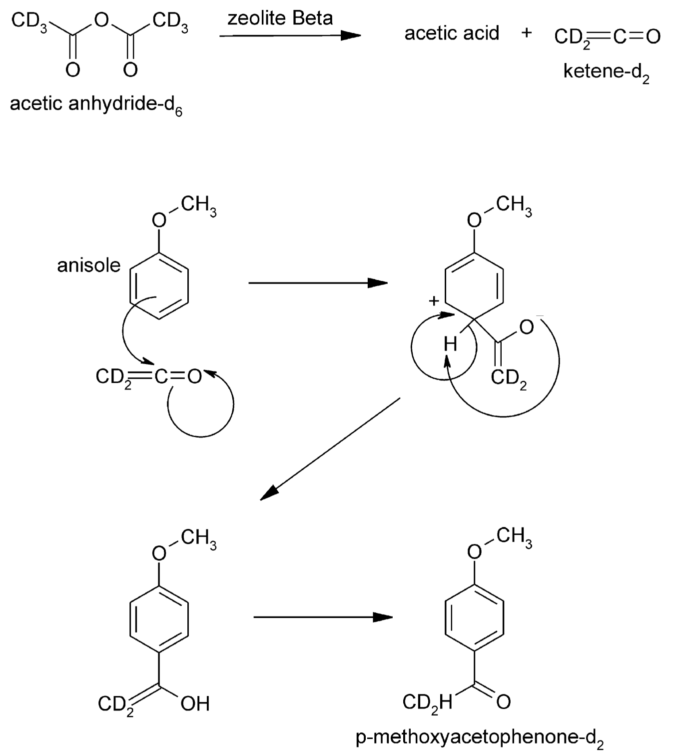

Fig. 2. Reaction pathway for the acylation of anisole with acetic anhydride via a ketene [3] formation using deuterated reagents.

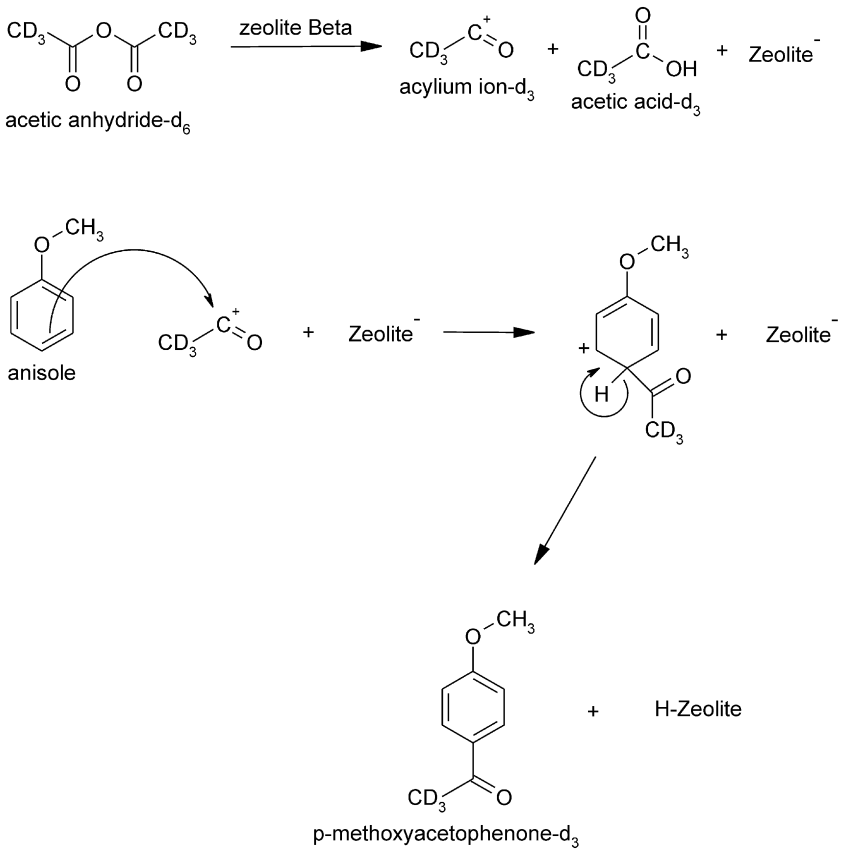

Fig. 1. Reaction pathway for the acylation of anisole via a acylium cation with acetic anhydride using deuterated reagents. The mechanism is derived from [1].