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A temperature programmed desorption study of the interaction of acetic anhydride with zeolite beta (BEA)

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Abstract

The interaction of acetic anhydride with the Na- and H-forms of zeolite BETA, as well as with materials where copper or iron has been introduced into BEA by ion exchange, has been studied by temperature programmed desorption (TPD). In all cases acetic acid is a main desorption product in the temperature range 370–570 K. Ketene desorption is also significant, although it is argued that much of it is retained in the zeolite pores, where it undergoes further decomposition into carbon monoxide, hydrogen and water. There is an inverse correlation between the quantity of ketene desorbed and the activity of the catalysts in the catalytic acylation of anisole by acetic anhydride to yield *p*-methoxyacetophenone. The significance of this observation is discussed and an acylation mechanism involving ketene is proposed.

Keywords: Acetic anhydride; Acylation catalysis; Thermal desorption; Ketene; Zeolite beta

1. Introduction

Zeolite beta has been shown to be an effective catalyst for the acylation of anisole to give *p*-methoxyacetophenone $\{CH_3–C(O)–C_6H_4–O–CH_3\}$ [1], with acetic anhydride as the preferred acylating agent. The reaction is catalysed by the acid form of the zeolite H-BEA, and has been assumed to occur by Brønsted acid catalysis [2]. However, one of us has recently shown that similar catalytic activity to that of the H-form is exhibited by Fe-BEA and Cu-BEA, where the transition metal is introduced by ion exchange and there is little residual Brønsted acidity [3]. These results suggest that other catalytic mechanisms than Brønsted catalysis may be available, and the importance of a reversible transformation from tetrahedral aluminium to octahedral coordination as a result of adsorption of the anhydride has been postulated [3].

We are thus interested to understand the interaction of acetic anhydride with the different catalytically active forms of zeolite beta, and have studied this by a number of techniques. Of these temperature programmed desorption (TPD) has turned out to be the most informative, and the TPD results are presented here. We are particularly interested to look for the formation of ketene (CH_2=CO) since an earlier study has shown that it can be formed from the interaction of acetic acid with Na-ZSM-5 [4], but not with, e.g. H-ZSM-5 [5]. We will suggest that ketene formed in situ may be an effective acylating agent.

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2. Experimental

H-BEA with a Si/Al ratio of 12.5/1 was obtained from Catal Ltd., Sheffield. Sodium, copper or iron were introduced by aqueous ion exchange. Approximately, 5 g of parent zeolite was added to 250 ml of a 1 M solution of the metal nitrate (Laboratory reagent grade) in distilled water. The solution was stirred at room temperature overnight. The catalyst was then separated by filtration, washed with distilled water and dried in air for 24 h at 298 K. This exchange procedure was then repeated twice. The iron and copper loadings in the zeolites were determined by dissolution of the zeolite in hydrofluoric acid, the resulting solution being analysed by atomic absorption spectroscopy.

TPD measurements were made in a compact, purpose built, stainless steel apparatus equipped with a $60\,\mathrm{l\,s^{-1}}$ turbo pump. The desorption cell was connected through a leak valve to an independently pumped, multiplexed Pfeiffer Prisma quadrupole mass spectrometer operating under computer control. The zeolite (ca. 50 mg) was introduced into the desorption cell, evacuated, heated to ca. 750 K at 5 K per minute and cooled to room temperature. After this, the base pressure in the apparatus was typically 5×10^{-6} Pa. Acetic anhydride (Aldrich, +99% purity) was further purified by freeze/thaw pumping cycles and exposed to the zeolite sample at room temperature and ca. 10^2 Pa pressure. After pumping back to the base pressure, the sample was heated to 875 K at 10 K per minute and the desorption spectra recorded.

Preliminary analysis of desorption results showed there are a wide range of significant reaction products from acetic anhydride, principally acetic acid, carbon monoxide, carbon dioxide, water, hydrogen and ketene. Ketene was identified from the cracking pattern published by Cornu and Massot [6], which shows that the parent m/e of 42 is the second largest feature, but that the strongest contribution is at $m/e = 14$, from the CH_2 fragment. We have used $m/e = 14$ in our analysis, although we have also shown that essentially the same results are obtained if $m/e = 42$ is considered instead. $m/e = 14$ also has the advantage that it receives only relatively small contributions from acetic acid and acetic anhydride.

Cracking patterns in the mass spectrometer were determined in situ for acetic anhydride, water and acetic acid. To quantify the relative amounts of the anhydride and the acid desorbing, the mass spectrum was measured of the vapour above a mixture of acetic anhydride and acetic acid, prepared such that their partial pressures at room temperature were equal.

The cracking patterns justify the following assumptions, which greatly facilitate the quantitative analysis of the desorption spectra:

1. The peak at $m/e = 60$ arises only from acetic acid.
2. The peak at $m/e = 43$ receives contributions from acetic acid and acetic anhydride, but not from ketene. Since acetic acid can be quantified from $m/e = 60$, its contribution to $m/e = 43$ can be calculated, and the amount of acetic anhydride desorbed determined by difference.
3. The peak at $m/e = 14$ receives contributions from ketene, acetic acid and acetic anhydride. Since the acid and the anhydride have already been quantified from the $m/e = 60$ and 43 peaks and their cracking patterns are known, the contribution of ketene to the $m/e = 42$ peak can be determined by subtraction.
4. The $m/e = 18$ peak arises only from the desorption of water. CO_2 was determined from the $m/e = 44$ peak, CO from the $m/e = 28$ peak and hydrogen from the $m/e = 2$ peak.

Amounts desorbed were normalised to take account of the mass of material under study. Two blank experiments were performed. Exposure of the empty TPD apparatus to acetic anhydride, followed by pumping and temperature ramping, showed that there was negligible adsorption on the apparatus walls. In a further experiment, H-BEA was heated to 750 K, cooled to room temperature, and temperature programmed again. There was no detectable desorption of water during this second heating, up to at least 750 K.

3. Results and discussion

Fig. 1 shows desorption spectra from H-BEA, which follow a pattern that is typical of all of the materials studied, although the relative quantities of different compounds desorbed change markedly. As Fig. 1a indicates, at around 370 K some desorption of acetic anhydride occurs. At a slightly higher temperature acetic acid desorption commences and dominates the desorption spectra in the range up to ca. 550 K. Ketene desorption starts at a similar temperature to

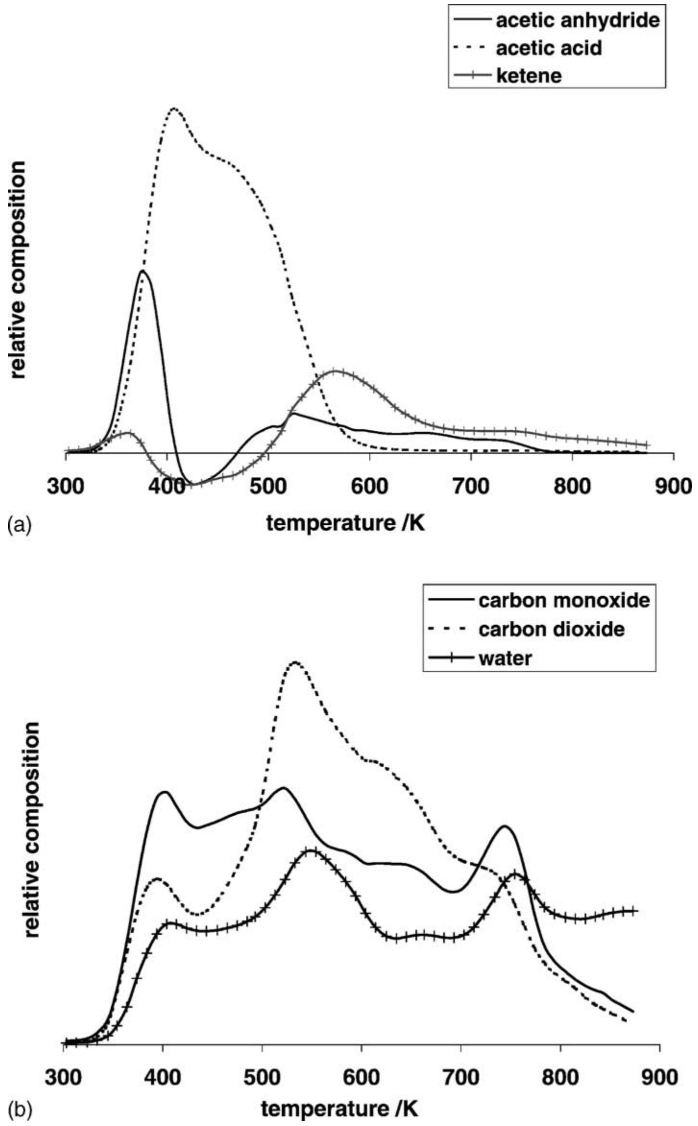


Fig. 1. Desorption results obtained after the adsorption of acetic anhydride at room temperature on H-BEA. (a) Curves for acetic anhydride, acetic acid and ketene; (b) curves for carbon monoxide, carbon dioxide and hydrogen.

acetic acid but continues to occur up to the highest temperature studied, and there is a broad feature due to water desorption (Fig. 1b). As noted already, there is no desorption of water in this region from the activated zeolite, so it must be a decomposition product from acetic anhydride. Fig. 1b shows the desorption results simultaneously obtained for water, carbon monoxide and carbon dioxide. Hydrogen desorption starts at ca. 370 K and continues in a rather featureless way up to the highest temperatures studied. Fig. 2a–c show the desorption results obtained, respectively, from Na-BEA, Cu-BEA and Fe-BEA, concentrating on the organic species. Small dips below the baseline in the desorption curves for acetic anhydride and ketene are thought to reflect small errors in our cracking patterns.

The results show that on all the samples studied only a small fraction of any acetic anhydride adsorbed desorbs intact, with the smallest amount observed

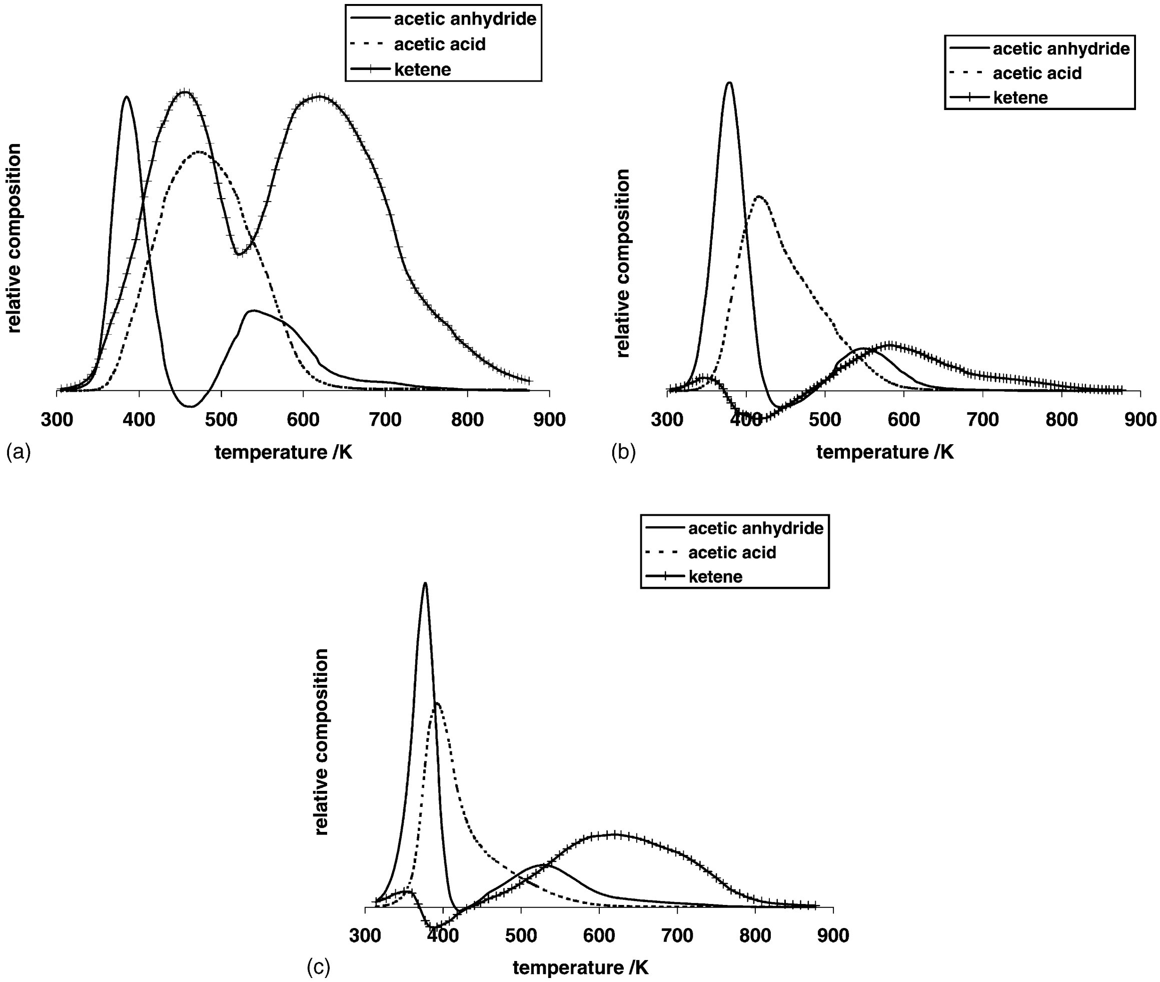


Fig. 2. Desorption results obtained after the adsorption of acetic anhydride at room temperature on (a) Na-BEA, (b) Cu-BEA and (c) Fe-BEA.

from H-BEA. Even on Na-BEA, which might be expected to be comparatively unreactive, much more acetic acid desorption is observed. Only from a purely siliceous MCM-41, which is not of direct relevance to the present study, have we found acetic anhydride to be the dominant desorption product.

Our results show that the primary decomposition mode of acetic anhydride is

$$\text{Acetic anhydride (ads)} \rightarrow \text{Acetic acid} + \text{Ketene (ads)}$$

The desorption spectra are consistent with this, since acetic acid and ketene are both adsorbed at relatively low temperatures. We also consider it to be significant that acetic anhydride is made industrially by the reverse reaction of acetic acid with ketene [7]. The majority of the acetic acid formed within the zeolite pores is quite rapidly desorbed but most of the ketene is retained. However, even at 500 K some acetic acid does stay adsorbed and some ketene starts to desorb, quite large amounts in the case of Na-BEA (Fig. 2a). As the temperature is further increased, there is evidence for the decomposition of adsorbed acetic acid into ketene and water. But much of the ketene remains adsorbed until temperatures above ca. 530 K, when it decomposes into fragments such as CO and hydrogen. Some carbon dioxide formation is also observed,

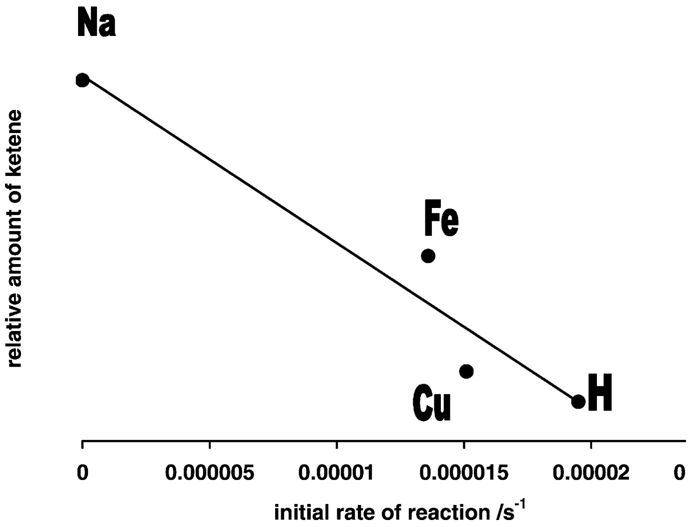
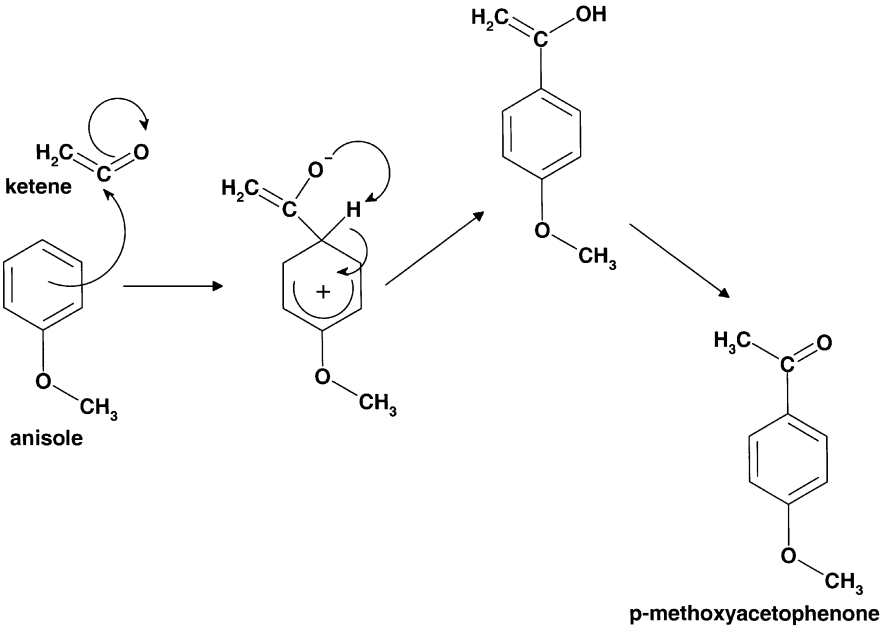


Fig. 3. The relation between the initial rate of acylation of anisole by acetic anhydride at 333 K (3), and the total amount of ketene desorbed from the catalyst.

which may result from the water gas shift reaction or through a bimolecular decomposition of ketene.

We have looked for correlations between our desorption results and the catalytic rate measurements of Apperley et al. [3]. Perhaps surprisingly, there is some inverse correlation between the initial rate of acylation and the amount of ketene desorbed intact for a number of catalysts, as shown in Fig. 3. There is no



Scheme 1. A possible mechanism for the acylation of anisole by ketene.

simple correlation between catalytic performance and the quantities of either acetic acid or acetic anhydride desorbed from the different catalysts.

It is tempting to see this correlation as evidence of the involvement of ketene in the acylation reaction, which is typically carried out at 330–400 K. There is a strong partial positive charge on the central carbon atom of the ketene molecule [8], which makes it an interesting possibility as an acylating agent through the mechanism shown in Scheme 1. The inverse correlation suggests that the strength of bonding of ketene to the zeolite, and hence perhaps its degree of polarisation, determines its effectiveness in the acylation catalysis.

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