

SELECTIVITY IN THE CONVERSION OF ACETIC ACID OVER MFI-TYPE ZEOLITES

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ABSTRACT

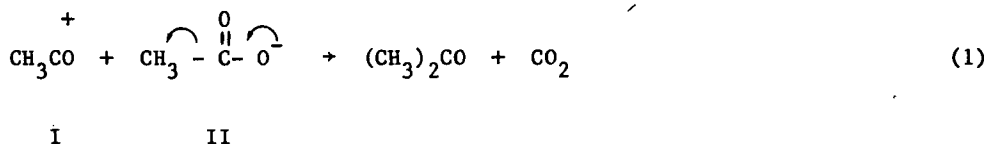
The product selectivity in the conversion of acetic acid over H-ZSM-5 zeolites with different Si/Al ratios was followed at atmospheric pressure in a continuous flow tubular reactor over a wide temperature range.

The primary carbon containing products in this conversion in every case were carbon dioxide and acetone formed via an acid-catalyzed aldolization and a decarboxylation.

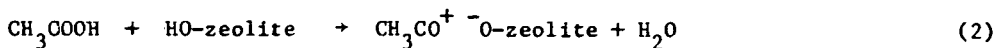
The nature of the secondary products was determined mainly by the Si/Al content of the ZSM-5 zeolite, and for a given ratio by the reaction temperature. Isophorone seems to be a key intermediate, which is either cracked to 1,2,4-trimethylbenzene in the very acidic zeolites or transformed into dimethylphenols via a dehydrodemethylation reaction on zeolites with intermediate acidity and Si/Al ratios.

INTRODUCTION

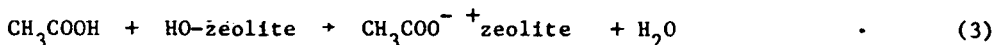
MFI zeolites seem to be able to convert acetic acid into a mixture of hydrocarbons [1]. The distribution of the products of this reaction can be rationalized in terms of a sequence of condensation, decarboxylation and dehydration reactions [2,3]. The primary products of this reaction are acetone and carbon dioxide, formed by a nucleophilic attack of an acyliumion (I) by an acetate anion (II) [4,5] :



Species I may be directly formed by the very acidic ZSM-5 zeolites [3] :

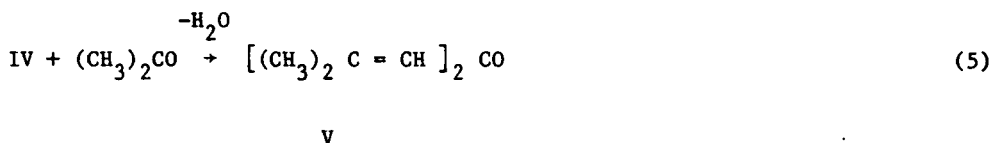
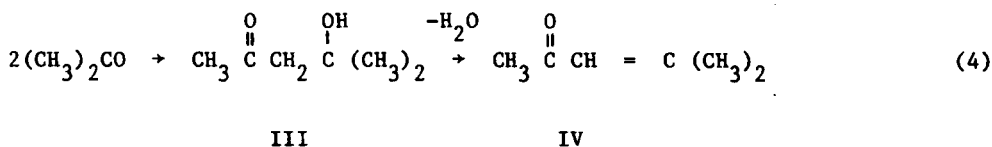


while acetate is formed upon zeolite dehydroxylation [6] :



Chang et al. [3] associate catalyst deactivation in the acetic acid conversion with the dehydroxylation of the zeolite which is evident from equation (3). This statement tacitly assumes that such a system should not be regenerable in the usual way. It should also be noted that a combination of equations (1) to (3) eventually explains the formation of acetone but does not take into account the regeneration of the catalyst Brønsted acidity.

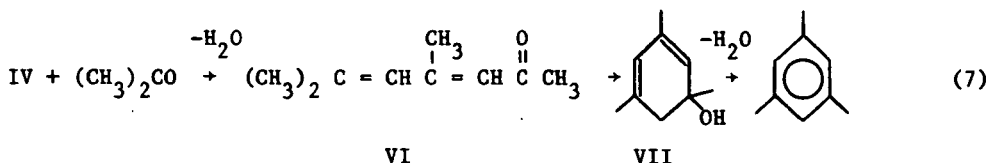
In acid conditions, acetone may undergo further aldolization and subsequent dehydration under formation of diacetone alcohol (III), mesityl oxide (IV) and phorone (V) [7-9] :



On H-ZSM-5 zeolites, the main products of the acetone condensation were reported to be isobutene and aromatics [1-3]. Isobutene can be formed by acid-catalyzed cracking of diacetone alcohol [2],



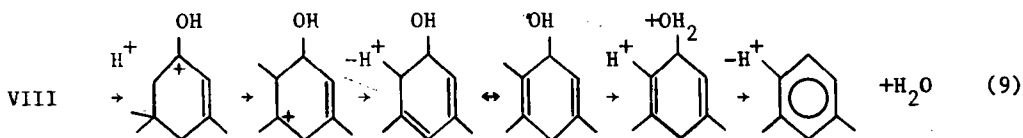
and acetic acid reenters the cycle. Mesitylene (1,3,5-trimethylbenzene) is known to be an acid-catalyzed condensation product of acetone [9] :



in which the cyclization of the dienone (VI) to an isophorone (VII) is the key step, which at the present time is incompletely understood [2]. Also phorone (V) can be cyclized in acid conditions to an isophorone [10] :

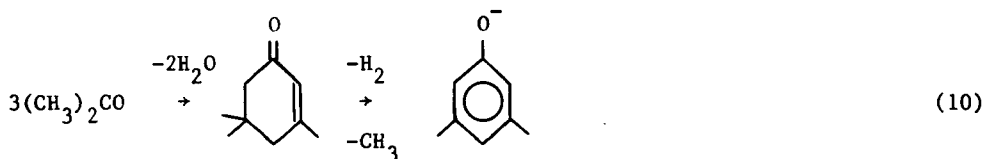


and gives via classical carbenium ion rearrangements and dehydration 1,2,4-trimethylbenzene :



Since the distribution of aromatics from acetic acid, acetone or methanol over H-ZSM-5 is very similar [1], these aromatics in case of acetic acid or acetone may stem from isobutene condensation-dehydrocyclization reactions rather than from equations (7) or (9).

In the decomposition products of acetic acid small quantities of oxygenated products are observed, not exceeding 4 % by weight [3] and consisting of mainly dimethylphenols. Their formation is explained via the following mechanism [3] :



Puzzled by this complex chemistry, we decided to investigate over a wide range of reaction temperatures, the influence of the number of acid sites in H-ZSM-5 upon the product distribution from acetic acid by changing the Si/Al ratio of the zeolite.

EXPERIMENTAL

H-ZSM-5 zeolites with different Si/Al ratio were synthesized in the presence of TPA-OH and glycerol and using aerosil as silica source, according to the method published by Von Ballmoos [11]. The Al/Si + Al percentage in the sample is given in brackets after the sample notation. After careful calcination, subsequent ammonium exchange and further deammoniation, as described earlier in detail [12], H-ZSM-5 samples were obtained characterized by a single surface hydroxyl group around 3600 cm^{-1} . X-ray diffraction showed that these samples were highly crystalline and phase pure. Scanning electron microscopy showed that they were devoid of any amorphous material and consisted of large isolated crystals ($15 \times 20\ \mu\text{m}$) with an hexagonal shape. Such samples are expected to have an Al-rich rim and silicon-rich core [13,14].

A powder sample of each material was compressed without any binder, crushed and sieved. The 0.25-0.5 mm fraction was used in the continuous flow tubular reactor.

Acetic acid from UCB (99.5 % purity) was vaporized and diluted with helium using a thermostatted saturator and a W/F_0 of $2016\text{ kg.s.mol}^{-1}$, W being the amount of catalyst and F_0 the acetic acid flow rate at the reactor inlet.

Product analysis was done on-line with a 1 m packed column of Chromosorb 102 (from Johns-Manville) for the separation of CO , CO_2 and $\text{C}_1 - \text{C}_2$ hydrocarbons, and with a 50 m fused silica column (CP Sil 5, chemically bound, from Chrompack) with 0.3 mm internal diameter for the heavier products. The latter column was temperature programmed between 338 and 973 K at a rate of 2 K per minute.

RESULTS AND DISCUSSION

Overall reaction rate. For the contact time used, acetic acid could be converted completely in the temperature range from 520 to 700 K. The variation of the initial rate for acetic acid decomposition with the Al content of the ZSM-5 zeolite is shown in Fig. 1.

Surprisingly, and in contrast to what is observed in several other cases [15-17], this particular reaction rate is in no way proportional to the amount of lattice aluminum. This behaviour can only be explained when for the reaction either a particular site strength or site density is needed.

Selectivity for acetone. The selectivity for the supposed primary products from acetic acid, acetone and carbon dioxide, is shown in Fig. 2.

From this figure, two general observations elude :

(1) The initial selectivities for CO_2 are constant, irrespective of the aluminum content of the sample and amount to approximately 45 wt %.

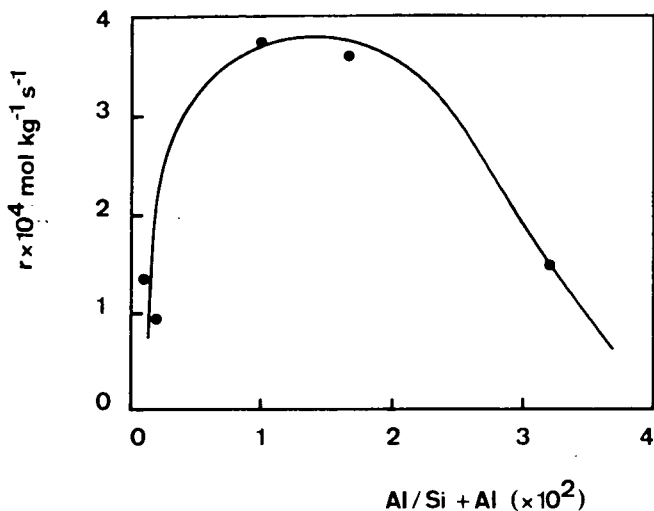


Fig. 1. Initial rate of CH_3COOH decomposition at 550 K for H-ZSM-5 zeolites with different Al content.

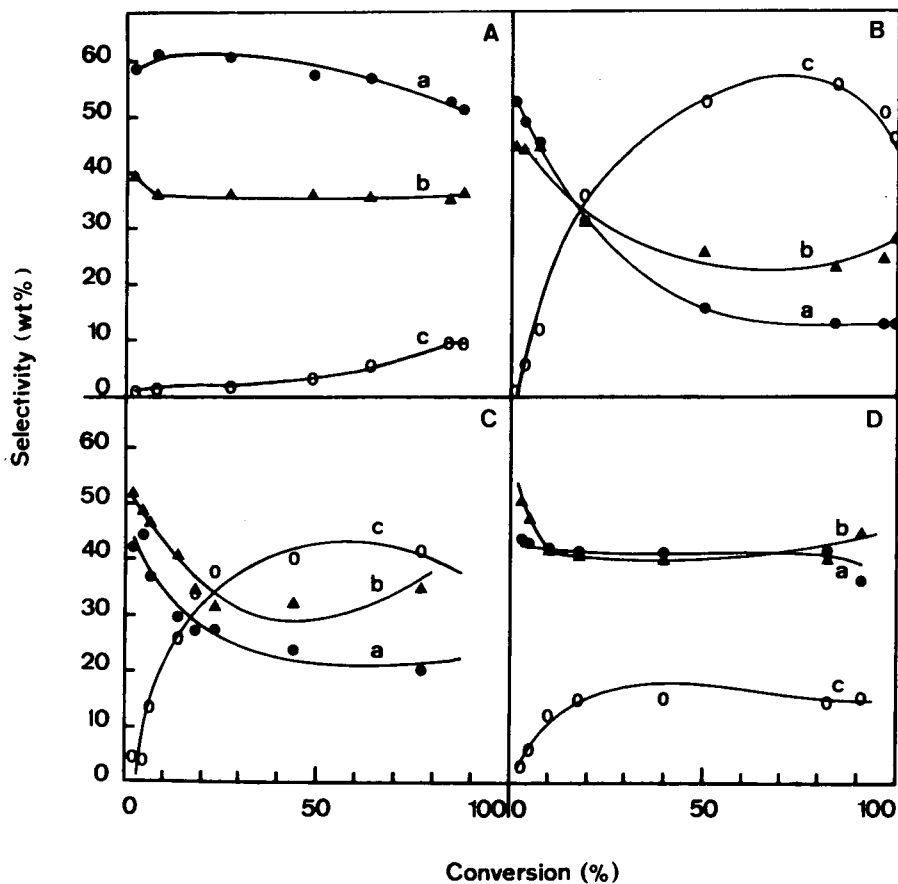
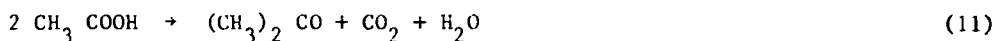


Fig. 2. Reaction selectivity for acetone (a), CO_2 (b) and secondary products (c) from acetic acid, over H-ZSM-5 with different Al/Al + Si fractions = (A) 0.1, (B) 1, (C) 1.6 and (D) 3.2 %.

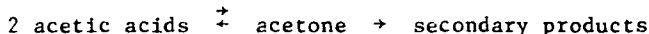
The theoretical CO₂ selectivity of the bimolecular reaction :



is equal to 43 wt % when water is not considered as reaction product.

(ii) The rate at which secondary products are formed is dependent on the Al content of the sample : at intermediate values for the Al content (approximately 1 Al per unit cell), the rate of formation of the secondary products as well as the overall rate of acetic acid decomposition are fastest.

The sequence of events can be kinetically represented as follows :



In other words, the decomposition of acetone is slower than its formation.

As is evident from the introduction, the presence of catalyst deactivation and the ability to regenerate the system will allow to decide whether the acetone formation can be rationalized by equations (1) to (3). In Fig. 3 time on stream data are plotted using a fresh catalyst.

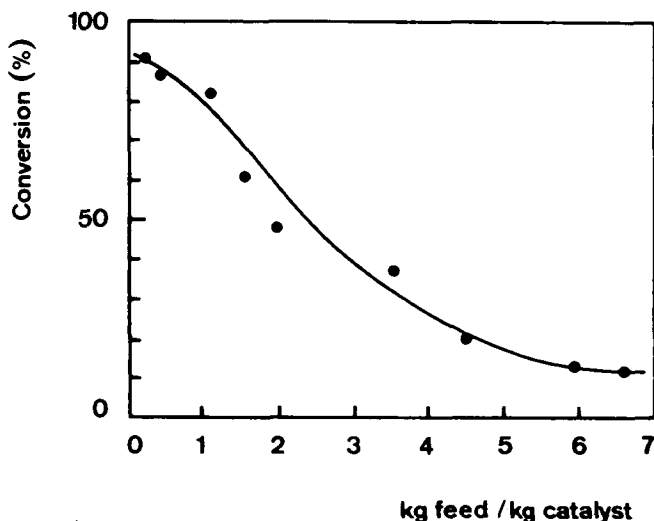
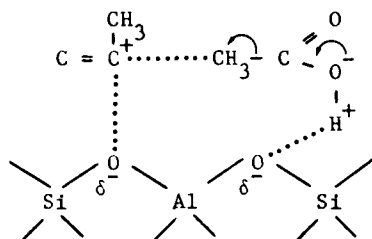


Fig. 3. Catalytic stability of H-ZSM-5 (1) at 633 K.

This catalyst H-ZSM-5 (1), after regeneration (oxygen treatment at reaction temperature), comes back to its original activity.

In agreement with the literature data [3], it is confirmed that all H-ZSM-5 zeolites coke up in a relatively short period, but are easily regenerable. If the mechanism occurs according to equations (1) to (3), the Brønsted acidity of the dehydroxylated zeolite should be restored by H₂O/CO₂ mixtures. Since there is no

direct proof in literature that this is possible for hydrogen zeolites, a alternative explanation for acetic acid activation is advanced using the following transition state :



The acylium is formed in the usual way (equation (2)), while the acetic acid is polarized by the diffuse negative charge. In such a way acetate and acyl are formed close to each other (possibly in a channel intersection) and may react upon complete reconstitution of the catalyst in its original state. Such a mechanism doesnot suffer from the drawbacks mentioned for equations (1) to (3).

Distribution of secondary products. The main secondary products formed from acetone are in the order of importance : alkylphenols, isobutene, aromatics and other hydrocarbons. The distribution of these products on the series of ZSM-5 samples is shown in Fig. 4.

This figure indicates that isobutene as well as the alkylphenols are primary products from acetone, while aromatics are only of a secondary origin. Selectivity for the oxygenated products is maximum for the ZSM-5 (1) sample, with intermediate aluminum content.

The formation of isobutene is easily accounted for by cracking of diacetone alcohol (equation (6)). The precursor of alkylphenols can be isophorone (VIII) (equations (8) and (10)). This molecule can be formed from acetone through an acid aldolization followed by dehydration (equations (4),(5),(8)). However, its conversion to dialkylphenols is difficult to explain using Brønsted catalyzed-reactions, since the overall conversion equation represents a dehydrodemethylation reaction. A competitive and Brønsted acid-catalyzed degradation of isophorone (VIII) gives mainly 1,2,4-trimethylbenzene (equation (9)). From the data of Fig. 2 it follows that if too few acid sites are present, the reaction stops when acetone is formed. When too many Brønsted sites are present (i.e. for high Al/Si + Al ratios), it follows from Fig. 4 that more aromatics and much less alkylphenols are formed. This may reflect that reaction (9) becomes fast on such catalysts. This is confirmed when the distribution of the aromatics is considered. The selectivity for 1,2,4-trimethylbenzene decreases with decreasing Al content of the ZSM-5 zeolites and is in any case over 50 wt %. In a given zeolite it increases with the reaction temperature. It can be concluded that reaction (9) is important compared to the formation of aromatics from isobutene and

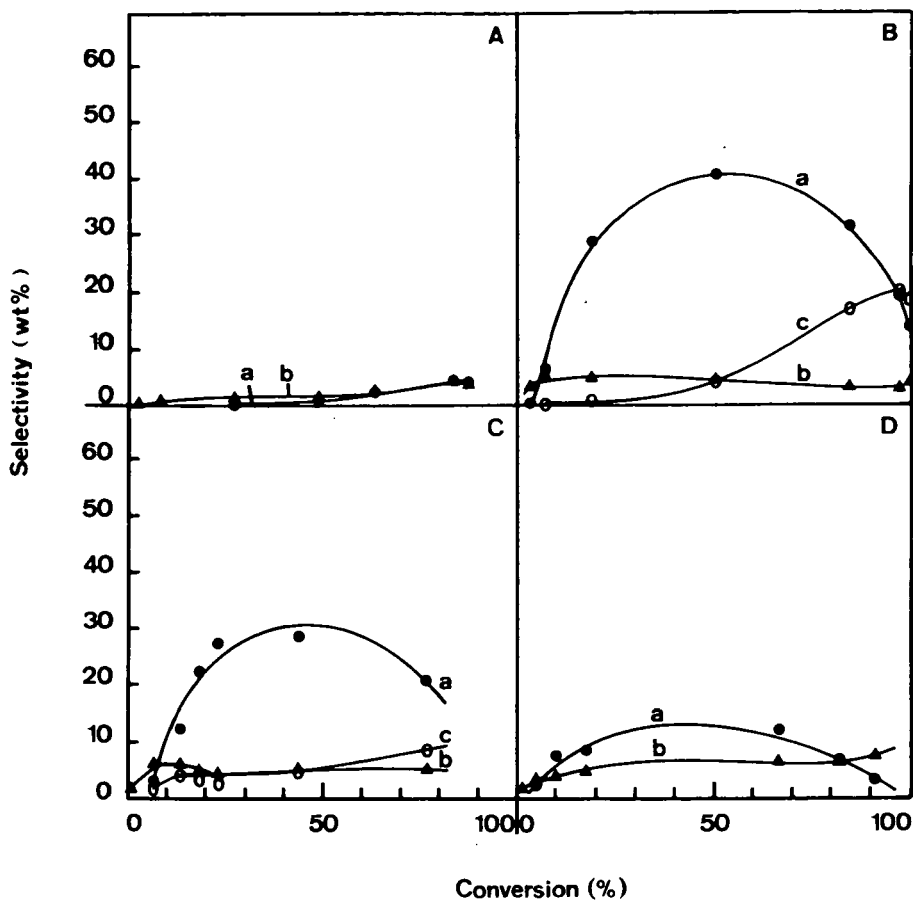
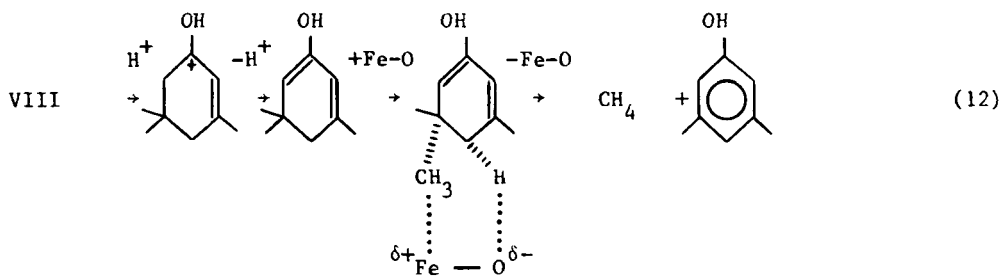


Fig. 4. Distribution of the secondary products from acetic acid : (a) alkylphenols, (b) isobutene and (c) aromatics. The H-ZSM-5 zeolites used contained (A) 0.1, (B) 1, (C) 1.6 and (D) 3.2 % of Al/Al + Si.

competes with the dehydrodemethylation reaction. This would explain the maximum in the yield of alkylphenols (Fig. 4). In the series of ZSM-5 zeolites with different Al content, the right degree of dilution of the Brønsted sites is needed to realize a maximum selectivity to alkylphenols. Whether at this particular dilution a maximum number of Brønsted sites of a given strength is present, is unknown at this time. Neither is known on what kind of site the dehydrodemethylation occurs. A potential active site could be occluded impurity iron.

Although this matter requires further research, at this stage it is believed that rather than by equation (10) the dehydrodemethylation reaction can be best rationalized when it is catalyzed by occluded iron-oxide in the following way :



Distribution of the alkylphenols. The maximum selectivity obtained for alkylphenols when untransformed acetone and CO_2 are not taken into account as products is approximately 80 wt % on H-ZSM-5 (1). The dominating product in this fraction is 2,4-dimethylphenol, with a maximum selectivity of 77 wt %. In analogy to the trimethylbenzenes [3], 2,4-xyleneol is expected to be the smallest of the dimethylphenol-isomers. Its formation is therefore governed by product diffusion shape selectivity. At high reaction temperatures, cresol as well as trimethylphenols appear in minor amounts. This represents evidence for a dismutation reaction.

CONCLUSION

Acetic acid is shown to be converted on H-ZSM-5 zeolites into acetone, carbon dioxide and water as primary products. The stoichiometrically expected CO_2 is recovered on all H-ZSM-5 zeolites, irrespective of their Al content. The data can be rationalized in terms of the interaction between a Brønsted acid generated acylium and an acetate ion. In contrast to previously proposed mechanism, no zeolite dehydroxylation has to be invoked.

Acetone is then either converted via a series of Brønsted acid-catalyzed aldolization and dehydration reactions into isophorone or via dimerization and cracking into isobutene. The selectivity for the first reaction is high for H-ZSM-5 samples rich in aluminum. For the high-silica samples, acetone is only cracked at very high reaction temperatures. The key step in the reaction network seems to be the decomposition pathway of isophorone. If this occurs via classical carbenium ion chemistry, 1,2,4-trimethylbenzene is the main product. On H-ZSM-5 zeolites with intermediate Al content (1 %) and at relatively low reaction temperatures, isophorone is via a dehydrodemethylation reaction converted into mainly dimethylphenols, in which fraction 2,4-xyleneol as a result of product diffusion shape selectivity is abundantly present.

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