

Dehydration of *t*-butanol over basic ETS-10, ETAS-10 and AM-6 catalysts

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Received 20 March 1998; accepted 21 May 1998

The *t*-butanol dehydration over basic ETS-10, ETAS-10 and AM-6 has been investigated. All these as-synthesised materials catalyse this reaction in a very similar fashion yielding remarkably high selectivities for isobutene, which are independent of both reaction conditions and conversion levels. The catalyst decay was more profound at lower reaction temperatures (ca. 200 °C), whereas no decay was observed at higher temperatures (ca. 300 °C). The basic sites of these materials are purported to be responsible for the excellent catalytic performance.

Keywords: dehydration, butanol, isobutene, ETS-10, ETAS-10, AM-6

1. Introduction

Dehydration of alcohols [1,2] may be catalysed by a plethora of inorganic solids, and among those crystalline zeolite/zeotype [3–8] and amorphous silica–alumina [7–10] materials constitute two major groups. In addition, amorphous and crystalline mesoporous aluminophosphate materials (AlPO₄) have also been recently reported [11] to catalyse this reaction. The catalytic performance of silica–alumina has been found [9] to be dependent upon the chemical composition of these catalysts, which defines the acid–base properties of these solids. Alumina-rich silica–alumina exhibits a rather weak acidity and, thus, dehydrates alcohols to the corresponding alkenes and ethers. On the other hand, silica-rich silica–alumina is far more acidic and, therefore, dehydrates alcohols to alkenes which undergo further isomerisation and oligomerisation reactions. Dehydration of alcohols over zeolite catalysts has been widely investigated [3–8] and various selectivities for ethers and olefins were found for different zeolites. A large number of factors such as structural properties, acidity/basicity and diffusion effects seem to dictate the catalytic behaviour of zeolite catalysts.

The dehydration of *t*-butanol has received particular attention in the literature [6] due to the fact that it leads to isobutene, an essential ingredient in the methyl *tert*-butyl ether (MTBE). Furthermore, *t*-butanol is an ideal probe molecule for investigation of the reaction mechanism as it entails stable tertiary carbenium ions or alkoxy-type intermediates which may be detected by various spectroscopic techniques.

ETS-10 (Engelhard titanosilicate structure 10) is potentially a very important new microporous inorganic titanosilicate framework material. The structure, which was first synthesised by Engelhard [12,13] and solved by Ander-

son et al. [14–16], consists of corner sharing octahedral titanium(IV) and tetrahedral silicon. ETS-10 is one of a small group of zeolite or zeotype materials which contain a three-dimensional 12-ring pore system. Additionally, isomorphous substitution to incorporate both aluminium [17] and gallium [18] into ETS-10, thus producing ETAS-10 and ETGS-10, respectively [19], has been reported. The most recent advance [20] in the ETS-10 chemistry has been the synthesis of AM-6, a material with the ETS-10 structure, but synthesised with vanadium rather than titanium.

The increasing interest in these inorganic solids with regard to catalysis results from their unique structural characteristics as well as their novel chemical composition, and a number of contributions have already reported on the catalytic properties of ETS-10 materials [21–26]. In this preliminary investigation, the *t*-butanol dehydration over basic ETS-10, ETAS-10 and AM-6 is described. All these as-synthesised materials catalyse this reaction in a very similar fashion yielding remarkably high selectivities for isobutene. The acid–base properties of these materials are suggested to be responsible for this excellent catalytic performance.

2. Experimental

2.1. Synthesis and characterisation

ETS-10 and ETAS-10 samples were synthesised according to the methods reported by Engelhard [12,13]. The AM-6 sample was synthesised using the synthesis procedure recently reported [20] in the literature by Rocha et al. All these materials were fully characterised by powder XRD, ²⁹Si, ²⁷Al and ¹H MAS NMR, N₂ adsorption measurements, electron-dispersive analysis of X-rays (EDAX) and electron microscopy. Catalytic tests on a silica–alumina sample were also performed in these studies for comparison

purposes, and the molar composition of this material was 86% SiO₂ and 13% Al₂O₃. Furthermore, the BET surface area of this sample was found to be 400 m²/g.

2.2. Catalysis

These experiments were performed in a fixed-bed stainless-steel reactor at atmospheric pressure. The reactor's length and internal diameter are 16 and 0.5 cm, respectively, and the reactor's bed measures 1 cm long and exhibits an internal diameter of 0.5 cm. The catalyst (50 mg) was activated at 350 °C in a flow of argon (30 ml/min) prior to reaction. To assess the effect of reaction temperature on this catalytic process, these experiments were carried out in the temperature range 100–300 °C. The reactant was fed by a syringe pump, and the Ar/reactant molar ratio was twenty. Residence times were adjusted by keeping the catalyst volume constant and altering the volumetric flow rate of the reactant and were calculated at the reaction conditions on a volume basis. In order to assess thermal reactivity, a blank test was performed at 300 °C in the absence of catalyst. A fresh catalyst was used for each run and products were analysed *in situ* using gas chromatography. These analyses were carried out isothermally at 45 °C by means of a 30 m long capillary column (DP1 fused silica phase) and an FID (flame ionisation detector). Conversions hereafter are calculated on a molar basis, and isobutene selectivities are calculated by dividing the isobutene yield by the *t*-butanol conversion.

3. Results and discussion

3.1. Characterisation of ETS-10, ETAS-10 and AM-6

The X-ray diffraction patterns of the as-synthesised materials, before and after the catalytic test, match very closely with those published earlier [14,16–20]. These results indicate that, although ETS-10 is thermally more stable than ETAS-10 and AM-6, all materials have remained intact during these catalytic tests.

Furthermore, the ²⁹Si and ²⁷Al MAS NMR spectra of these materials agree with those published earlier [14,16, 17], and the ¹H MAS NMR spectra exhibit lines in the chemical shift region of 1.0–3.0 ppm assigned to terminal non-acidic protons [26].

EDAX analysis shows that, within experimental error, the Si/Ti ratio in ETS-10 and ETAS-10 is ca. 4.8, and the Si/Al ratio in ETAS-10 is ca. 20. The Si/V ratio in the AM-6 sample is ca. 5. In addition, ETS-10 and AM-6 materials were found to contain similar Na/K ratios (Na/K = 3.4), whereas ETAS-10 appears to accommodate more K cations (Na/K = 2).

Finally, N₂ adsorption experiments on these materials yield isotherms of type I, characteristic of microporosity with maximum uptakes of ca. 12–15% w/w.

Table 1

A comparison between the catalytic performance of the ETS-10 materials and that of silica–alumina at identical reaction conditions.^a

Catalyst	ETS-10/ETAS-10	AM-6	Silica–alumina
Conversion (mol%)	100.0	100.0	100.0
C ₁ –C ₃	0.1	0.2	2.0
<i>isobutene</i>	99.0	95.0	83.0
isobutane	0.1	0.2	1.0
<i>n</i> -C ₄ 's	0.4	0.6	2.6
C ₅ –C ₉	0.4	4.0	11.4

^a Residence time: 0.4 s, TOS: 1 h, *T*: 300 °C.

3.2. Catalytic activity of ETS-10, ETAS-10 and AM-6

As mentioned above, all these as-synthesised basic solids, ETS-10, ETAS-10 and AM-6, catalyse this reaction in a remarkably similar fashion yielding selectivities for isobutene of 95–99 mol%. It was also found that this uncommonly high selectivity for isobutene was independent of the reaction conditions. In other words, whereas conversion levels were very dependent upon the residence time and the reaction temperature, the product distribution remained unchanged at all various experimental conditions investigated.

Table 1 illustrates the catalytic performance of ETS-10, ETAS-10 and AM-6, hereafter defined as ETS-10 type of materials, in comparison with that of silica–alumina. It is clearly shown that, at the same reaction conditions and conversion levels (100 mol%), the ETS-10 materials are more selective than silica–alumina. Furthermore, AM-6 was found to be slightly less selective than ETS-10 and ETAS-10. Due to the higher acidity of silica–alumina, isobutene is suggested [6,8] to undergo secondary reactions such as isomerisation, oligomerisation and cracking, thereby decreasing the final selectivity of this catalyst for isobutene.

3.3. Effect of temperature and residence time

The effect of the reaction temperature on the conversion of the ETS-10 catalyst is depicted in figure 1(a). Furthermore, table 2 illustrates a comparison among the conversion levels of the three catalysts at various reaction temperatures, indicating that these ETS-10 type catalysts are equally active. While the conversion is limited to less than 30 mol% at temperatures lower than 200 °C, a noticeable increase is observed in the temperature range 200–300 °C. Conversion levels were also dependent upon residence times and this is illustrated in figure 1(b), where a variety of conversions were achieved by altering the residence time at 250 °C. A linear correlation between residence time and conversion was found, which is indicative of a zero-order reaction. This suggests that the reaction rate is independent of the reactant concentration and, thus, the former decreases linearly with the residence time. The selectivity for isobutene in all these experiments was in the range of 97–99 mol%.

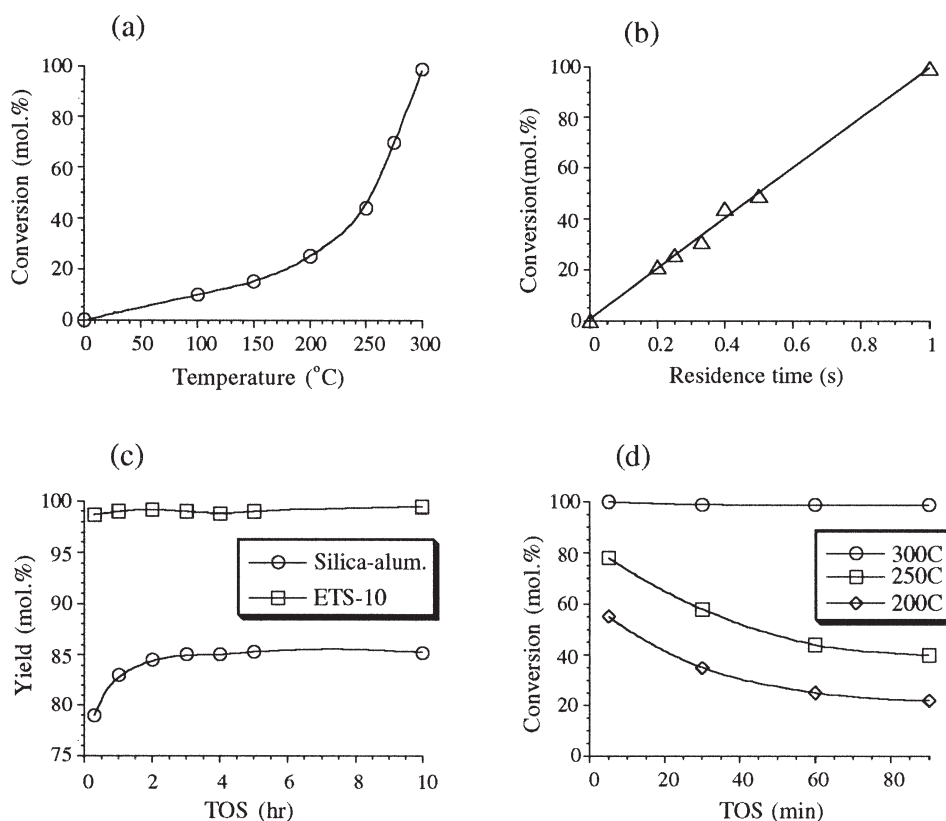


Figure 1. (a) The effect of reaction temperature on the *t*-butanol dehydration catalysed by the ETS-10 catalyst. (b) The effect of residence time on the *t*-butanol dehydration catalysed by the ETS-10 catalyst. (c) The effect of TOS on the selectivity for isobutene in the *t*-butanol dehydration catalysed by the ETS-10 catalyst and silica-alumina. (d) The catalyst decay in the *t*-butanol dehydration catalysed by the ETS-10 catalyst at various reaction temperatures. (a) Residence time: 0.4 s, TOS: 1 h, selectivity for isobutene: 97–99 mol%; (b) *T*: 250 °C, TOS: 1 h, selectivity for isobutene: 97–99 mol%; (c) residence time: 0.4 s, *T*: 300 °C; (d) residence time: 0.4 s, selectivity for isobutene: 97–99 mol%.

Table 2

A comparison among the conversion levels of the ETS-10 materials.^a

	ETS-10	ETAS-10	AM-6
Conversion (mol%) at 200 °C	25.0	24.0	23.0
Conversion (mol%) at 250 °C	44.0	45.0	43.0
Conversion (mol%) at 300 °C	100.0	100.0	100.0

^a Residence time: 0.4 s, TOS: 1 h.

3.4. Effect of time on stream (TOS)

Besides the high catalytic activity and selectivity of the ETS-10 materials for this reaction, it is worth looking at the effect of TOS on this catalytic process. Figure 1(c) shows the effect of TOS on the selectivity of both ETS-10 and silica-alumina. It becomes apparent that even after 10 h the selectivity of the ETS-10 materials for isobutene is approximately 99 mol% at 300 °C. The conversion levels in this experiment were 100 mol%, and no decay was observed at these conditions. However, at lower reaction temperatures striking decays with TOS were observed, as shown in figure 1(d), and the lower the reaction temperature the more pronounced the catalyst decay. The catalyst deactivation at low reaction temperatures might result from active site poisoning by water molecules. These active centres which are poisoned by water remain inactive at lower temperatures, whereas they would regenerate at higher temperatures.

3.5. Active sites in the ETS-10 type of materials

Overall, these experimental findings point to an excellent catalytic behaviour which may only be accomplished by a very few catalysts. Dehydration of alcohols to olefins is known to be catalysed by acidic materials, where a reactant alcohol interacts with a Brønsted acid site and dehydrates to the corresponding alkene via a carbenium ion mechanism. The stability of the intermediate ions coupled with structure and diffusion characteristics dictate the catalyst activity and selectivity. However, alcohols may also, but less conventionally, dehydrate over basic catalysts via alkoxy intermediates [27–30]. The catalyst structure and the electronic nature of the basic sites were reported [27,28] to be of great significance for the mechanistic pathway of alcohols dehydration over basic systems.

Both spectroscopic evidence (¹H MAS NMR) and acid-catalysed reaction tests, such as paraffin cracking, performed on the as-synthesised ETS-10 materials suggest that the acidity of these solids is very weak. It follows that such a high catalytic activity for the *t*-butanol dehydration cannot be explained on grounds of acidity. Conversely, these as-synthesised materials possess a large number of Na and K cations balancing the anionic framework oxygen charge. Thus, these cations furnish the ETS-10 materials with considerable basicity, which is purported to be responsible for

the remarkable catalytic performance. Further evidence for this argument rests with the high selectivity of these solids for isobutene. If the reaction was catalysed by acid sites, isobutene, formed after the dehydration of *t*-butanol, would inevitably undergo secondary reactions such as isomerisation, oligomerisation, cracking, etc. at the expense of the final selectivity for isobutene. By contrast, isobutene is inert over basic catalysts at these relatively mild reaction conditions. Hence, the high selectivity of these catalysts for isobutene may also be explained by the fact that *t*-butanol dehydrates to isobutene over basic sites. As a result, isobutene, formed after the dehydration of *t*-butanol, fails to undergo any further reactions in the basic environment and, thus, desorbs as the main product of this catalytic process. The intermediacy of alkoxides in the base-catalysed dehydration of alcohols, as previously suggested [27–30], could be a step of this reaction pathway, though this matter requires further investigation.

Acknowledgement

We thank Mr. Zhi Lin and Miss Paula Brandao (Department of Chemistry, University of Aveiro) for synthesising the ETAS-10 and AM-6 samples.

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