# The strong basicity of the microporous titanosilicate ETS-10

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Base-catalysed reactions in general are of great importance. In zeolite chemistry, alkali-metal-exchanged zeolites, such as zeolite X, display very strong basicity coupled with high catalytic activity. However, in order to achieve this strong basicity, considerable post-synthesis modification is necessary. In this report, it is shown that strong basicity is exhibited by the microporous titanosilicate ETS-10 in the as-prepared form which is superior to the presently known suite of zeolite catalysts. This opens up a new class of material for heterogeneous base catalysis.

**Keywords:** ETS-10, basicity, catalysis

## 1. Introduction

In the zeolite family, zeolite X is widely accepted as one of the most basic zeolites, and ion exchange of the as-synthesised Na-X with larger monovalent cations to either K-X or Cs-X increases the zeolite basicity markedly [1]. Further increase in the zeolite basicity may also be achieved by impregnating the porous solids with cesium oxide [2] and thus forming additional extra-framework basic sites.

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 [3,4] and solved by Anderson et al. [5,6], 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. Owing to the high framework charge associated with the octahedral Ti, ETS-10 also exhibits a very high cation-exchange capacity which, in the as-prepared material, consists of 75 mol% sodium and 25 mol% potassium.

The increasing interest in these inorganic solids with regard to catalysis stems from their unique structural characteristics as well as their novel chemical composition, and a number of contributions [7–14] have already reported on the catalytic properties of ETS-10 materials. The acidity of these materials is rather modest [10] and so is their acid catalytic activity. Conversely, these materials were recently found to be excellent basic catalysts for reforming chemistry [12,14].

The basicity of a solid catalyst may be assessed in various ways, with catalytic tests using probe reactions considered to be one of the most reliable measures [1]. A probe reaction which defines basicity is the conversion of isopropanol [1,2] producing acetone and propene. The selectivity for acetone relates to the catalyst basicity as it results from base-catalysed dehydrogenation, whereas propene is the product of acid-catalysed dehydration.

In the present contribution, the basicity of ETS-10 type materials is assessed by means of isopropanol conversion and compared with that of zeolite X. Further characterisation of the basic catalytic activity of these titanosilicates was carried out by a $^{13}$C solid-state NMR investigation of methanol decomposition over these inorganic solids.

## 2. Experimental

### 2.1. Materials

ETS-10 and ETAS-10 were prepared using the procedures described in the literature [3,4]. Zeolite Na-X was obtained from a commercially available source (13X, with Si/Al = 1.3). The ETS-10 and Na-X samples were partially exchanged to produce Cs-ETS-10 and Cs-X using 0.5 M aqueous solution of CsOH at 60 °C (30 ml sol. per 1 g solid). The Cs-exchanged samples were impregnated with cesium acetate using the procedure reported by Hathaway et al. [2] and then calcined at 450 °C to produce the $Cs_2O$/Cs-ETS-10 and $Cs_2O$/Cs-X catalysts. Zeolite K-X was prepared by ion exchange of Na-X with 0.5 M aqueous solution of KOH and the conditions described above. All these materials were characterised by powder X-ray diffraction, $^{29}$Si MAS NMR, $N_2$ adsorption experiments and chemical analysis.

### 2.2. Catalysis

The isopropanol conversion experiments were performed in a fixed-bed stainless-steel reactor at atmospheric pressure and 350 °C. The catalyst (50 mg) was activated at 400 °C in a flow of argon (10 ml/min) prior to reaction. The reactant was fed by a syringe pump and the Ar/reactant molar ratio was 16. The various conversion levels and weight hourly space velocities (WHSV) were controlled by keeping the catalyst mass constant and altering the mass flow rate of the reactant. A fresh catalyst was used for each run and products were analysed *in situ* using gas chromatography. The $^{13}$C MAS NMR experiments were carried out on sealed ampoules containing [16,18] the catalysts loaded with a controlled amount of methanol (10 moles per unit cell).

## 3. Results and discussion

### 3.1. Characterisation of the ETS-10 type catalysts

The X-ray diffraction patterns and the $^{29}$Si MAS NMR spectra of the as-synthesised ETS-10 materials match very closely with those published earlier [3–6]. A small loss of crystallinity was observed in both, the X-ray diffractograms and the $^{29}$Si MAS NMR spectra of the ion-exchanged and impregnated samples. $N_2$ adsorption experiments on these materials yield isotherms of type I, characteristic of microporosity with maximum uptakes of ca. 12–15% w/w. Finally, the catalysts cation compositions (mol%) were obtained by wet chemical analysis techniques and are illustrated in table 1.

### 3.2. The basicity of ETS-10

Table 2 illustrates the product distribution of isopropanol conversion over zeolite X materials and these results constitute the reference for the basicity comparisons. The basicity of these materials is monitored by assessing acetone selectivities at relatively low conversion levels (<30 wt%). The selectivity for acetone is less than 20% for as-prepared Na-X, whereas it increases considerably to ca. 62% for K-X and then drops to ca. 49% for Cs-X. The decreased basicity [2] of Cs-X compared to that of K-X is unexpected and relates to the degree of ion exchange of these solids. The large size of cesium cations limits the sodium exchange capacity compared to that for potassium and this is clearly manifested in the overall basicity of these microporous solids (see section 2 for chemical compositions). The impregnation of Cs-X with $Cs_2O$ leads to formation of additional extra-framework basic sites and thus to a considerable increase in the catalyst basicity.

Table 1
The catalysts chemical composition (unit cell mol%).

| | |
|---|---|
| ETS-10 | $[Si_{78}Ti_{16}O_{208}]Na_{23}K_9$ |
| ETAS-10 | $[Si_{73}Al_4Ti_{16}O_{208}]Na_{19}K_{13}$ |
| Cs-ETS-10 | $[Si_{78}Ti_{16}O_{208}]Na_{17}K_4Cs_{11}$ |
| $Cs_2O$/Cs-ETS-10 | $[Si_{78}Ti_{16}O_{208}]Na_{15}K_4Cs_{13}(Cs_2O)$ |
| Na-X | $[Al_{84}Si_{108}O_{384}]Na_{84}$ |
| K-X | $[Al_{84}Si_{108}O_{384}]Na_4K_{80}$ |
| Cs-X | $[Al_{84}Si_{108}O_{384}]Na_{40}Cs_{44}$ |
| $Cs_2O$/Cs-X | $[Al_{84}Si_{108}O_{384}]Na_{35}Cs_{49}(Cs_2O)$ |

Table 2
Isopropanol conversion over zeolite X.[a]

| | Na-X[b] | K-X[c] | Cs-X[c] | $Cs_2O$/Cs-X[c] |
|---|---|---|---|---|
| Conversion (wt%) | 23.6 | 18.5 | 24.9 | 17.0 |
| Propene (wt%) | 18.9 | 7.0 | 12.6 | 3.4 |
| Acetone (wt%) | 4.7 | 11.5 | 12.3 | 13.6 |
| Selectivity for acetone | 19.9 | 62.2 | 49.4 | 80.0 |

[a] $T = 350\,^\circ$C, TOS = 60 min.
[b] WHSV = 10 $h^{-1}$.
[c] WHSV = 2 $h^{-1}$.

Table 3 illustrates the product distribution of isopropanol conversion over ETS-10 type materials. These experimental findings were obtained at identical reaction conditions as those for zeolite X, so that a valid comparison may be gained. Of great interest is a comparison between the basicity of the as-synthesised ETS-10 with that of the as-synthesised Na-X. Based on acetone selectivities, ETS-10 is found to be approximately four times more basic than Na-X and, if one considers the ion-exchange capacity of ETS-10 which is approximately half that of Na-X, the basic strength of this as-prepared titanosilicate is remarkably high. A closer look to these results reveals that the basicity of the as-prepared ETS-10 is comparable to that of $Cs_2O$-impregnated Cs-X, a material which has undergone a number of chemical treatments in order to yield that level of basicity. Incorporation of aluminium [15] in the ETS-10 framework to form ETAS-10 has a very little effect on the basicity of this solid whereas ion exchange with cesium, followed by impregnation with $Cs_2O$ leads to a further increase in basicity.

Further evidence as to the strong basicity of ETS-10 type materials rests with the methanol decomposition over these solids. Methanol decomposition over zeolite X has been investigated by $^{13}$C MAS NMR [16] and several other spectroscopic techniques [17]. These results indicate that methanol mainly dehydrates to dimethyl ether over Na-X, whereas it dehydrogenates to formaldehyde which in turn decomposes to carbon monoxide and hydrogen only over the more basic K-X and Cs-X. Thus, the formation of carbon monoxide, as a result of basic dehydrogenation, is a manifestation of strong basic catalytic activity. In all three catalysts, several surface species and methane were also observed [16].

Figure 1 illustrates the $^{13}$C MAS NMR spectra of methanol decomposition over ETS-10 type materials. Evidently, the as-synthesised ETS-10 exhibits a very strong basicity as it does dehydrogenate methanol to carbon monoxide giving rise to a line at ca. 183 ppm (see figure 1(a))

Table 3
Isopropanol conversion over ETS-10 type materials.[a]

| | ETS-10 | ETAS-10 | Cs-ETS-10 | $Cs_2O$/Cs-ETS-10 |
|---|---|---|---|---|
| Conversion (wt%) | 28.5 | 25.8 | 24.8 | 28.5 |
| Propene (wt%) | 6.3 | 6.2 | 3.6 | 3.4 |
| Acetone (wt%) | 22.2 | 19.6 | 21.2 | 25.1 |
| Selectivity for acetone | 77.9 | 76.0 | 85.5 | 88.1 |

[a] $T = 350\,^\circ$C, TOS = 60 min, WHSV = 2 $h^{-1}$.

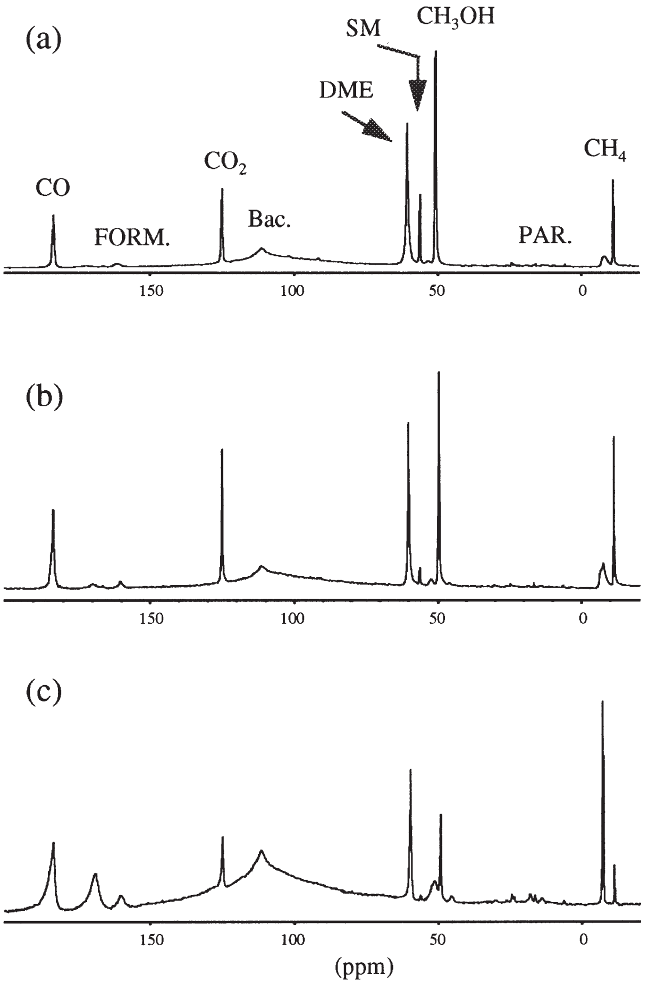

Figure 1. $^{13}C$ MAS NMR spectrum of methanol decomposition at 425 °C over (a) ETS-10, (b) Cs-ETS-10 and (c) $Cs_2O$/Cs-ETS-10; PAR. = paraffins, SM = surface methoxy, DME = dimethyl ether, Bac. = background, FORM. = formates.

while a number of other reactions also take place. Dehydration of methanol to dimethyl ether (60 ppm) and the formation of methane ($-8$ and $-11$ ppm), surface methoxy groups (53 and 56 ppm) and formates (162 ppm) also proceed over ETS-10, while the carbon dioxide peak at 125 ppm is an interesting feature in this spectrum. The formation of carbon dioxide is not yet fully understood, as it has not been previously observed in methanol decomposition over basic zeolite X catalysts and might relate to secondary oxidation reactions of carbon monoxide. Figure 1(b) illustrates the $^{13}C$ MAS NMR spectrum of methanol decomposition over Cs-ETS-10 and the spectrum shown is very similar to the one described above. The $^{13}C$ MAS NMR spectrum of methanol decomposition over $Cs_2O$-impregnated Cs-ETS-10 is shown in figure 1(c). This spectrum exhibits all the features described above and additionally a broad line at 169 ppm, which is assigned to formate species formed on extra-framework basic sites.

In conclusion, the basicity of the ETS-10 type materials is found to be considerably stronger than that of the zeolite X type catalyst, one of the most basic systems in the zeolite family. The basicity of ETS-10 may be further enhanced by ion exchange with Cs cations and impregnation with $Cs_2O$. The strong basicity of ETS-10 materials is also confirmed by a spectroscopic study of methanol decomposition over these inorganic solids. The implications of these experimental findings in the area of base catalysis are of great significance.

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