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Enantioselective dehydration of butan-2-ol using zeolite Y modified with dithiane oxides: comments on the nature of the active site *

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Modification of zeolite H-Y by dithiane oxides (2-R-1,3-dithiane 1-oxide, R = H, CH_3, C_6H_5) is shown to enhance significantly its activity for the acid-catalysed gas phase dehydration of butan-2-ol. The rate enhancement is observed for catalysts that are prepared using two commercial samples of zeolite H-Y. The origin of this effect is examined using in situ FTIR spectroscopy and ^{27}Al and ^{29}Si MAS NMR spectroscopy studies of the modified zeolite. The rate enhancement is considered to result from a specific interaction between the dithiane oxide modifier with both the extra-framework and framework aluminium in the zeolite.

Keywords: dehydration of butan-2-ol, modified zeolite Y, enantioselective dehydration

1. Introduction

The identification of effective asymmetric catalysts for the synthesis of pure enantiomers continues to be a topic of intense research interest. Most previous research involved homogeneous catalysts, leading to the design of chiral catalysts for such applications as the synthesis of L-Dopa [1] and epoxidation [2]. More recently, however, attention has focused on the design of heterogeneous asymmetric catalysts, since these may be more suitable for use in industrial applications.

To date, three experimental approaches have been used in the design of enantioselective heterogeneous catalysts: (i) the use of a chiral support for an achiral metal catalyst; (ii) the immobilization of an asymmetric homogeneous catalyst onto an achiral support; and (iii) modification of an achiral heterogeneous catalyst using a chiral cofactor. The first approach was pioneered by Schwab in 1932 [3,4]. Using Cu, Ni, Pd and Pt supported on enantiomers of quartz he demonstrated low enantioselection in the dehydration of butan-2-ol. A number of other chiral supports have been examined, e.g. natural fibres and chiral polymers, and this work led to the development of polypeptides as catalysts for the enantioselective epoxidation of chalcones [5]. Most recently, attention has focused on using zeolite β, since it is possible that a chiral form of this zeolite could be synthesised [6]. The second approach has been particularly effective for enantioselective hydrogenation reactions using zeolites as supports for asymmetric Ru and Rh catalysts [7]. In addition, Wan and Davis [8] have immobilized a homogeneous hydrogenation catalyst with retention of both the high activity and enantioselection of the non-immobilised catalyst. The third approach, involving the creation of a chiral catalyst surface by the adsorption of a chiral modifier onto an achiral catalyst, has been successful in a number of studies, again particularly for enantioselective hydrogenation. For example, the modification of platinum catalysts with cinchona alkaloids for the hydrogenation of prochiral α-ketoesters [9–11], and the modification of Raney nickel catalysts with diethyl tartrate, used for the hydrogenation of prochiral β-dicarbonyl compounds [12], have been extensively studied.

In our initial work, we have also used the third approach, but we consider that for the optimal catalyst design, the achiral catalyst should have a well defined structure, and for this reason we have selected zeolites. Modification of zeolite H-Y with chiral dithiane 1-oxides has been shown to give catalysts that are capable of enantioselection in the dehydration of butan-2-ol in the temperature range 110–150°C [13–15]. A feature of this catalytic system is the observation of a significant rate enhancement for the acid catalysed dehydration reaction, and we believe this to be of crucial importance with respect to the origin of the enantioselection. In this paper we describe infrared and NMR spectroscopic studies and comment on the possible structure of the active site.

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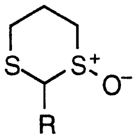
2. Experimental

2.1. Catalyst preparation

Enantiomerically pure or enriched (R)- or (S)-2-substituted-1,3-dithiane 1-oxides **I**, which are chiral at sulphur, were prepared according to standard procedures [16].



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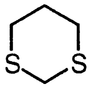

II

Samples where R = H, CH_3, Ph were prepared in both the racemic and enantiomerically enriched forms. When R = CH_3 or Ph a second chiral centre is present but the relative configuration was always controlled and in the materials used in this study only the trans configuration was utilised. The achiral 1,3-dithiane **II** was obtained commercially.

Two commercial samples of zeolite Y were used in this study: (a) H-Y (Union Carbide, LZY82) with a $SiO_2 : Al_2O_3$ ratio of 4.8, and (b) Na-Y (Crosfield) with a $SiO_2 : Al_2O_3$ ratio of 5.52. The latter sample was ion-exchanged three times with aqueous ammonium nitrate (0.1 mol/ℓ, 10 ml/g zeolite), recovered by filtration, and calcined (400°C, 8 h) to convert it into the H-Y form.

Zeolite Y (2.0 g) was treated with a solution of 1,3-dithiane 1-oxide (0.144 g) in deionised water (30 ml) at 50°C for 2 h. The modified zeolite was filtered, dried (100°C, 2 h), pelleted and sieved to give particles with diameter 0.6–1 mm. This procedure achieved an average loading of one modifier per zeolite supercage (determined by elemental analysis) and this loading was used throughout this study.

2.2. Catalyst characterisation

The catalysts were characterised using powder X-ray diffraction, NMR spectroscopy and in situ FTIR spectroscopy. MAS NMR spectroscopy studies were carried out using a ChemMagnetics 300 LITE spectrometer and all spectra were recorded at ambient temperature. Samples were spun in standard 7 mm zirconia rotors on a bearing of air. ^{27}Al MAS NMR spectra were obtained using a 1 s pulse delay and 1000 scans with samples spun at 7 kHz, and ^{29}Si MAS NMR spectra were obtained using a 5 s pulse delay and 5000 scans with samples spun at 5 kHz. Infrared spectroscopy studies were carried out as follows. Catalyst (ca. 100 mg) was compressed at 80 MN m^{-2} between two polished stainless-steel dies into self-supporting discs of diameter 25 mm. These were mounted in an infrared cell fitted with fluorite windows and glassblown to conventional glass vacuum apparatus fitted with grease-free taps. The infrared cell could be heated to a temperature of 400°C with the disc in the infrared beam, and contained a thermocouple used for temperature monitoring. Once mounted in the cell, the catalyst was evacuated at ambient temperature for 1 h before raising the temperature to 150°C until no further evidence of adsorbed water was observed (approximately 2 h). The sample was then allowed to cool to ambient temperature, before the disc was exposed to butan-2-ol vapour. Infrared spectra of the discs were recorded with a resolution of 4 cm^{-1} at varying temperatures using a Perkin-Elmer 1750 FTIR spectrometer.

2.3. Catalyst testing

Catalysts (0.3 g) were tested in a glass microreactor, and all reactant and product lines were heated. Butan-2-ol was introduced into the reactor using a calibrated syringe pump and prevaporized prior to dilution with a nitrogen carrier gas. The reactor exit gases were analysed with on-line gas chromatography using a flame ionization detector. A heated sixteen loop sample valve was used to store samples prior to analysis. The hydrocarbons, together with racemic butan-2-ol, were analysed using a GS-Q megabore column (30 m).

3. Results

3.1. Conversion of butan-2-ol over zeolite Y modified with dithiane oxide

A range of catalysts was prepared by the adsorption of 2-substituted 1,3-dithiane 1-oxides (substituent R = H, CH_3, C_6H_5) using the two zeolite samples, and these were used as catalysts for the dehydration of racemic butan-2-ol. The results for butan-2-ol conversion are shown in figure 1, together with those for the unmodified zeolites (in this case the modified zeolites were treated with water in an analogous procedure to the zeolites modified with dithiane 1-oxide) and for zeolite H-Y modified with 1,3-dithiane (1 molecule/supercage). It is apparent that modification of both zeolites with the dithiane 1-oxide leads to a significant enhancement in the butan-2-ol conversion and this is not observed when the zeolite is modified with 1,3-dithiane. For example, at 115°C both of the unmodified zeolites are inactive, whereas the modified zeolites demonstrate significant activity. In addition, the rate enhancement is more pronounced for the samples prepared with the ultra-stabilized zeolite (LZY 82, Union Carbide). Subsequent ^{27}Al MAS NMR confirmed that this zeolite sample contained markedly more extra-framework aluminium than the ion-exchanged sample (Crosfield). The enhanced activity was maintained for many hours and turnover numbers of > 1200 (based on the dithiane 1-oxide) were readily observed for the conversion of butan-2-ol over

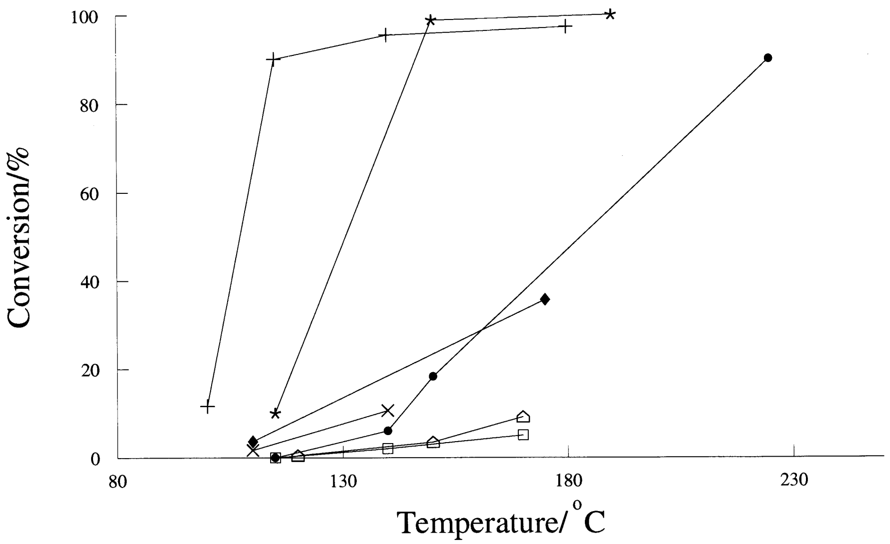

Figure 1. Effect of temperature on the conversion of butan-2-ol over zeolite, key: (●) Zeolite H-Y (LZY 82, Union Carbide), (+) Zeolite H-Y (LZY 82, Union Carbide) after modification with 1,3-dithiane 1-oxide, (∗) Zeolite H-Y (LZY 82, Union Carbide) after modification with 2-methyl-1,3-dithiane 1-oxide, (□) Zeolite H-Y (Crosfield), (×) Zeolite H-Y (Crosfield) after modification with 1,3-dithiane 1-oxide, (⌂) Zeolite H-Y (Crosfield) after modification with (S)-2-phenyl-1,3-dithiane 1-oxide, (◆) Zeolite H-Y (LZY 82, Union Carbide) after modification with 1,3-dithiane; reaction conditions: catalyst (0.3 g) reacted with butan-2-ol (3.2×10^{-3} mol h^{-1}) prevaporised in nitrogen (4.3×10^{-2} mol h^{-1}).

the modified zeolite, indicating that the enhanced activity is a sustained catalytic effect. Modifiers prepared by substitution of the dithiane 1-oxide in the 2-position did not lead to such a pronounced rate enhancement, although the modified catalyst still gave a higher activity than the unmodified zeolite. Following reaction, all the catalysts were analysed by powder X-ray diffraction, and some loss of crystallinity was apparent. The zeolites had coked during the reaction, but the dithiane oxide modifier could still be recovered by soxhlet extraction, and, if used in the enantiomerically pure form, no racemization was observed following use in the catalytic reaction.

3.2. In situ FTIR spectroscopic studies

To gain an improved understanding of the observed rate enhancement, in situ FTIR studies were carried out to probe the interaction of the butan-2-ol with the modified zeolite. The adsorption of racemic butan-2-ol unmodified zeolite H-Y (Crosfield) at 50°C leads to the formation of hydrogen bonded species. Figure 2 shows the IR spectra of zeolite H-Y at 50°C, before and after exposure to butan-2-ol vapour. In the hydroxyl region two stretching vibrations are observed at 3632 and 3543 cm^{-1}, and these are denoted high (HF) and low (LF) frequency bands respectively. Previous studies of zeolite Y by van Santen et al. have shown that the protons associated with the LF band are hydrogen bonded to other lattice oxygen atoms [17]. In our case, adsorption of butan-2-ol at 50°C leads to the HF zeolite hydroxyl band decreasing in integrated intensity with respect to the LF band, which we consider to be due to the formation of hydrogen bonds between the adsorbate and the Brønsted acidic zeolite hydroxyl group. Direct comparison of band intensity is not valid in this case as the extinction coefficients of bands originating

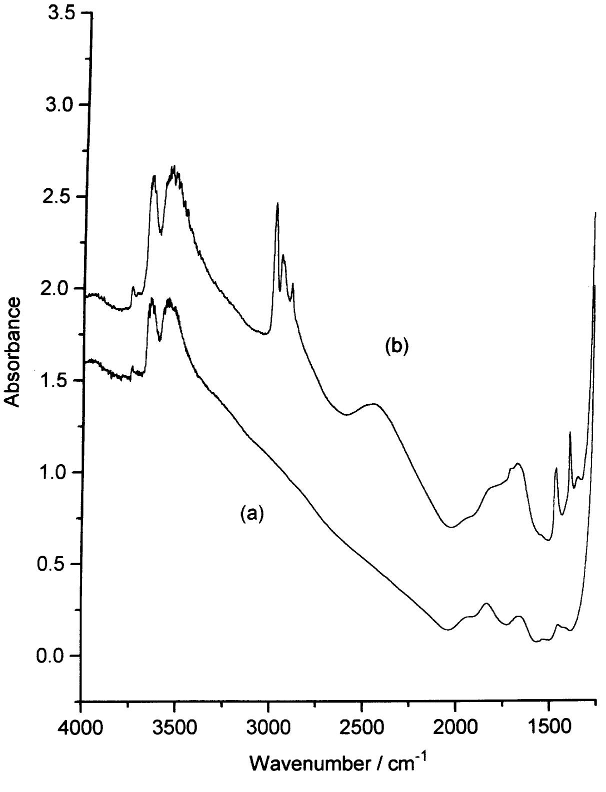

Figure 2. FTIR spectra of zeolite H-Y at 50°C (a) before and (b) after exposure to butan-2-ol (133 N m^{-2}).

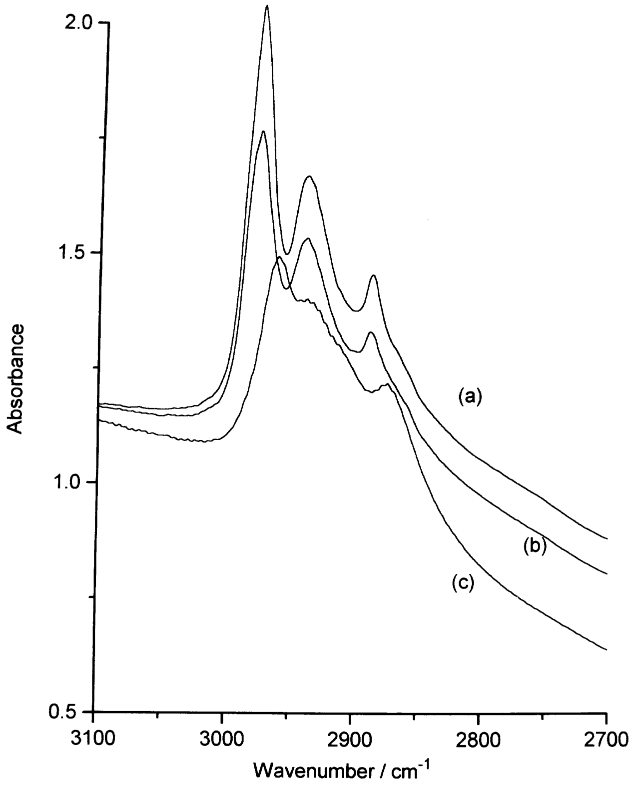

Figure 3. FTIR spectra of zeolite H-Y after exposure to butan-2-ol (133 N m^{-2}) at (a) 50°C and then subsequently heating to (b) 80°C, and (c) 90°C.

from hydrogen bonded species are significantly increased compared to those of the free molecular species [18]. The other spectral features, i.e. the broad bands centred around 2400 and 1700 cm^{-1}, are characteristic bands formed by species strongly hydrogen bonded to zeolites [19–21]. Heating this sample under a static vacuum leads to a decrease in the integrated intensities of all the absorption bands associated with butan-2-ol, indicating that some of the adsorbed butan-2-ol desorbs. In addition, a small amount of butanone is also formed, indicated by the presence of a new C=O stretch band centred at 1705 cm^{-1}. At 90°C, water is eliminated and a surface bound butoxide species is formed. The water loss is signified by the large increase in intensity of the water deformation band at 1645 cm^{-1}. At the same time, a shift occurs in the CH_3, and CH_2 band positions (figure 3). For hydrogen bonded molecules, the asymmetric and symmetric CH_3 stretch bands of adsorbed butanol appear at 2976 and 2888 cm^{-1}, and these bands are observed below 90°C. Above 90°C, these bands shift to 2960 and 2873 cm^{-1}, and this is indicative of the formation of butoxide species [22].

When butan-2-ol was adsorbed onto the zeolite modified with 1,3-dithiane 1-oxide at 50°C, the same initial hydrogen bonded species was formed, giving bands for CH_2 and CH_3 deformations in the same position as the unmodified zeolite. However, on heating, the elimination of water and the band shift characteristic of butoxide formation, described above, occurred at 70°C, rather than at 90°C (figure 4). A blank experiment in which the zeolite H-Y was treated with water at 50°C for 2 h in a procedure analogous to that used in the preparation of the dithiane oxide modified zeolite did not give this effect. Modification with higher loadings of dithiane-1-oxide did not lead to a further decrease in the temperature of butoxide formation. For the water-treated zeolite H-Y, the butoxide species was still formed at 90°C, indicating that the observed decrease in the temperature of formation of the butoxide species was due to the modification of zeolite Y by the 1,3-dithiane 1-oxide. This is clear evidence that the acid catalysed elimination of water from butan-2-ol is promoted by the presence of the dithiane 1-oxide, and this is consistent with the enhanced reaction rate observed for the modified zeolites.

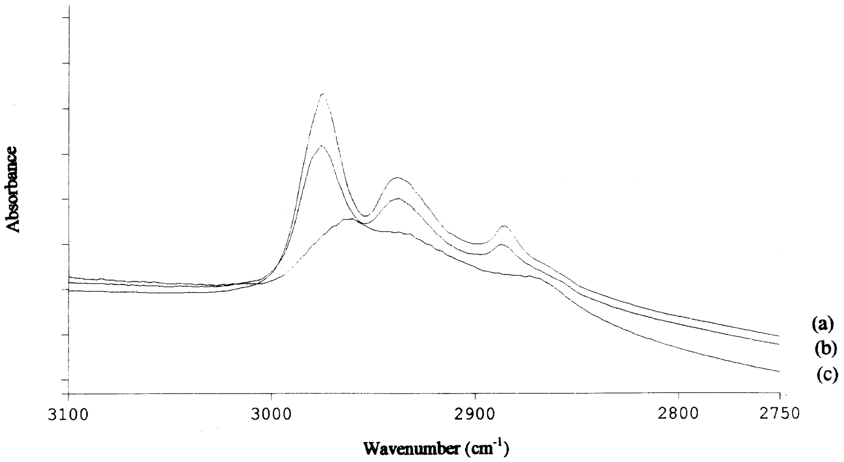

Figure 4. FTIR spectra of zeolite H-Y modified with 1,3-dithiane 1-oxide after exposure to butan-2-ol (133 N m^{-2}) at (a) 50°C, and then subsequently heating to (b) 80°C, and (c) 90°C.

3.3. MAS NMR studies

^{27}Al and ^{29}Si MAS NMR spectra were recorded for the unmodified zeolite H-Y (Crosfield), and for the zeolite modified with 1,3-dithiane 1-oxide and 1,3-dithiane (1 molecule/supercage), and these are shown in figures 5 and 6. From the ^{29}Si MAS NMR spectra it is apparent that no differences are induced when the zeolite is modified by the sulphur compound. In particular, no dealumination of the zeolite lattice is observed. The ^{27}Al spectra show that when the zeolite is modified with 1,3-dithiane 1-oxide, an increase is observed in intensity of the resonance at 0 ppm, which is associated with the octahedral (extra-framework) aluminium. This is not observed when the zeolite is modified with 1,3-dithiane. Since the ^{29}Si NMR spectra do not show evidence of dealumination of the zeolite, this increase in intensity is considered to result from a specific interaction between the extra-framework aluminium and the 1,3-dithiane 1-oxide.

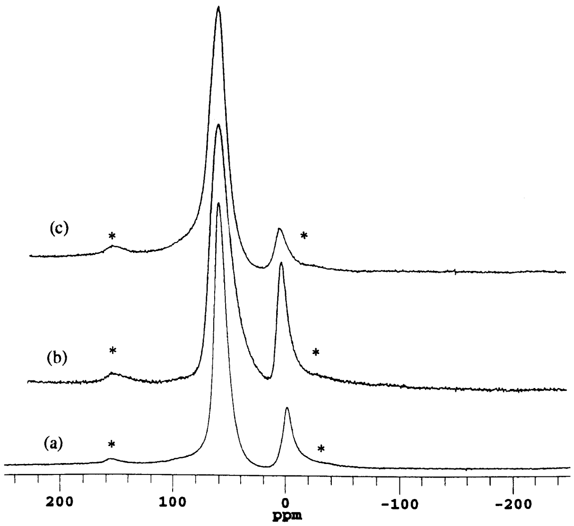

Figure 6. ^{27}Al MAS NMR spectra. (a) Zeolite H-Y (Crosfield), (b) after modification with 1,3-dithiane 1-oxide, (c) after modification with 1,3-dithiane.

4. Discussion

The experimental data show that the modification of zeolite H-Y with dithiane oxides leads to a significant rate enhancement for the acid catalysed dehydration of butan-2-ol. Our previous studies [13–15] have shown that the dithiane oxide is molecularly adsorbed within the zeolite, and that it is particularly stable in this environment, and that it is not decomposed thermally below 400°C. All these data indicate that when the dithiane oxide is added to the zeolite a new high activity site is formed, and this involves the molecularly adsorbed dithiane oxide. The model studies using in situ FTIR spectroscopy confirm this rate enhancement and indicate that the effect is correlated with the formation of the butoxide species at a lower temperature for the modified zeolite.

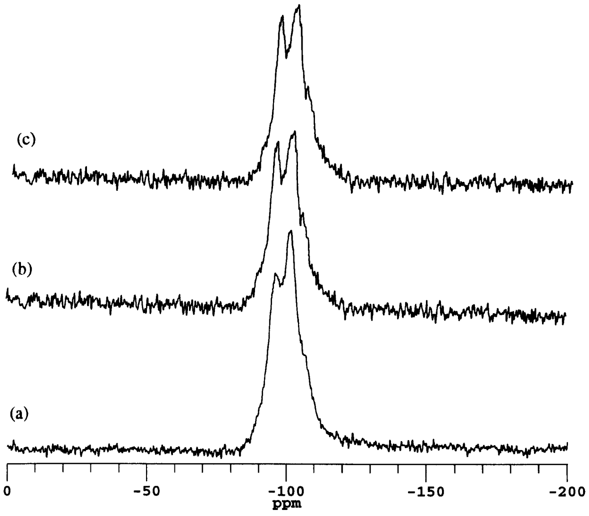

Figure 5. ^{29}Si MAS NMR spectra. (a) Zeolite H-Y (Crosfield), (b) after modification with 1,3-dithiane 1-oxide, (c) after modification with 1,3-dithiane (1 molecule/supercage).

The catalytic studies indicate that the observed rate enhancement is greatest for the zeolite Y (Union Carbide LZY 82). This is an ultrastabilized zeolite Y that has been formed by steaming, and consequently contains significant amounts of non-framework aluminium. The rate enhancement is less pronounced, but still significant, with the modification of the zeolite Y (Crosfield). The proton form of this zeolite was obtained by ion-exchange of the commercially supplied Na-Y sample. The original Na-Y sample contained no extra-framework aluminium but the ion-exchange procedure adopted in our studies led to dealumination of the framework but the extent was much less marked than for the steamed ultrastabilized zeolite. Hence, the degree of enhancement observed is considered to be related to the presence of extra-framework aluminium. This must, however, act in combination with the Brønsted acid site of the bridging hydroxyl group associated with the zeolite framework aluminium, since the dehydration reaction investigated is catalysed by Brønsted acidity. Previous work has indicated that a combination of extra-framework (Lewis acid sites) and framework (Brønsted acid sites) aluminium, formed by steaming a zeolite, can give enhanced acidity in zeolite catalysts. For example, Haag and Lago [23] showed that steaming zeolites at 500°C with low levels of water vapour can lead to an increase in the activity of the zeolite for acid catalysed reactions. This effect was subsequently explained by Fritz and Lunsford [24] in terms of the initial dealumination of the zeolite by water vapour to form non-framework aluminium that imparts, presumably through an

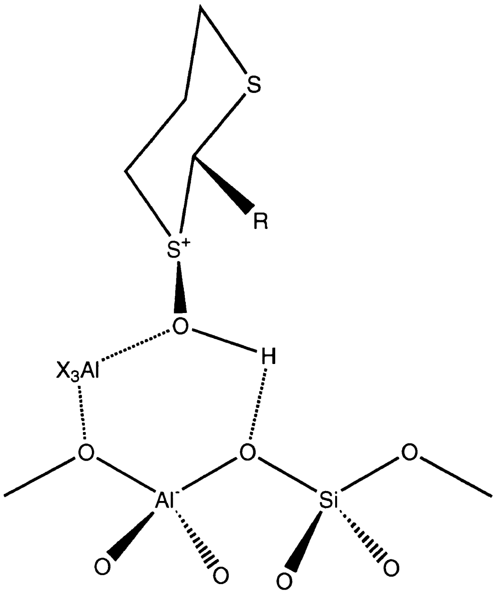

Figure 7. Schematic representation of the structure of the high activity site formed on addition of 1,3-dithiane 1-oxide to zeolite H-Y (Al^+X_3 denotes extra-framework aluminium species).

electrostatic effect, strong acidity to the remaining framework Brønsted acid sites. This leads to an increase in acidity of the zeolite, and, for simple acid catalysed reactions such as cracking, an enhanced activity is observed. This effect is observed in the current study for the unmodified zeolites (figure 1) since the zeolite Y (LZY 82), which has the highest concentration of extra-framework aluminium is three times more active than zeolite Y (Crosfield) at 140°C, although both zeolites are inactive at 115°C. When the dithiane oxide is added the rate enhancement is much more pronounced. This high activity site is considered to be formed by the specific interaction of the dithiane oxide with both the extra-framework aluminium and the Brønsted acid site associated with the framework aluminium. A schematic model for this high activity site is shown in figure 7. Supporting evidence for this proposed model comes from the ^{27}Al MAS NMR spectroscopy studies which show that the dithiane oxide interacts strongly with the extra-framework aluminium atoms (figure 6). The formation of the high activity acid sites enables these modified zeolites to be used as enantioselective catalysts, since, although only one active site per supercage is modified, it is many orders of magnitude more active than the remaining unmodified sites. The enantioselection arises from the chiral environment created by the dithiane oxide, and molecular simulation studies [14,25] indicate that preferential adsorption of one enantiomer of butan-2-ol also plays a role.

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