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Enantioselective Dehydration of Butan-2-ol Using Zeolite Y Modified with Dithiane Oxides

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Modification of zeolite H–Y by dithiane oxides (2-R-1,3-dithiane 1-oxide; $R = \mathrm{H}, \mathrm{CH_3}, \mathrm{C_6H_5}$) 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 by adding the dithiane oxide to the zeolite synthesis gel or by adsorption of the dithiane oxide onto commercial samples of zeolite H–Y. The origin of 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. Modification of zeolite H–Y with (*R*)-1,3-dithiane 1-oxide enhances the conversion of (*S*)-butan-2-ol compared to (*R*)-butan-2-ol in the temperature range 110–150°C when the two enantiomers are reacted separately. Modification with (*S*)-2-phenyl-1,3-dithiane 1-oxide gives a catalyst for which (*R*)-butan-2-ol is the most reactive of the two enantiomers. Reaction of racemic butan-2-ol over these chirally modified H–Y zeolites demonstrates that this modification procedure makes the zeolite enantiomerically discriminating and one enantiomer preferentially reacts, although both are present in the micropores under the reaction conditions. This effect is considered to be due to enantioselective rate enhancement, since, although the rate of dehydration of both enantiomers is enhanced in the chiral environment, the dehydration rate of one enantiomer is accelerated relative to the other. It is suggested that the effect is due to preferential adsorption at the chiral active site. © 1997 Academic Press

INTRODUCTION

Interest in asymmetric synthesis continues to increase, and this has highlighted the need for the design of highly selective asymmetric catalysts. Most of this research activity concerns homogeneous catalysts and has led, for example, to the design of catalysts for the synthesis of L-Dopa (1) and to the Sharpless epoxidation and dihydroxylation processes (2). More recently, increased attention has been given to the identification of suitable heterogeneous asymmetric catalysts (3–7), since such catalysts readily overcome the problems typically encountered with homogeneous systems, namely product recovery and catalyst separation. A heterogeneous asymmetric catalyst must not only activate the substrates but must exert stereochemical control, and this requires the preferential formation of a particular diastereoisomeric transition state. To date, three approaches have been taken in the design of heterogeneous enantioselective catalysts: (i) the use of a chiral support for an achiral metal catalyst, (ii) modification of an achiral heterogeneous catalyst using a chiral cofactor, and (iii) the immobilisation of a homogeneous catalyst. Early studies in this field adopted the first of these approaches. In 1932, Schwab *et al.* (8, 9) demonstrated that supporting Cu, Ni, Pd, and Pt on the enantiomers of quartz gave a catalyst capable of the enantioselective dehydration of butan-2-ol, and the best results were obtained from a catalyst with submonolayer coverage of the metal. Subsequently, natural fibres were used as catalyst supports including silk and cellulose. Synthetic chiral polymers were also evaluated as supports, but the early work experienced a range of problems including lack of reproducibility and low enantioselection. These studies have, however, recently led to the eventual development of polypeptides as catalysts, for example, in the epoxidation of chalcones with enantiomeric excesses of *ca.* 99% (10).

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, particularly for enantioselective hydrogenation. For example, the modification of platinum catalysts with cinchona alkaloids for the hydogenation of prochiral α-ketoesters (11–13), and the modification of Raney nickel catalysts with diethyl tartrate, used for the hydrogenation of prochiral β-dicarbonyl compounds (14), have been extensively studied. The immobilisation of an enantioselective homogeneous catalyst on to an achiral support, such as a zeolite, has also proved to be a viable approach. For example, Wan and Davis (15) have immobilised a homogeneous hydrogenation catalyst with retention of both the high activity and the enantioselection of the nonimmobilised catalyst. Very recently Bein and co-workers (16) have encapsulated

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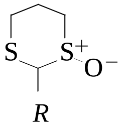
chiral Mn (III) salen complexes in zeolite Y and have reported high enantiomeric excesses for epoxidation of *cis*-β-methylstyrene with sodium hypochlorite.

These early studies demonstrate that very high levels of enantioselection can be achieved using heterogeneous asymmetric catalysts. Most of these catalysts tend to be very specific, however, and small changes to the nature of the catalyst, the modifier or the substrate can lead to a loss of enantioselectivity. We therefore consider that a generic approach to the design of heterogeneous asymmetric catalysts would have an immense benefit for this field. We believe that this can be provided by heterogeneous catalysts with well-defined structures. For this reason we have concentrated our initial research (17) on the chiral modification of zeolite catalysts since these microporous materials are well-defined crystalline solids and the nature of the modified surface can be probed with a range of spectroscopic techniques. In this paper we describe a method by which zeolite Y can be made enantiomerically discriminating for the dehydration of racemic butan-2-ol.

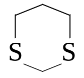
EXPERIMENTAL

Catalyst Preparation

Preparation of dithiane oxides. Enantiomerically pure or enriched (*R*)- or (*S*)-2-substituted-1,3-dithiane 1-oxides **I**, which are asymmetric at sulphur, were prepared according to standard procedures (18).



I



II

Samples where $R = \mathrm{H}$, $\mathrm{CH_3}$, or Ph were prepared in both the racemic and enantiomerically enriched forms (ee of enantiomerically enriched forms: $R = \mathrm{H}$, 83% (*R*)-enantiomer; $R = \mathrm{Ph}$, 99% (*S*)-enantiomer). When $R = \mathrm{CH_3}$ 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.

In situ incorporation of a chiral modifier during zeolite synthesis. Zeolite Y was synthesised from a gel formed by the addition of two solutions. Solution A was formed by mixing fumed silica (33.04 g) with distilled water (120 mL) with stirring to form an opaque gel. Solution B was formed by dissolving aluminium powder (1.45 g) in aqueous sodium hydroxide (19.80 g NaOH, 25.67 mL H_2O). Solutions A and B were mixed thoroughly with stirring to form a homogeneous gel with composition $11\mathrm{SiO_2} : \mathrm{Al_2O_3} : 10\mathrm{NaOH} : 162\mathrm{H_2O}$, and this was aged (25°C, 120 h). After ageing, the gel was heated in an autoclave (95°C, 48 h), cooled, and the product recovered by filtration, washed with distilled water and calcined (400°C, 12 h). Incorporation of a dithiane oxide modifier was achieved by dissolving 1,3-dithiane 1-oxide (0.153 g) in the minimum amount of water and adding this together with solutions A and B prior to the formation of the gel with composition $11\mathrm{SiO_2} : \mathrm{Al_2O_3} : 10\mathrm{NaOH} : 0.02\mathrm{C_4H_8S_2O} : 162\mathrm{H_2O}$.

Modification of zeolite Y by adsorption of dithiane oxides. Two commercial samples of zeolite Y were used in this study: (a) H–Y (Union Carbide, LZY82) with a $\mathrm{SiO_2} : \mathrm{Al_2O_3}$ ratio of 4.8, and (b) Na–Y (Crosfield) with a $\mathrm{SiO_2} : \mathrm{Al_2O_3}$ ratio of 5.52. The latter sample was ion-exchanged three times with aqueous ammonium nitrate (0.1 mol/liter, 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 dithiane molecule per zeolite supercage and appropriate modifications were used to obtain materials with a higher loading.

Catalyst characterisation. The catalysts were characterised using powder X-ray diffraction, ^{13}C, ^{27}Al, and ^{29}Si MAS NMR spectroscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy (XPS), and electron impact mass spectroscopy (EIMS).

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 prevaporised prior to dilution with a nitrogen carrier gas. The reactor exit gases were analysed with on-line gas chromatography using a flame ionisation detector. A heated 16-loop sample valve was used to store samples prior to analysis. Two analytical methods were adopted. First, for analysis of the hydrocarbons together with racemic butan-2-ol, a GS-Q megabore column (30 m) was employed. Second, for separation of the butan-2-ol enantiomers, a γ-cyclodextrin trifluoroacetyl capillary column (40 m) was employed with a column temperature of 25°C and split ratio of 120 : 1. These conditions reliably give baseline separation of the (*R*)- and (*S*)-butan-2-ol; for example, the separation of racemic butan-2-ol can be achieved with an accuracy for each enantiomer of ±0.05%.

Infrared Spectroscopy Studies

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 glass blown 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 control.

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, 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 with a Perkin–Elmer 1750 FTIR spectrometer.

RESULTS

Conversion of Butan-2-ol over Zeolite Y Modified with Dithiane Oxide during Synthesis

Samples of zeolite Y were prepared in the presence and absence of a racemic sample of 1,3-dithiane 1-oxide. The samples were characterised by powder X-ray diffraction and both were found to be crystalline; ^{27}Al MAS NMR spectroscopy confirmed that all aluminium atoms were tetrahedrally coordinated. ^{29}Si MAS NMR spectroscopy was used to determine the framework Si/Al ratio of the zeolite. For the zeolite Y made in the absence of the dithiane oxide the Si/Al ratio was 2.7, which is similar to commercial samples of zeolite Y. For the zeolite synthesised in the presence of dithiane oxide, the framework Si/Al ratio was significantly lower, at 2.0, indicating that the presence of the dithiane in the synthesis gel increases the incorporation of aluminium into the framework. ^{13}C MAS NMR spectroscopy of a sample prepared using 1,3-dithiane 1-oxide in the synthesis gel showed signals characteristic of the 1,3-dithiane 1-oxide, confirming that the modifier was incorporated in the zeolite. These materials were found to be inactive for the dehydration of racemic butan-2-ol, and conversions typically of $<8\%$ were observed even at temperatures as high as 200°C (Table 1). The presence of the dithiane oxide modifier leads to a decrease in activity, and no effect on the chemoselectivity was observed. In this case we consider that the zeolite is present in the sodium ion-exchanged form, and hence the concentration of Brønsted acid sites is very low. The materials were then ion-exchanged with ammonium nitrate and calcined for a short time at 400°C to give the proton exchanged forms. The dehydration of racemic butan-2-ol was then examined using the ion-exchanged materials (Table 1). The proton forms are much more active than the Na^+ forms, and the proton form of the dithiane oxide-modified zeolite is much more active than the unmodified zeolite, and also gives a somewhat higher selectivity for production of but-1-ene.

These results show that modified catalysts can be prepared by the incorporation of dithiane oxide modifiers in the synthesis gel of zeolites. However, only low levels of the modifier are incorporated by this method, as evidenced by the integrated intensities of the ^{13}C MAS NMR spectra. In addition, to prepare catalytically active materials it is necessary to carry out ion exchange of the Na^+ form of the zeolite with NH_4^+ cations and to form the active proton form by a calcination procedure. During this process, it can be expected that some of the protonated dithiane oxide will also be exchanged as the cation and an equilibrium will be established between the concentrations of Na^+, NH_4^+, and $C_4H_9S_2O^+$ as counter-cations in the zeolite. In addition, the calcination procedure required for the conversion of the NH_4^+ form to the H^+ form could lead to thermal decomposition of the dithiane oxide. For these reasons, we decided not to pursue this method of catalyst synthesis, and instead a postsynthesis modification procedure was investigated.

TABLE 1

Catalytic Performance of Zeolite Y Modified by the Addition of 1,3-Dithiane 1-Oxide to the Synthesis Gel for the Dehydration of Butan-2-ol[a]

Catalyst[b]	Temperature (°C)	Conversion (%)	Product composition (%)		
			But-1-ene	*c*-But-2-ene	*t*-But-2-ene
Na–Y	190	7.1	16.1	36.4	47.5
H–Y	140	1.0	15.7	28.7	55.6
	160	4.0	17.0	36.0	47.0
	180	16.0	17.4	37.4	45.2
Na–SO–Y	190	3.7	17.4	36.3	46.3
H–SO–Y	140	1.8	25.9	27.7	46.4
	160	16.4	22.6	29.8	47.6
	200	42.4	22.0	33.2	44.8

[a] Catalyst (0.3 g) reacted with butan-2-ol (3.2×10^{-3} mol h^{-1}) prevaporised in diluent nitrogen (4.3×10^{-2} mol h^{-1}).

[b] Zeolites synthesised as described under Experimental. Na– denotes that the zeolite is in the sodium-exchanged form, H– denotes that the zeolite is in the proton-exchanged form, and SO– denotes that 1,3-dithiane 1-oxide has been added to the synthesis gel.

Conversion of Butan-2-ol over Zeolite Y Modified with Dithiane Oxide Postsynthesis

Catalyst stability. Samples of zeolite H–Y modified by adsorption of 1,3-dithiane 1-oxides at one molecule per supercage were prepared and characterised by powder X-ray diffraction and ^{13}C MAS NMR spectroscopy. Powder X-ray diffraction showed that the modification process had not caused any significant loss of crystallinity. The ^{27}Al MAS NMR spectra of both the unmodified zeolites indicated the presence of nonframework aluminium, but this was not significantly increased by the adsorption of the dithiane oxide. ^{13}C MAS NMR spectroscopy of the modified zeolite, when compared with the solution NMR spectra of the equivalent dithiane oxide (Fig. 1), indicated that the dithiane oxide was molecularly adsorbed within the zeolite. The stability

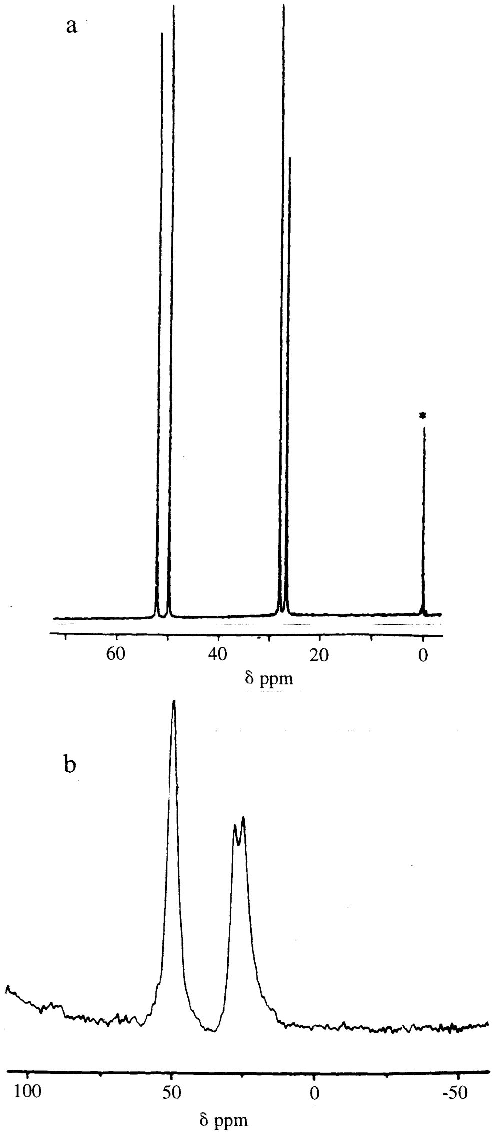


FIG. 1. ^{13}C NMR spectra (a) 1,3-dithiane 1-oxide dissolved in $CDC1_3$; *TMS; (b) 1,3-dithiane 1-oxide adsorbed in zeolite Y (LZY 82, Union Carbide; one molecule/supercage).

TABLE 2

EIMS Analysis for 2-Phenyl-1,3-dithiane 1-oxide-Modified Zeolite Y

	m/z			
Temperature (°C):	40–100	200–300	300–400	400–500
Zeolite−HY	46, 44	—	ND	—
2-Phenyl-1,3-dithiane 1-oxide	46, 44	212, 121, 90, 45	ND	—
Zeolite HY 2-Phenyl-1,3-dithiane 1-oxide	46, 45, 44	—	ND	106, 91, 78, 64, 45

Note. ND, not detected.

of the modified zeolites was then investigated with a range of techniques. First, the modified zeolites were examined with EIMS. The samples were gradually heated at a constant rate (2°C/min), and the evolved gases were analysed. The results for 2-phenyl-1,3-dithiane 1-oxide as modifier are shown in Table 2, and the results are compared with the pure modifier and the unmodified zeolite. The pure dithiane oxide decomposed in the region 200–300°C, whereas the zeolite-modified sample did not show any decomposition products below 400°C; at this temperature there was no evidence for the molecular ion (*m/e* 212), which indicates that the dithiane oxide decomposes at this temperature rather than simply desorbing. The unmodified zeolite, as expected, did not show any desorption or decomposition products in this temperature region. Secondly, the modified samples were heated (180°C, 2 h) in a fixed-bed microreactor under flowing nitrogen. The samples were cooled and then extracted with deuteriated chloroform using a soxhlet procedure. Analysis of the extract by ^1H NMR spectroscopy confirmed that the dithiane modifier could be recovered unchanged by this procedure. Thirdly, thermogravometric analysis (heating rate 10°C/min) was employed to assess further the stability of the modifier in the zeolite. A comparative analysis of the unmodified zeolite H−Y and zeolite H−Y modified with 1,3-dithiane 1-oxide is shown in Fig. 2. Both samples show similar weight loss below ca. 250°C due to water loss. The modified zeolite does show an additional weight loss at ca. 450°C. This behaviour is consistent with the results of the EIMS study.

To assess whether the modifier was evenly distributed throughout the microporous structure of the zeolite, an XPS study was conducted for zeolite H−Y modified with 1,3-dithiane 1-oxide at one molecule per supercage. Analysis of the peak areas of the S_{2p} and the Si_{2p} peaks were used to determine the S/Si ratio (19), which was found to be 0.07. The calculated value of the ratio expected for the bulk of the

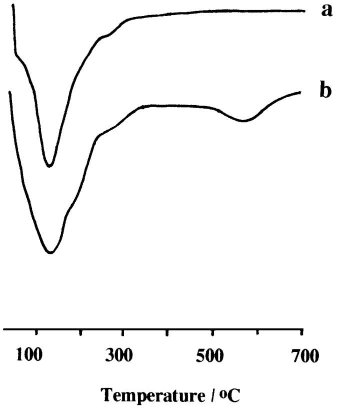


FIG. 2. TGA of (a) zeolite Y and (b) 1,3-dithiane 1-oxide adsorbed in zeolite Y (LZY 82, Union Carbide; one molecule/supercage).

TABLE 3

Catalytic Performance of Dithiane Oxide-Modified Zeolite Y[a]

Catalyst[b]	Temperature (°C)	Conversion (%)	Product composition (%)		
			But-1-ene	*c*-But-2-ene	*t*-But-2-ene
US–Y	115	0	—	—	—
	140	6.0	16.0	47.4	36.6
	150	18.2	15.6	51.2	33.2
SOUS–Y	100	11.6	24.4	51.3	24.3
($R = \mathrm{H}$)	140	95.4	15.0	46.0	39.0
	180	97.3	13.3	44.2	42.5
SOUS–Y	115	10.0	15.9	33.6	50.5
($R = \mathrm{CH_3}$)	150	98.8	13.7	38.5	47.8
	190	100	12.4	35.3	52.3
H–Y	115	0	—	—	—
	140	2.0	17.0	36.0	47.0
	170	5.0	17.0	37.0	46.0
SOH–Y	110	1.7	14.6	28.3	57.0
($R = \mathrm{H}$)	140	10.6	12.5	29.2	58.3
SOUS–Y	120	0.5	17.2	31.0	51.7
($R = \mathrm{C_6H_5}$)	153	3.5	15.9	34.5	49.6
	170	9.1	16.5	36.5	47.0

[a] Catalyst (0.3 g) reacted with butan-2-ol (3.2×10^{-3} mol h^{-1}) prevaporised in diluent nitrogen (4.3×10^{-2} mol h^{-1}).

[b] Key to catalysts: US–Y, LZY 82, Union Carbide; H–Y, ion-exchanged NaY, Crosfield; SO denotes the zeolite has been modified by addition of 2-*R*-1,3-dithiane 1-oxide (one molecule per supercage, $R = \mathrm{H}, \mathrm{CH_3}, \mathrm{C_6H_5}$).

sample for uniform distribution is 0.07, and the agreement between these values indicates that the modifier is indeed uniformly distributed.

Catalytic performance of dithiane oxide-modified zeolites for the dehydration of butan-2-ol. A range of catalysts was prepared by the adsorption of racemic 2-substituted-1,3-dithiane 1-oxides (substituent $R = \mathrm{H}, \mathrm{CH_3}, \mathrm{C_6H_5}$; one molecule/supercage), and these were used as catalysts for the dehydration of racemic butan-2-ol. The results are shown in Table 3 together with those for the unmodified zeolites. It is apparent that modification of zeolite H–Y (LZY 82, Union Carbide) with 1,3-dithiane 1-oxide gives considerably higher catalytic activity than zeolite H–Y (Crosfield) modified in the same way. However, both modified samples displayed an enhanced catalytic activity when compared with their respective unmodified zeolite. This enhanced activity was maintained for many hours, whereas the unmodified zeolites were rapidly deactivated under the reaction conditions. Turnover numbers of >1200 based on the dithiane 1-oxide were observed for the conversion of butan-2-ol over the modified zeolite, indicating that the enhanced activity is a sustained catalytic effect. Modification with 2-methyl-1,3-dithiane 1-oxide gave similar results, but 2-phenyl-1,3-dithiane 1-oxide did not lead to such a pronounced rate enhancement, although it 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 were found to have coked during the reaction, but the dithiane oxide modifier could still be recovered by soxhlet extraction using deuteriated chloroform.

A range of control experiments was carried out to probe the origin of this rate enhancement (Table 4). Modification of zeolite Y with 1,3-dithiane (compound **II**) using an analogous procedure led to a small rate enhancement, significantly lower than that observed for modification by the equivalent dithiane oxide, indicating the importance of the sulphoxide oxygen atom as a vital component of the catalytically active site. Investigation of a nonmicroporous $\mathrm{SiO_2/Al_2O_3}$ catalyst indicated that in this case the dithiane oxide modifier acted as a poison. In addition, the same reaction carried out over dithiane oxide supported on an inactive support, BN, indicated that the dithiane oxide by

TABLE 4

Reaction of Racemic Butan-2-ol over Modified Catalysts[a]

Catalyst:	Y[b]		Y–SO[c]	Y–S[d]		$\mathrm{SiO_2/Al_2O_3}$[e]	$\mathrm{SiO_2/Al_2O_3}$[f]	BN–SO[g]	
Temperature (°C)	115	225	115	110	175	200	200	115	225
Conversion (%)	0	90	90	3.6	35.6	31.5	24.5	0	0
Selectivity (%)									
But-1-ene	—	17.7	8.3	15.4	14.7	16.5	21.6	—	—
trans-But-2-ene	—	40.6	53.8	53.8	46.5	31.7	33.9	—	—
cis-But-2-ene	—	41.6	37.8	30.7	38.8	51.8	46.5	—	—

[a] Catalysts (0.3 g) tested in a conventional glass microreactor using on-line GC analysis with butan-2-ol (3.3×10^{-3} mol h^{-1}) prevaporized in a nitrogen diluent (3.7×10^{-2} mol h^{-1}).

[b] Zeolite Y (ultrastabilized LZY 82, Union Carbide).

[c] Zeolite Y modified with (±)-1,3-dithiane 1-oxide, one molecule per supercage (7.6 wt%).

[d] Zeolite Y modified with 1,3-dithiane, one molecule per supercage (7.2 wt%).

[e] Nonmicroporous silica alumina, $\mathrm{SiO_2/Al_2O_3} = 5.7$.

[f] Nonmicroporous silica alumina, $\mathrm{SiO_2/Al_2O_3} = 5.7$, modified with 1,3-dithiane 1-oxide (6.9 wt%).

[g] Boron nitride modified with 1,3-dithiane 1-oxide (7.4 wt%) under these conditions unmodified BN was also inactive.

itself does not exhibit any catalytic activity for this reaction. These control experiments demonstrate that it is the combination of the microporous zeolite together with the dithiane oxide that is important for the creation of the enhanced activity catalytic site observed with the modified zeolites.

In situ FTIR spectroscopic investigation of butan-2-ol dehydration over dithiane oxide-modified zeolite H–Y. The adsorption of racemic butan-2-ol on unmodified zeolite H–Y (Crosfield) at 50°C leads to the formation of hydrogen-bonded species. Figure 3 shows the IR spectra of H–Y at 50°C, before and after exposure to butan-2-ol vapour. Two hydroxyl stretching vibrations are observed, at 3632 and 3543 cm^{-1}, denoted high (HF) and low (LF) frequency bands, respectively. van Santen *et al.* have shown that the protons of the LF band are hydrogen bonded to other lattice oxygen atoms (20). Adsorption of butan-2-ol leads to the formation of hydrogen bonds between the adsorbate and the Brønsted acidic zeolite hydroxyl groups as evidenced by the HF zeolite hydroxyl band decreasing in integrated intensity with respect to the LF band. Direct comparison of band intensity is not valid in this case as the extinction coefficients of bands originating from hydrogen-bonded species are significantly increased compared to those of the free molecular species (21). The broad bands centred around 2400 and 1700 cm^{-1} are two of the three characteristic bands formed by species strongly hydrogen bonded to zeolites (22–24).

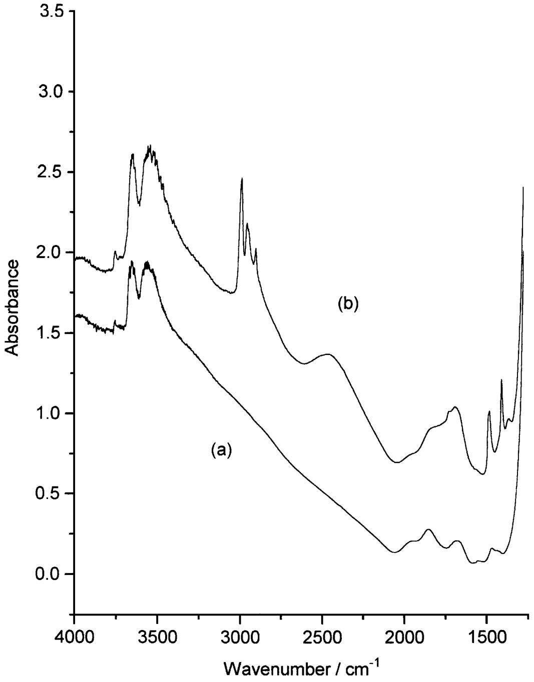


FIG. 3. FTIR spectra of zeolite H–Y at 50°C (a) before and (b) after exposure to butan-2-ol (133 N m^{-2}).

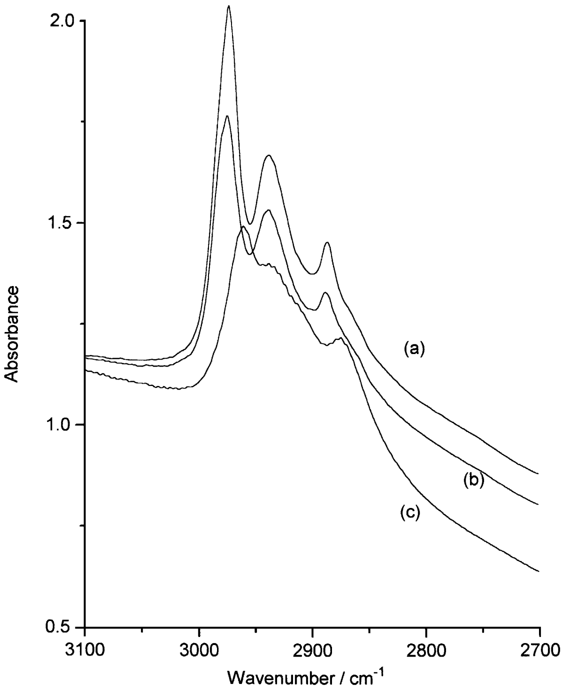


FIG. 4. FTIR spectra of zeolite H–Y after exposure to butan-2-ol (133 N m^{-2}) at (a) 50°C, (b) 80°C, and (c) 90°C.

On heating under a static vacuum, some of the adsorbed butan-2-ol desorbs. A small amount of butanone is also formed, indicated by the presence of a C=O stretch band centred at 1705 cm^{-1}. However, at 90°C water is eliminated, 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 (Fig. 4). For hydrogen-bonded molecules, the asymmetric and symmetric CH_3 stretch bands of adsorbed butanol appear at 2976 and 2888 cm^{-1}; above 90°C, these bands shift to 2960 and 2873 cm^{-1}. This is indicative of the formation of butoxide species (25).

When butan-2-ol was adsorbed on to the zeolite modified with 1,3-dithiane 1-oxide (one molecule/supercage), the same initial hydrogen-bonded species was formed. However, on heating, the elimination of water and the band shift characteristic of butoxide formation, described above, occurred at 70°C, rather than 90°C. Modification with higher loadings of dithiane-1-oxide did not lead to a further decrease in the temperature of butoxide formation. 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. 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.

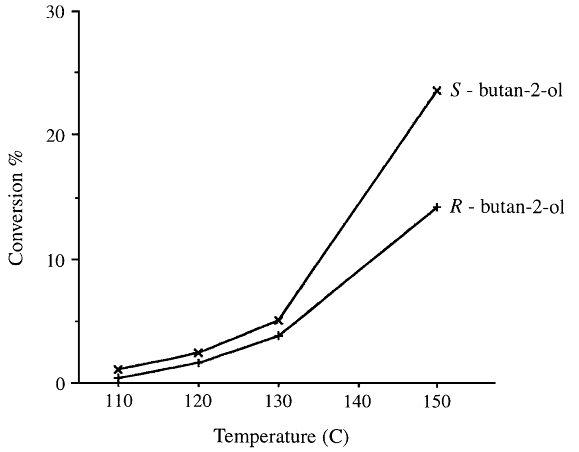


FIG. 5. Effect of temperature on the conversion of (*R*)-butan-2-ol and (*S*)-butan-2-ol over zeolite H−Y (Crosfield) modified with (*R*)-1,3-dithiane 1-oxide (one molecule/supercage); reaction conditions as in Table 6.

TABLE 5

Effect of Reactant Feed Rate on the Conversion of (*R*)- and (*S*)-Butan-2-ol to Alkenes over Zeolite Y Modified with (*R*)-1,3-Dithiane 1-oxide[a]

Reactant flow rate (10^{-2} mol h^{-1})	Conversion (%)	
	(*R*)-Butan-2-ol	(*S*)-Butan-2-ol
2.1	5.7	12.2
6.6	4.5	8.0
13.0	1.48	4.75
18.0	0.01	1.05

[a] Zeolite Y (ion-exchanged Na−Y ex Crosfield modified with one molecule per supercage of (*R*)-1,3-dithiane-1-oxide, 0.3 g) reacted separately with (*R*)- and (*S*)-butan-2-ol prevaporised in diluent nitrogen (5.6 × 10^{-2} mol h^{-1}) at 110°C.

Reaction of R-butan-2-ol and S-butan-2ol over zeolite Y modified with enantiomerically enriched dithiane oxides. A catalyst was prepared by adsorbing enantiomerically enriched (*R*)-1,3-dithiane 1-oxide (enantiomeric excess 83%) in zeolite H−Y (Crosfield, one molecule/supercage). A series of control experiments were carried out in which enantiomerically pure (*R*)- and (*S*)-butan-2-ol were reacted over the modified zeolite, and it was determined that, in the temperature range investigated (110–150°C), no racemisation of the butan-2-ol occurred. In addition, following reaction with either enantiomerically pure (*R*)- or (*S*)-butan-2-ol, or racemic butan-2-ol, the chiral modifier was extracted with deuteriated chloroform, as described above, and was investigated by ^{1}H NMR spectroscopy in the presence of a chiral shift reagent. In this way it was determined that these treatments had not induced racemisation of the chiral modifier.

A series of experiments were then carried at increasing temperatures for the separate reactions of (*R*)- and (*S*)-butan-2-ol over the chirally modified zeolite; the results for conversion and selectivity are shown in Figs. 5 and 6. It is clear that when the zeolite is modified with (*R*)-1,3-dithiane 1-oxide, (*S*)-butan-2-ol is more reactive over the entire temperature range compared with (*R*)-butan-2-ol. In a further set of experiments, the temperature was maintained at 110°C, and the flow rates of the (*R*)- and (*S*)-butan-2-ols were separately varied (Table 5). Enhanced reactivity of (*S*)-butan-2-ol was again observed.

A similar set of experiments was conducted with zeolite Y (LZY, 82, Union Carbide) modified with enantiomerically enriched (*S*)-2-phenyl-1,3-dithiane 1-oxide (enantiomeric excess 99%) at a loading of one molecule/supercage; the results for the separate reactions of (*R*)- and (*S*)-butan-2-ols with increasing temperatures are shown in Fig. 7. In this case it is apparent that (*R*)-butan-2-ol is more reactive than (*S*)-butan-2-ol over the temperature range. Over both modified zeolites, the activation energies for the separate conversions of (*R*)- and (*S*)-butan-2-ols are very similar (105 ± 5 kJ mol^{-1}).

Reaction of racemic butan-2-ol over zeolite Y modified with enantiomerically enriched dithiane oxides. The difference in reaction rate observed for the reaction of the

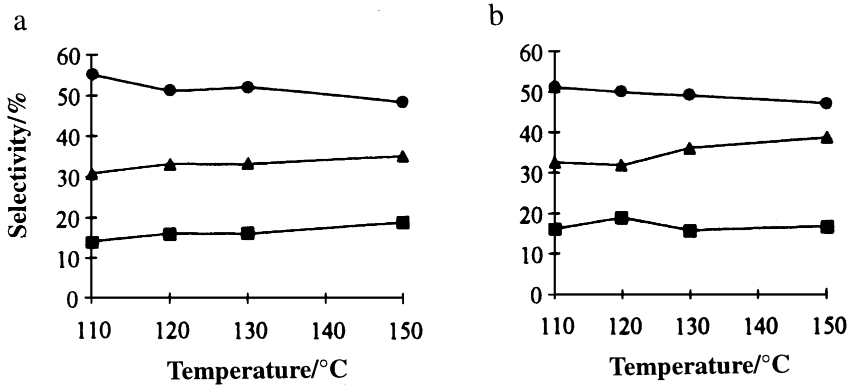


FIG. 6. Effect of temperature on selectivity (a) (*R*)-butan-2-ol and (b) (*S*)-butan-2-ol over zeolite H−Y (Crosfield) modified with (*R*)-1,3-dithiane 1-oxide (one molecule/supercage); reaction conditions as in Table 6; product selectivity: ●, but-1-ene; ▲, *cis*-but-2-ene; ■, *trans*-but-2-ene.

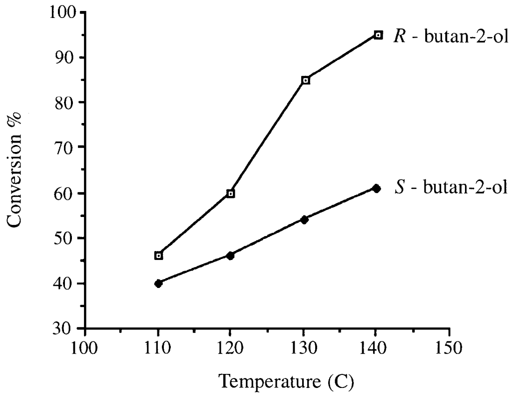


FIG. 7. Effect of temperature on the conversion of (*R*)-butan-2-ol and (*S*)-butan-2-ol over zeolite H–Y (LZY 82, Union Carbide) modified with (*S*)-2 phenyl-1, 3-dithiane 1-oxide (one molecule/supercage); reaction conditions as in Table 6.

enantiomerically pure (*R*)- and (*S*)-butan-2-ol suggests that this catalyst system should be able to discriminate between the two enantiomers of racemic butan-2-ol. Hence, a series of experiments were carried out for the reaction of racemic butan-2-ol over zeolite H–Y modified with enantiomerically enriched dithiane oxides; the results are given in Table 6. As observed previously with the enantiomerically pure (*R*)- and (*S*)-butan-2-ols, when the zeolite is modified with (*R*)-1,3-dithiane 1-oxide, it is apparent that (*S*)-butan-2-ol reacts in preference to (*R*)-butan-2-ol. In addition, when the zeolite is modified with (*S*)-2-phenyl-1,3-dithiane 1-oxide, (*R*)-butan-2-ol reacts in preference to (*S*)-butan-2-ol. In both these sets of experiments, enantioselection was observed for a number of turnovers, although the effect was short-lived at the higher temperatures (turnover numbers, 17 and 2, respectively (based on dithiane 1-oxide) at 110 and 150°C, respectively).

DISCUSSION

Modification of zeolite H–Y with dithiane oxides leads to the creation of a catalyst that has enhanced activity for the acid-catalysed dehydration of butan-2-ol when compared with the unmodified zeolite. This effect is observed both for samples prepared by addition of the modifier to the synthesis gel and for the postsynthesis modification of two different commercial samples of zeolite Y (Crosfield and Union Carbide). When the modifier is added to the synthesis gel, the resulting zeolite contains only a small quantity of the modifier, but the effect is still apparent.

The interaction of alcohols with the acid forms of zeolites has been particularly well studied in recent years (26, 27), and it is generally considered that the adsorbed species that is formed initially is an alkoxide. *In situ* FTIR spectroscopy confirmed that, in the present study, an alkoxide species is formed on reaction of the butan-2-ol with both the unmodified zeolite and the dithiane oxide-modified zeolite. Consistent with the enhanced reactivity observed with the flow reactor studies, the *in situ* FTIR spectroscopy experiments reveal that the alkoxide species is formed at a significantly lower temperature for the dithiane oxide modified zeolite than for the unmodified zeolite.

Dehydration of butan-2-ol leads to the formation of but-1-ene, *cis*-but-2-ene and *trans*-but-2-ene. At equilibrium, but-1-ene becomes the major product at temperatures >950°C, and, for the conditions used in this study, the equilibrium compositions are 47.5 : 35 : 17.5, for *trans*-but-2-ene, *cis*-but-2-ene, and but-1-ene, respectively. When the modified zeolites are used as catalysts, product compositions that are very close to the equilibrium values are observed, and consequently it is not possible to draw any mechanistic information from the observed chemoselectivity. However, it is interesting to note that for the sulphoxide-modified catalyst as the temperature increases the yield of but-1-ene

TABLE 6

Reaction of Racemic Butan-2-ol over Zeolite Y Modified by Enantiomerically Enriched Dithiane Oxides

Catalyst		Temp. (°C)	Conversion (%)[a]	Product composition[b] ($\times 10^{-3}$ mol h^{-1})				Butan-2-ol conversion (%)		
zeolite	modifier			But-1-ene	But-2-ene	*R*-Butan-2-ol	*S*-Butan-2-ol	*R*	*S*	Relative rate
Y[c]	(*R*-)-**I**, *R* = H	110	0.5	—	0.037	3.673	3.640	0.002	0.035	1 : 17.5
Y[c]	(*R*-)-**I**, *R* = H	120	1.3	0.015	0.085	3.669	3.581	0.006	0.094	1 : 15.7
Y[c]	(*R*-)-**I**, *R* = H	150	9.9	0.105	0.620	3.657	2.968	0.018	0.707	1 : 39.3
Y[d]	(*S*-)-**I**, *R* = Ph	110	4.2	0.020	0.271	3.399	3.660	0.276	0.015	18.4 : 1
Y[d]	(*S*-)-**I**, *R* = Ph	120	7.5	0.044	0.507	3.260	3.594	0.415	0.081	5.1 : 1

[a] Total conversion of *R*- and *S*-butan-2-ol.

[b] Flow rate, 10^{-3} mol h^{-1}.

[c] Zeolite Y (Crosfield NaY, ion exchanged with NH_4NO_3 and calcined at 550°C), modified with *R*-1,3-dithiane 1-oxide, one molecule per supercage (0.1 g), tested in a convential glass microreactor with racemic butan-2-ol (7.35×10^{-3} mol h^{-1}), prevaporized in a nitrogen diluent (6.7×10^{-3} mol h^{-1}).

[d] Zeolite Y (ultrastabilized LZY 82, Union Carbide) modified with *S*-2-phenyl-1,3-dithiane 1-oxide, one molecule per supercage (0.1 g), tested in a convential glass microreactor with racemic butan-2-ol (7.35×10^{-3} mol h^{-1}), prevaporized in a nitrogen diluent (6.2×10^{-3} mol h^{-1}).

increases slightly whereas the yield of *trans*-but-2-ene decreases (Fig. 6). This is the reverse of the expected trend based on equilibrium data (28, 29) and indicates that the modified catalysts are exerting some slight kinetic control.

All these data indicate that when the dithiane oxide is added to the zeolite, a new high activity site is formed. It is apparent that the enhancement in activity is greatest for the sample of zeolite Y supplied by Union Carbide (LZY 82). This is an ultrastabilised zeolite Y that has been steamed and consequently contains significant amounts of nonframework aluminium. The rate enhancement is less pronounced, but still significant, with the modification of the zeolite Y supplied by Crosfield. The proton form of this zeolite was obtained by ion exchange of the commercially supplied Na–Y sample which originally contained no extraframework aluminium. The ion-exchange procedure adopted led to dealumination of the framework, but the extent was much less marked than with zeolite H–Y (LZY-82). Hence, the degree of enhancement observed may be related to the presence of extraframework 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. A number of studies have indicated that a combination of extraframework (Lewis acid sites) and framework (Brønsted acid sites) aluminium can give enhanced acidity in zeolite catalysts. Haag and Lago (30) 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. Mirodatos and Bartemeuf (31) showed that superacid sites could be created in mordenite by a steaming procedure. These effects were subsequently explained by Fritz and Lunsford (32) in terms of the initial dealumination of the zeolite to form nonframework aluminium that imparts, presumably through an electrostatic effect, strong acidity of 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. In the present work, the high activity site is considered to be formed by the specific interaction of the dithiane oxide with both the extraframework aluminium and the Brønsted acid site associated with the framework aluminium. Supporting evidence for this proposed model comes from detailed ^{27}Al MAS NMR spectroscopy studies (33) and molecular simulations (34) that have shown that the dithiane oxide interacts strongly with the extraframework aluminium atoms.

The formation of 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. When the dithiane oxide is used in the enantiomerically enriched form, the active sites are able to discriminate between the enantiomers of butan-2-ol. This important effect is achieved by enantioselective rate enhancement, i.e., both enantiomers react faster in the chiral environment than in the absence of the chiral modifier, but one reacts faster than the other. The observation that modification leads to the formation of a high activity site has also been observed for the cinchona alkaloid modification of platinum for the enantioselective hydrogenation of prochiral α,β-ketoesters. In the case of cinchona modification, rate enhancements of three orders of magnitude are observed (11), and hence the observation of a rate enhancement effect may be a prerequisite for the design of effective enantioselective catalysts.

It is observed that the activation energies for the dehydration of the separate enantiomers over the zeolites doped with the enantiomerically enriched dithiane oxides are identical within experimental error (105 ± 5 kJ mol^{-1}). In addition, it should be noted that the enantiomeric discrimination obtained from the reaction of racemic butan-2-ol is higher than that based on the conversions of the separate enantiomers. The apparent inconsistency can be resolved by regarding the modified zeolite as if it were an enzyme (a zeozyme?) operating with its active sites saturated with substrate. The conversions of the separate enantiomers then yield the relative reactivities in the catalytic step, whereas the results using the racemate reflect the enantioselection not only of the catalytic step but also of the competitive binding of the substrates. Present indications, supported by molecular modelling studies, are that the latter effect is the larger.

It is important to note that the reactants and products in this reaction are gas phase. However, the reactant butan-2-ol is present at high partial pressures, and, at the lower temperature used in this study, which is only 12°C above the boiling point of butan-2-ol, it is possible that condensation may occur in the micropores of the zeolite. This effect would not, however, be expected to contribute significantly to the results obtained at the higher temperatures, where enantioselection is still observed. We consider that these results provide the first example of a gas-phase enantioselective reaction heterogeneously catalysed by a zeolite. Although the initial approach has been to design a catalyst that consumes chiral molecules, the study is, in effect, a proof of the concept that a zeolite can be modified so that it preferentially catalyses reaction of one enantiomer of a chiral substrate in the presence of both. In view of the immense range of microporous zeolites available together with the large number of enantiomerically pure modifiers, we consider that this approach will provide the basis for the generic design of a new type of enantioselective catalysts.

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