

Stereoselective Meerwein–Ponndorf–Verley and Oppenauer reactions catalysed by zeolite BEA¹

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Abstract

Zeolite BEA has been studied as catalyst in the Meerwein–Ponndorf–Verley and Oppenauer (MPVO) reactions of substituted cyclohexanones and cyclohexanols. In the MPV reduction of 4-*tert*-butylcyclohexanone to 4-*tert*-butylcyclohexanol a high stereoselectivity (> 95%) to the thermodynamically less stable *cis*-isomer was obtained while in the complementary Oppenauer oxidation the *cis*-alcohol was preferentially converted. This stereoselectivity is explained by transition-state selectivity imposed by the zeolite structure. The catalytic activity is related to Lewis-acid aluminium sites which are located in the micropores. FT-IR results indicate that these sites are related to aluminium atoms which are only partially bonded to the framework. The mechanism is proposed to involve a six-membered transition state in which both the alcohol and the carbonyl are coordinated to the same aluminium.

Keywords: Meerwein–Ponndorf–Verley reduction; Oppenauer oxidation; Zeolite BEA; Stereoselectivity; Transition-state selectivity; 4-*tert*-butylcyclohexanone; *cis*-4-*tert*-butylcyclohexanol; Lewis acidity

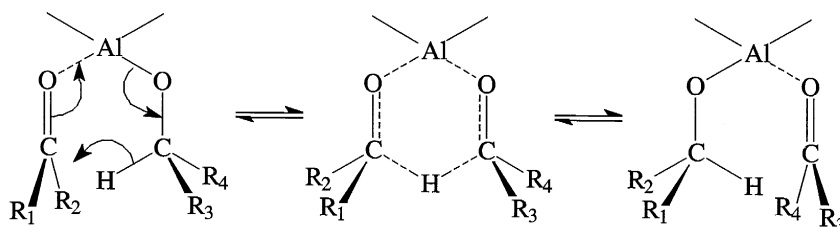
1. Introduction

The Meerwein–Ponndorf–Verley reduction of aldehydes and ketones and the Oppenauer oxidation of alcohols are reactions that can be performed under mild conditions. Furthermore, the MPVO reactions can be applied without the risk of reducing or oxidising other functional groups. The hydrogen donors are easily oxidisable secondary alcohols (e.g. isopropanol) while the oxidants are simple ketones (e.g. acetone). The MPVO reactions are usually catalysed by metal alkoxides such as Al(OPr^{*i*})₃. The activity of these catalysts is related to their Lewis acidic

character in combination with ligand exchangeability. The reaction mechanism of the homogeneous MPVO reactions proceeds via a cyclic six-membered transition state in which both the reductant and the oxidant are coordinated to the metal centre of a metal alkoxide catalyst (Scheme 1). The alcohol reactant is coordinated as alkoxide. Activation of the carbonyl by coordination to Al(III) initiates the hydride transfer reaction from the alcoholate to the carbonyl. The formed alkoxide may leave the catalyst via an alcoholysis reaction with the bulk alcohol (see Ref. [1] for a review).

A major advantage of heterogeneous over homogeneous catalysed MPVO reactions is that the catalysts can easily be separated from the liquid reaction mixture. However, only a few

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Scheme 1. Reaction mechanism for the MPVO reaction.

examples of heterogeneously catalysed MPVO reactions have been reported [1]. Recently, Ivanov et al. reported on the use of various metal oxides in the MPV reduction [2]. Two different reaction schemes were proposed for the catalysts, which exhibited either Lewis acid or basic properties. The proposed mechanisms had in common that the first step consisted of the formation of an alkoxide-like species, while the reactions proceeded via cyclic six-membered transition states, comparable to those in homogeneous systems. The coordination of the carbonyl, however, was assumed to occur by hydrogen bonding to an acidic hydroxy group instead of to the metal.

Zeolites are crystalline metal oxides which have potential as recyclable heterogeneous catalysts in various organic reactions [3]. Furthermore, because of their unique microporous structure, zeolites are expected to show various types of shape-selectivity. As far as we know, however, only a very few examples on the use of zeolites in the MPVO reaction have been reported [4–6]. These reactions were carried out in the gas-phase over zeolites A, X and Y exchanged or impregnated with alkali and alkaline-earth cations. Furthermore, only one example of shape-selectivity appears to exist. Shabtai et al. showed that the conversion of citronellal under MPV conditions could be tuned by the size of the metal ion [4]. In NaX there was enough space for the substrate to perform an intramolecular ring closure to isopulegol whereas over CsX, reduction to the linear citronellol was observed. Similar steric effects were found for various other substrates.

Recently, we have reported on the first stereoselective MPV reduction of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol catalysed by zeolite BEA [7]. This reaction is of commercial interest because the *cis*-isomer is in use on a substantial scale as an intermediate in the fragrance industry. Here we present full details on the catalytic properties of the zeolite-based catalyst, followed by an investigation into the origin of the catalytic activity. Furthermore, the observed high selectivity to the thermodynamically less stable *cis*-alcohol will be explained and a reaction mechanism proposed.

2. Experimental

2.1. Synthesis of the BEA catalysts

Zeolite BEA (Si/Al = 12) was synthesised according to Wadlinger and Kerr [8].

Calcination of the parent material to remove the organic template was performed following three different procedures. Heating rates were 1°C/min in all cases.

Zeolite BEA(1) was obtained by calcination of 10 g of parent material, spread out in a thin layer, in a horizontal tubular reactor under a constant flow of dry air at 525°C for 12 h (shallow-bed conditions).

Zeolite BEA(2) was made by calcination of 20 g of parent material, put into a crucible with a diameter of 12 cm, in a stationary oven using ambient air at 550°C for 12 h (deep-bed conditions).

Zeolite BEA(3) was obtained by a method which largely prevents the extraction of framework aluminium, first applied for the calcination of boron-containing MFI and BEA [9,10]. The parent material (2 g) was first calcined in a flow of ammonia (15 ml/min) at 450°C for 2 h. The brownish sample was then ion-exchanged with 2 M aqueous sodium chloride at reflux temperature for 4 h (1 g/100 ml), according to Bourgeat-Lami et al. [11]. After washing and drying the sample was calcined in a flow of about 1 vol% ozone in dry oxygen (200 ml/min) at 120°C for 1 h, followed by calcination in a flow of dry oxygen (200 ml/min) at 400°C for 2 h. The Na/Al ratio was 0.8. In order to study the hydroxy groups of this material by FT-IR, the zeolite was ion exchanged with 2 M aqueous ammonium nitrate (200 mg/25 ml) at room temperature. After washing and drying the catalyst was activated in situ to 450°C in vacuo (Section 2.3).

The ammonium forms of BEA(1) and BEA(2) were obtained by ion exchange with 1 M aqueous ammonium nitrate at 80°C for 24 h; the Na/Al ratios were below 0.01. The acid forms were made by calcination of NH_4 -BEA at 500°C for 6 h. The sodium forms of both zeolites were made according to Bourgeat-Lami et al. [11], as described above. The Na/Al ratios were 0.9 and 0.7 for Na-BEA(1) and Na-BEA(2), respectively.

The series Li-, Na-, K-, Rb- and Cs-BEA(2) was made by two subsequent ion exchanges of the calcined zeolite with 0.1 M aqueous alkali metal chloride (50 ml/g) for 12 h at reflux temperature. The M/Al ratios (M = alkali metal) were 0.4 for Li, 0.5 for Na and 0.6 for K, Rb and Cs.

2.2. Other catalysts

Zeolite Na-Y and USY (both Si/Al = 2.5) and a silica-alumina catalyst (HA-HPV, Si/Al = 2) were kindly donated by AKZO-Nobel Chemicals, Amsterdam. The ammonium form

of zeolite Y was obtained by three subsequent ion-exchanges of Na-Y with 1 M ammonium nitrate (1 g/50 ml) at 80°C. The Na/Al ratio was 0.3.

Mordenite (CBV-10A, Si/Al = 6.5, Na-form) was obtained from PQ zeolites. The ammonium form was obtained as described in Section 2.1 for zeolite BEA. Dealuminated mordenite (Si/Al = 33.3) was prepared by refluxing the mordenite in 6 M aqueous nitric acid according to a patent of Dow Chemical [12].

Mesoporous MCM-41 (Si/Al = 15) was synthesised according to Janicke et al. [13]. The sodium form was made as described elsewhere [14].

Zeolite H-MCM-22 (Si/Al = 15) was synthesised as described by Unverricht et al. [15].

The synthesis of the all-silica form of zeolite BEA (Si/Al > 5000) was reported by van der Waal et al. [16].

2.3. Characterisation of the catalysts

The metal contents and exchange stoichiometries of the zeolite-based catalysts were determined, before and after reaction, by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS).

X-ray powder diffraction analysis (XRD) was performed on all zeolite-based catalysts in order to check their crystallinity after all preparation and activation procedures. The powder patterns were recorded on a Philips PW 1877 diffractometer using monochromatic $\text{Cu K}\alpha$ radiation. Patterns were recorded from 5° to 50° (2θ) with a resolution of 0.02° and a count time of 2 s at each point.

High resolution scanning electron microscopy (HRSEM) analysis of the as-synthesised zeolite was carried out at the Shell Research and Technology Centre, Amsterdam. A JEOL JSM-840A scanning electron microscope was used.

Multipoint BET surface areas and pore volumes were calculated from nitrogen adsorp-

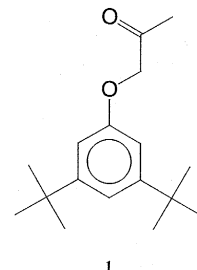
tion/desorption isotherms, measured at -196°C using a Quantachrome Autosorb-6B instrument. The samples were outgassed for 16 h in vacuum at 350°C prior to use.

Solid-state ^{27}Al MAS-NMR spectra were recorded at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe. A resonance frequency of 104.21 MHz, a recycle delay of 0.1 s, and short $3\ \mu\text{s}$ pulses (45° pulses of $3\ \mu\text{s}$), a spectral width of 50 kHz and a spin rate of 6.2 kHz were applied. The lines were referenced to $\text{Al}(\text{NO}_3)_3$ (0 ppm). All samples were fully hydrated in a desiccator over aqueous saturated ammonium nitrate (80% relative humidity).

Infrared spectra were recorded on a BioRad FTS 175 FT-IR spectrometer with a resolution of $2\ \text{cm}^{-1}$. The zeolite samples were pressed into disks with a diameter of 18 mm and a weight of 25 mg. The samples were heated in a quartz IR cell to 450°C (heating rate $10^{\circ}\text{C}/\text{min}$) in vacuo. After cooling to 150°C a reference spectrum was recorded. The wafers were treated with about 15 Torr (1 Torr is 1.333×10^2 Pa) pyridine at 150°C for 15 min after which the pyridine was pumped off (better than 10^{-5} Torr) for 15 min and a spectrum was recorded. Spectra were also recorded at 150°C after 15 min desorption at 300 and 450°C , respectively. Difference spectra were obtained by subtracting the reference spectrum from the spectra obtained after pyridine adsorption. The concentrations of acid sites were calculated from the integral absorbances using the integrated molar extinction coefficients of Emeis [17] for Brønsted acid and Lewis acid bonded pyridine (1.67 and $2.22\ \text{cm}/\mu\text{mol}$, respectively).

The spectra of adsorbed ethanol were measured in a comparable way, however, all spectra were recorded at 25°C . About 45 Torr ethanol was admitted to the sample at 25°C for 15 min after which the excess was pumped off. The infrared measurements were performed at the Shell Research and Technology Centre, Amsterdam.

2.4. Synthesis of 1-(3,5-di-*tert*-butylphenoxy)propan-2-one (**1**)



The synthesis of this probe molecule was based on a general method of McKillop et al. [18] for the preparation of phenol ethers using phase-transfer catalysis, followed by the rearrangement of the intermediate epoxide to the ketone catalysed by lithium iodide, as described by An et al. [19].

To a solution of 18.0 g (0.45 mol) NaOH in 150 ml of water were successively added 5.0 g (40% solution in water, 7.7 mmol) of tetrabutylammonium hydroxide, 30.9 g (0.15 mol) of 3,5-di-*tert*-butylphenol, 150 ml of dichloromethane and 27.8 g (0.3 mol) of epichlorohydrin. The mixture was vigorously stirred at 40°C for 48 h; after 24 h another 14 g (0.15 mol) of epichlorohydrin was added to the reaction mixture. The organic layer was then separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water and saturated sodium chloride solution and dried with sodium sulphate. After removal of the solvent under reduced pressure, the desired epoxide (2-(3,5-di-*tert*-butylphenoxy)methyl)oxirane) was obtained as a yellow oil in a nearly quantitative yield and a purity of about 84%. The other products were mainly dimers and chlorine-containing isomers of the epoxide.

To 10 g of the yellow oil were added 20 g of dry (sodium sulphate) diglyme and 100 mg lithium iodide. The reaction mixture was vigorously stirred under nitrogen and heated to 130°C

for 16 h; during reaction the colour changed from brown to orange. After removal of the solvent an oil was obtained which was purified by silica gel column chromatography with hexane/ethyl acetate (10/1) as the eluent. After removal of the solvent under reduced pressure an oil (6.6 g) was obtained which contained the desired ketone (1-(3,5-di-*tert*-butylphenoxy)propan-2-one (1)) with a purity of about 85%. Distillation under reduced pressure (100°C/0.15 mm Hg) gave 4.2 g of (1) with a purity of about 95%, which crystallised at room temperature.

2.5. Catalytic reactions; general procedure

The MPV reductions were carried out in a 100 ml three-necked, round-bottomed flask equipped with a magnetic stirrer and a condenser with a calcium chloride guard tube. To 25 ml of secondary alcohol, dried on molecular sieve KA, were added 2.5 mmol ketone and about 1 mmol 1,3,5-tri-*tert*-butylbenzene (bulky internal standard). The reaction mixture was heated to reflux temperature (2-propanol) or to 80°C (higher boiling secondary alcohols) and stirred (1000 rpm). The reaction was started by the introduction of the activated catalysts (50–500 mg, dependent on the activity). Aliquots were taken during the reaction and analysed by gas chromatography (GC) using a Chromopack CP WAX 52 CB column (50 m × 0.53 mm i.d.). Products were identified by gas chromatography–mass spectrometry (GC-MS) and by comparison with authentic reference compounds.

The Oppenauer oxidation was performed in the same apparatus. To 25 ml acetone, dried over molecular sieve KA, were added 5 mmol 4-*tert*-butylcyclohexanol (*cis/trans* = 52.7/47.3) and about 1 mmol 1,3,5-tri-*tert*-butylbenzene. The mixture was heated to reflux temperature and stirred. The reaction was started by the introduction of 500 mg activated (500°C) Na–BEA(2). The progress of the reaction was monitored as described above.

Activation of the catalysts was performed in

a stationary oven. The catalyst was heated from room temperature to the final activation temperature (500°C, unless otherwise mentioned) at 1°C/min and held at this temperature for 6 h. Then, the catalyst was cooled down to 200°C and transferred to a vacuum desiccator where it was allowed to cool to room temperature.

2.6. Origin of the chemicals

All chemicals used were purchased from Aldrich, Acros or Baker and used without further purification. Ludox LS-30 was kindly donated by Du Pont. Sodium aluminate was obtained from Riedel de Haen.

3. Results and discussion

3.1. Catalytic results

3.1.1. Comparison of various heterogeneous catalysts

For the MPV reduction of 4-*tert*-butylcyclohexanone, results obtained with various heterogeneous catalysts are presented in Table 1. It is seen that neither mordenite (NH₄- or dealumi-

Table 1
MPV reduction of 4-*tert*-butylcyclohexanone with isopropanol to 4-*tert*-butylcyclohexanol over various heterogeneous catalysts^a

Catalyst ^b	Si/Al	Conv. (%)	Sel. (%)	<i>Cis:trans</i>
Na–BEA(1)	12.5	32	> 95	96:4
NH ₄ –BEA(1)	12.5	30	> 95	95:5
Al–Si BEA	> 5000	0	—	—
Na–Y	2.5	0	—	—
NH ₄ –Y	2.5	0	—	—
USY	2.5 (bulk)	24.4	ca. 85	9:91
NH ₄ –MOR ^c	6.5	0	—	—
Deal–MOR ^c	6.5	0	—	—
H–MCM-41 ^c	15	10	ca. 80	10:90
Na–MCM-41 ^c	15	10	> 95	10:90
H–MCM-22	15	33	ca. 25	24:76
HA–HPV	2	19	> 95	9:91
γ-Al ₂ O ₃	—	45	> 95	9:91

^a Formulation see experimental part; reaction time 6 h.

^b Activation temperature 500°C.

^c Activation temperature 430°C.

nated forms) or Y (NH₄- or Na-forms) are active for this reaction. For mordenite, this might be explained by the limited pore size of this type of zeolite (7.0 × 6.5 Å), in combination with its uni-dimensionality. Adsorption experiments indeed indicated that 4-*tert*-butylcyclohexanone (6.4 × 5.8 × 9.6 Å, Corey–Pauling–Koltun model [20]) is not able to reach a detectable concentration in the micropores of the zeolite at the temperatures applied. However, the fact that 2-butanone, which can enter the pores of mordenite unhindered, could also not be reduced by isopropanol over either of the mordenites, suggests that mordenite may not have catalytic sites capable of catalysing the MPV reduction. The same argument might be valid for Na- and NH₄-Y, for which the pore entrances are large enough (7.4 Å) for both 4-*tert*-butylcyclohexanone to enter, and 4-*tert*-butylcyclohexanol to leave, the three dimensionally interconnected supercages. The observation that Y zeolite is not active towards MPV reaction is in agreement with the results obtained by Ivanov et al. [2] and can be attributed to the absence of Lewis acid aluminium sites. For activity in the MPV reaction, coordinatively unsaturated (Lewis acid) aluminium sites are required, which can react with an alcohol to form an activated alkoxide species. Such aluminium might consist of extra-framework aluminium species, or ‘satellite’ aluminium which is partially hydrolysed from the framework resulting in framework defects (see below). This explains why zeolite USY, which is made by a steaming procedure, is an active catalyst. Its bulk composition shows it to contain extra-framework alumina. Similar arguments hold for less crystalline materials like MCM-41.

Selectivities to the corresponding alcohol are generally high (> 95%). However, for the Brønsted acid catalysts (H-form) some 4-*tert*-butylcyclohexenyl isopropyl ether and traces of 4-*tert*-butylcyclohexene were also observed, resulting in lower selectivities. This is explained by the acid catalysed acetalisation of 4-*tert*-butylcyclohexanone with isopropanol, followed

by dehydration, and by the acid-catalysed dehydration of 4-*tert*-butylcyclohexanol. These side reactions did not occur on a significant scale when NH₄-BEA was applied as the catalyst; presumably the transition state required for acetalisation cannot be accommodated in the straight channels of this zeolite (7.6 × 6.4 Å). For H-MCM-22 the main product formed was 4-*tert*-butylcyclohexyl isopropyl ether (*cis:trans* = 40:60). This compound might be formed by a hydride transfer to the cation resulting from the acid catalysed dehydration of the hemi-acetal of 4-*tert*-butylcyclohexanone and isopropanol.

In contrast to the other catalysts investigated, zeolite BEA was found to be highly selective towards the thermodynamically less stable *cis*-alcohol. However, all-silica BEA proved to be inactive, indicating the necessity of aluminium sites. The present industrial process involves the hydrogenation of 4-*tert*-butylphenol with low selectivity (70%) to the desired *cis*-isomer.

Scanning electron microscopy measurements on BEA, presented in Fig. 1, show that the catalyst consists of aggregates of primary crystallites with a diameter of about 1.5 μm. Most of these primary crystallites are smaller than 50 nm, indicating a large external surface area, which is in agreement with recent literature data [21]. As it is known that the external surface activity of zeolites can have a major impact on the overall selectivity of catalytic reactions [21,22], a catalytic test reaction for external surface activity was carried out. A probe molecule, 1-(3,5-di-*tert*-butylphenoxy)propan-2-one (**1**), which is too bulky to enter the micropores of zeolite BEA (cf. the isomorphous probe molecule in Ref. [22]), did not undergo reduction over zeolite BEA, though it was converted to the corresponding alcohol over HA-HPV, mesoporous MCM-41 and homogeneous Al(OPr^{*i*})₃. This demonstrates that the MPV reduction, catalysed by zeolite BEA, proceeds in the micropores only. It is therefore proposed that steric constraints imposed by the zeolite structure play a role in the observed stereoselectivity. Furthermore, the absence of outer surface

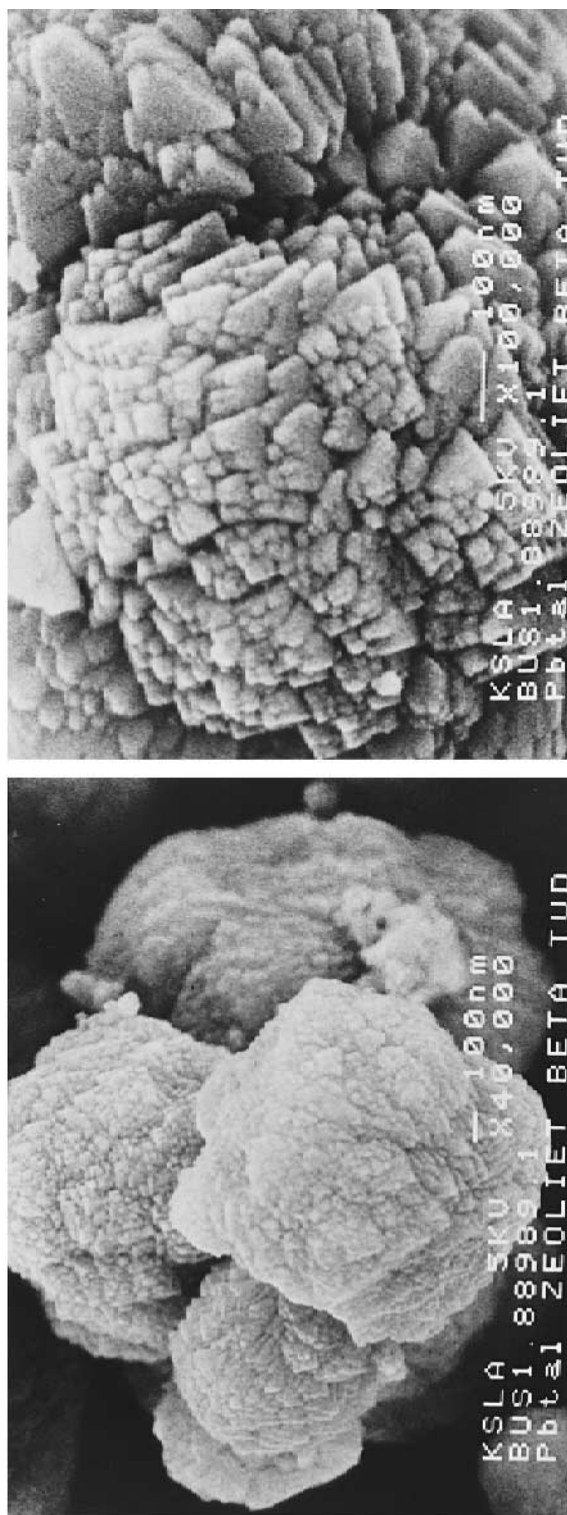


Fig. 1. HRSEM picture, two enlargements, of the parent zeolite BEA sample.

activity indicates that the active site might consist of aluminium which is still bound to the zeolite lattice and not of extra-framework aluminium, which is expected to be present on the external surface also [23].

3.1.2. Catalytic properties of zeolite BEA

The activity of zeolite BEA was found to increase with the activation temperature, as demonstrated for H-BEA(1) in Fig. 2. Activation at temperatures up to 700°C was found to be possible without significant loss in XRD crystallinity, indicating that the long range ordering is maintained. Essentially complete conversion of the ketone to 4-*tert*-butylcyclohexanol (*cis:trans* 95:5) was obtained within one hour over the 700°C-activated H-BEA(1) while the high selectivity (> 95%) was also maintained. For this experiment, the TON (total turnover number of a catalytic site) was determined to be 3.8, based on the participation of all aluminium sites, though probably only a small proportion is involved. In a typical upscaled experiment, using 12.5 mmol ketone instead of 2.5 mmol, the TON was found to be 19. Increase of the catalytic activity with the activation temperature was also found for γ -Al₂O₃ [2,24], and is a further indication that the activity of zeolite BEA in the MPV reduction is related to Lewis acid sites. These sites are known to be formed

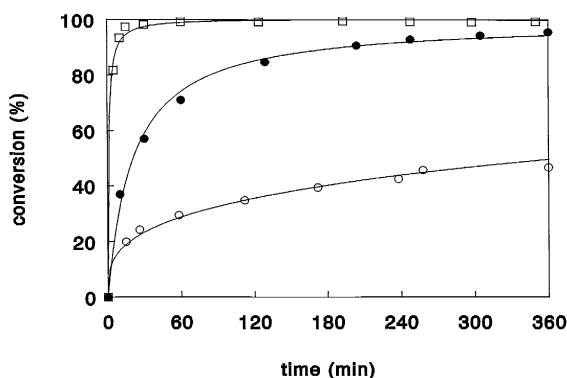


Fig. 2. Effect of the activation temperature on the MPV activity of H-BEA(1); (○) 500°C, (●) 600°C, (□) 700°C. Reaction conditions: 2.5 mmol 4-*tert*-butylcyclohexanone, 25 ml isopropanol, 0.5 g catalyst, under reflux and stirring.

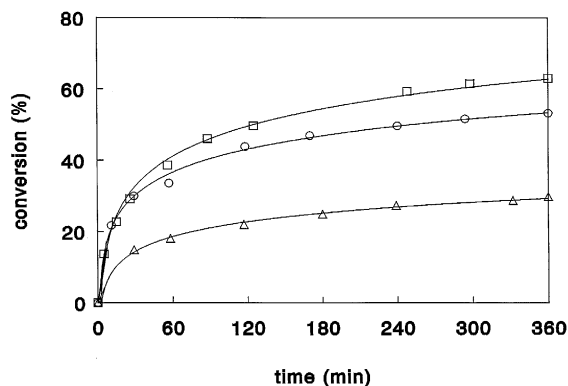


Fig. 3. Re-use of zeolite NH₄-BEA(1) activated at 500°C; (Δ) cycle 1, (○) cycle 2, (□) cycle 3. Reaction conditions: 2.5 mmol 4-*tert*-butylcyclohexanone, 25 ml isopropanol, 0.5 g catalyst, under reflux and stirring.

by dehydroxylation at high temperatures which results in auto-steaming of the zeolite. As a consequence, extra-framework aluminium and partially hydrolysed aluminium sites, often referred to as 'satellite aluminium', are formed. Both types of aluminium are proposed to contribute to Lewis acidity of the zeolite-based catalyst.

Recently, Ivanov et al. [2] showed that the Lewis acid sites on the γ -Al₂O₃ catalyst used in the MPV reaction could be poisoned with the base piperidine, resulting in a complete deactivation of the catalyst. Infrared experiments clearly showed that ethanol was not able to displace piperidine from the blocked Lewis sites, explaining why the poisoning was irreversible. A similar experiment was carried out for NH₄-BEA(1). Addition of 250 μ l piperidine to the reaction mixture resulted in a complete deactivation of the catalyst while the addition of a similar amount of water also caused a dramatic decrease in activity.

Re-use of the H-BEA catalyst was found to be possible. The catalyst was isolated from the reaction mixture by filtration and reactivated at 500°C. The activity of the catalyst was found to be slightly improved after reactivation, which can be explained by the formation of extra catalytic sites by the thermal treatment (Fig. 3). The selectivity, however, was maintained. After

three cycles, no loss in XRD crystallinity was observed. The Si/Al ratios also remained constant, indicating that no aluminium was leached during reaction.

Besides isopropanol, also 2-butanol, 2-pentanol and 2-hexanol were applied as hydrogen donors in the MPV reduction of 4-*tert*-butylcyclohexanone over zeolite BEA. All alcohols were able to carry out the reduction, indicating that there is enough space in the zeolite channels for these alcohols to coordinate to the active site, and to be an active intermediate in the reduction reaction. Furthermore, the chain length of the alcohol did not have any influence on the selectivity of the reaction. Changing the size of the R-group at the 4-position of the substrate also had no effect on the stereoselectivity; 4-methylcyclohexanone was also found to be reduced to the corresponding *cis*-alcohol with > 95% selectivity. For 3-methylcyclohexanone a stereoselectivity to the axial alcohol of 68% was observed. However, 2-*tert*-butylcyclohexanone could not be reduced over zeolite BEA, presumably owing to steric hindrance at the active site.

The stereoselectivity of zeolite BEA in the MPV reduction of 4-*tert*-butylcyclohexanone to the corresponding *cis*-alcohol could be tuned by changing the size of the cation (Table 2), which is another indication that the reaction proceeds in the micropores. In the presence of the larger alkaline earth cations almost absolute stereoselectivity is obtained. No differences between the

Table 2

Influence of the cations in zeolite BEA on the stereoselectivity in the MPV reduction of 4-*tert*-butylcyclohexanone with isopropanol to *cis*-4-*tert*-butylcyclohexanol

Cation in BEA(2)	Ionic radius ^a (Å)	<i>Cis:trans</i> ^b
Li ⁺	0.90	95:5
Na ⁺	1.16	96:4
K ⁺	1.52	98:2
Rb ⁺	1.66	99:1
Cs ⁺	1.81	99:1

^a Selected from [39]; coordination number is 6.

^b Determined at conversions > 95%; selectivity to 4-*tert*-butylcyclohexanol > 95% in all cases.

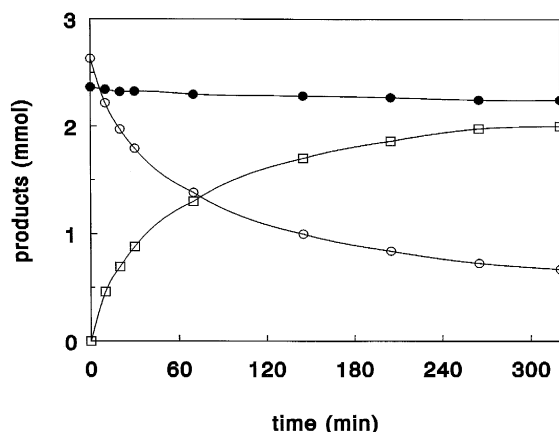


Fig. 4. Oppenauer oxidation of 4-*tert*-butylcyclohexanol catalysed by Na-BEA(2) activated at 500°C; (○) *cis*-4-*tert*-butylcyclohexanol, (●) *trans*-4-*tert*-butylcyclohexanol, (□) 4-*tert*-butylcyclohexanone. Reaction conditions: 5 mmol 4-*tert*-butylcyclohexanone (*cis/trans* = 52.7/47.3), 25 ml acetone, 0.5 g catalyst, under reflux and stirring.

activities of the various alkali cation forms of the catalyst were observed, which excludes a basic reaction mechanism such as proposed by Shabtai et al. [4] for zeolite M-X (Si/Al = 1, M is alkali metal). The basicity of a zeolite, however, does not only depend on the type of (alkali) cations but also on the Si/Al ratio. Zeolites with Si/Al much higher than one, which contain a stoichiometric amount of alkali cation, cannot be considered to be basic catalysts [25].

Zeolite BEA was also found to be an active and stereoselective catalyst in the Oppenauer oxidation of 4-*tert*-butylcyclohexanol to 4-*tert*-butylcyclohexanone, the reverse reaction. In a competitive experiment, using an almost equimolar mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanol, and acetone as the oxidant the *cis*-isomer was almost exclusively converted to the corresponding ketone, the *trans*-isomer remaining essentially unchanged (Fig. 4).

3.1.3. Effect of template calcination procedure on activity

The catalytic activity of zeolite BEA(2), made by deep-bed calcination of the as-synthesised material, was found to be much higher than the

activity of zeolite BEA(1), made by calcination under shallow-bed conditions. Comparison of the initial MPV reduction rates over $\text{NH}_4\text{-BEA(1)}$ and $\text{NH}_4\text{-BEA(2)}$, both activated at 500°C , by assuming that the reaction exhibits first-order kinetics in ketone concentration [1], indicates that the catalytic activity of $\text{NH}_4\text{-BEA(2)}$ is about 80 times higher. Similar results were obtained for the Na-forms of BEA(1) and BEA(2). The MPV reduction of 4-*tert*-butylcyclohexanone (2.5 mmol) could be performed using only 50 mg of 500°C -activated $\text{NH}_4\text{-BEA(2)}$, which gave complete conversion of the ketone to the *cis*-alcohol within three hours, corresponding to a TON of 38. Analysis of the reaction mixture proved the absence of any by-products, within the analytical limits.

The nitrogen adsorption data, presented in Table 3, show that the mesopore volume of zeolite H-BEA(2) is somewhat larger than that of H-BEA(1), which indicates that during deep-bed calcination more mesopores have been formed. This increase in mesopores, however, is considered to be insufficient to explain the large increase in the catalytic activity of BEA(2). A more plausible explanation might be that the different calcination procedures result in a different number of catalytic sites. Recent results of Jia et al. [26] indicate that the extent and type of framework damage in zeolite BEA, consisting of both neutral and charged extra-framework aluminium clusters, and aluminium species still connected to the framework by one or more bonds, depends on the harshness of the thermal treatment. Furthermore, zeolite Na-BEA(3), from which the template had been removed by a procedure which largely prevents dealumination of the framework, proved to be inactive in the

MPV reduction of 4-*tert*-butylcyclohexanone, clearly indicating the necessity of coordinatively unsaturated aluminium species for catalytic activity.

3.2. ^{27}Al MAS-NMR study

Recently, it was observed by ^{27}Al MAS-NMR studies that some of the framework aluminium atoms in H-BEA, formed by high temperature treatment of $\text{NH}_4\text{-BEA}$, can be transformed from tetrahedral to octahedral coordination by exposure to oxygen ligands such as water or acetylacetonate (acac) [11]. This transformation was found to be totally reversible since the tetrahedral coordination of the aluminium sites could be restored by exchange with Na-, K- or NH_4 -salts. This implies that the zeolite lattice has some flexibility and indicates the presence of crystallographic sites which are able to undergo local distortion. As indicated by Fajula [27], the change in symmetry of some of the aluminium sites could be important for reactions involving polar substrates in the presence of solvents. As it is generally accepted that MPV reactions proceed via a complex in which both the carbonyl and the reducing alcohol are coordinated to the aluminium-site, it seemed logical to propose octahedrally coordinated framework aluminium sites to be the active sites for the MPV reduction over H-BEA [7].

In order to further investigate this possibility, ^{27}Al MAS-NMR was applied. All H-BEA samples showed a signal at about 60 ppm, ascribed to aluminium in a tetrahedral coordination (Td), and a signal at about 0 ppm, which is assigned to aluminium in octahedral coordination (Oh), both framework and extra-framework [11,26–28]. The relative amounts of octahedral and tetrahedral aluminium in zeolite H-BEA(1) after activation at 500°C , 600°C and 700°C , respectively, were found to be about 85:15 (Td:Oh) for all samples (Table 4). Furthermore, the same ratio was found for zeolite H-BEA(2) after activation at 500°C , the catalytic activity of which was found to be much higher than that

Table 3
Nitrogen adsorption data

Catalyst	Micropore volume (ml/g)	Mesopore ^a volume (ml/g)	S_{BET} (m^2/g)
H-BEA(1)	0.262	0.086	644
H-BEA(2)	0.264	0.126	640

^a Pore diameter between 2 and 100 nm.

Table 4
 ^{27}Al MAS–NMR and FT-IR characterisation of the BEA catalysts

Catalyst	T_{act} ^a (°C)	^{27}Al NMR data (mol%)		Acidity ^c ($\mu\text{mol/g}$)		Relative integrals OH bands		
		Td ^b	Oh ^b	Brønsted	Lewis	3610 cm^{-1}	3660 cm^{-1}	3780 cm^{-1}
H–BEA(1)	500	85	15	390/320/100	220/180/180	7.0	0	0.55
H–BEA(1)	600	88	12	300/240/70	230/200/225	4.7	0.2	0.75
H–BEA(1)	700	84	16	190/130/25	225/180/165	1.2	0.7	0.9
H–BEA(2)	500	86	14	290/210/60	260/220/210	3.0	0.4	1.0
H–BEA(3)	450	—	—	730/665/260	65/70/180	18	0	0

^a Activation temperature of the catalysts; the wafers were activated in situ to 450°C in vacuo prior to the measurements.

^b Relative amount of tetrahedral and octahedral aluminium.

^c Measured at 150/300/450°C.

of zeolite BEA(1). This means that we are unable to observe a correlation between the amount of octahedral aluminium present in the zeolite and the differences in catalytic activity. Jia et al. also obtained identical ^{27}Al MAS–NMR data for both deep- and shallow-bed calcined zeolite BEA [26]. It is possible that both extra-framework aluminium and six-coordinated framework aluminium appear at about 0 ppm, making it impossible to discriminate between these different species.

The ^{27}Al MAS–NMR spectra of the 500°C-activated sodium forms of zeolite BEA, both Na–BEA(1) and Na–BEA(2), showed only a single signal at about 60 ppm, indicating that the tetrahedral coordination of all framework aluminium has been restored. However, both samples were still found to be active catalysts in the MPV reduction, which makes it impossible for octahedrally coordinated framework aluminium to be the active site. The impregnation of these catalysts with acac or a mixture of 4-methylcyclohexanone and isopropanol also did not transform tetrahedral aluminium into octahedral coordination. The absence of octahedrally coordinated aluminium, even after the impregnation with acac, indicates that the active Na–BEA catalysts are essentially free of extra-framework aluminium, which means that octahedrally coordinated extra-framework aluminium also cannot be considered to be the active site in the MPV reaction.

The absence of a correlation between the

catalytic activity of the different H–BEA samples and the relative amounts of octahedral coordinated aluminium in these samples, together with the absence of octahedral aluminium in the active Na–BEA catalysts, leads to the conclusion that the existence of octahedrally coordinated framework aluminium is not a requirement for catalytic activity. Moreover, extra-framework aluminium is also not believed to be responsible for the catalytic activity. However, our ^{27}Al MAS–NMR measurements support earlier observations leading to the more general conclusion that the lattice of zeolite BEA is very flexible and that partial hydrolysis of Al–O bonds in the H-form, especially during template calcination, is likely to occur [11,26–28].

3.3. IR study

The FT-IR spectrum obtained after ethanol chemisorption on activated H–BEA(2), followed by evacuation, is shown in Fig. 5. IR bands are observed at 2983, 2936, 2915 and 2885 cm^{-1} , which can be ascribed to C–H stretching vibrations of the ethyl group. Also clearly visible are the bands at 1450 and 1394 cm^{-1} , which are due to C–H and C–H₂ bending vibrations of the ethyl group. Similar spectra were reported in the literature for ethanol chemisorbed on alumina [29–32]. Furthermore, comparison of these spectra with the spectrum of aluminium ethoxide indicates that surface ethoxide species are predominantly formed [29].

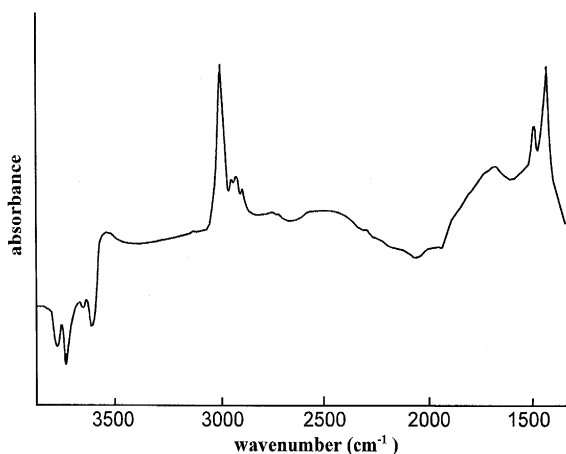


Fig. 5. IR difference spectra (loaded minus unloaded) of activated H-BEA(2) after adsorption of EtOH and evacuation at room temperature.

Such surface alkoxydes are active intermediates in the MPV reduction which can serve as hydrogen donors.

Infrared spectra of the hydroxyl region of the H-BEA catalysts are presented in Fig. 6. Vibrations are observed at about 3610, 3660, 3745 and 3780 cm^{-1} . The relative intensities of these bands are presented in Table 4. Infrared studies of the hydroxy groups in zeolite BEA have been reported recently [11,26,28,33]. The classical absorptions at 3610 and 3745 cm^{-1} are described to framework bridging acidic OH and internal and external SiOH groups. The two other bands, at ≈ 3660 and ≈ 3780 cm^{-1} , show correlation with the observed differences in activities. The band at 3660 cm^{-1} was recently ascribed to extra-framework aluminium. However, the true nature of these species is still a matter of debate. From infrared studies with the aid of various probe molecules it was concluded that this OH is less acidic than the bridging OH [28]. Finally, the band at 3780 cm^{-1} was recently ascribed to AlOH species near one or more SiOH groups, generated when aluminium leaves the framework. It may reflect low acidity AlOH species of intermediate (transient) products leaving the framework. As the frequency of this band is very high for zeolites, it was designated the VHF band. Since the VHF

vibration shifts upon interaction with basic molecules, it was considered to be more acidic than terminal silanols [28]. Furthermore, it was only observed for samples which were slightly dealuminated and it has been reported that samples possessing the VHF band exhibit enhanced catalytic activity [34,35].

From Table 4 it can be observed that the intensity of the 3610 cm^{-1} vibration is strongly related to both the activation temperature and the conditions employed for template removal. A more severe thermal treatment results in a dramatic decrease in the amount of Brønsted acid sites which is also evident from the results of pyridine adsorption (1540 cm^{-1}). This observation is in agreement with literature data [26]. As ^{27}Al MAS-NMR data indicate a maximum framework dealumination of about 15%, the dramatic decrease in Brønsted acidity cannot be ascribed to severe framework dealumination only. Significant neutralisation of framework acid sites by extra-framework aluminium has been suggested for various zeolites including zeolite BEA [26,33–36]. This possibility is supported by the increase in intensity of the 3660

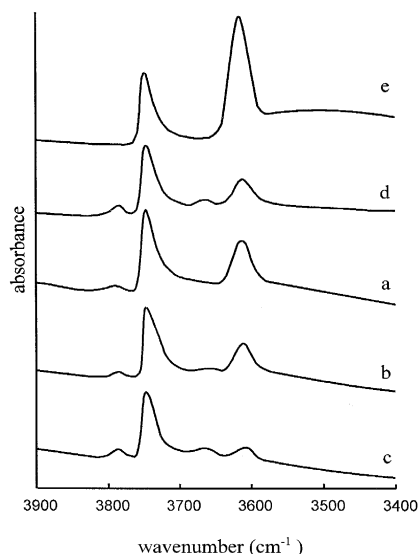


Fig. 6. IR spectra of the hydroxyl region of the H-BEA catalysts measured at 150°C under vacuo. (a) H-BEA(1)/500°C; (b) H-BEA(1)/600°C; (c) H-BEA(1)/700°C; (d) H-BEA(2)/500°C; (e) H-BEA(3)/450°C.

cm^{-1} band, associated with extra-framework aluminium.

A remarkable observation is the large difference in intensity of the 3780 cm^{-1} band between the shallow- and deep-bed calcined samples and the increase in intensity of this vibration after activation at higher temperatures. The observed trend is in line with the increase in activity found for the zeolite catalysts. Indeed, comparison of the initial activities of H-BEA(1) activated at 700°C , and H-BEA(2) activated at 500°C , shows comparable initial hydrogenation rates, in agreement with the very similar 3780 cm^{-1} intensities. No VHF band was observed for H-BEA(3), the catalyst that proved to be inactive. We therefore propose that the catalytic activity in the MPVO reaction of the zeolite BEA catalysts is related to aluminium which is partially attached to the zeolite framework and possesses Lewis acid properties.

Adsorption of pyridine resulted in the disappearance of all hydroxyl bands, except for the 3745 cm^{-1} vibration. Upon heating under vacuum, first the 3664 cm^{-1} band and later also the 3610 cm^{-1} reappeared; the 3780 cm^{-1} vibration, however, failed to reappear, even on heating to 450°C . This observation is in agreement with data reported in the literature [26,28]. Recent studies of the acidity of the hydroxyl groups of zeolite BEA revealed that the hydroxyls responsible for the VHF vibration are more acidic than the terminal silanols, but less acidic than the hydroxyls associated with extra-framework aluminium. This indicates that the vanishing of the VHF band after adsorption of pyridine, followed by desorption at 450°C in vacuo, is related to a strong adsorption of pyridine, stronger than that on a Brønsted acid site. Recently, such a strong adsorption mode has been proposed by Flego et al. to explain the shoulder at 1462 cm^{-1} on the 1455 cm^{-1} band [37]. This shoulder appears at higher temperatures when partial pyridine desorption has occurred, and was also observed for all our zeolite BEA samples after desorption in vacuo at increasing temperatures. The proposed strong adsorption mode

consists of the simultaneous interaction of pyridine with both a Lewis acid aluminium and an OH group bonded to the same aluminium. Such a simultaneous interaction of a base (ammonia, water, pyridine) with a Lewis acid metal site and the metal–OH was also recently proposed to explain the disappearance of the OH stretching band in cloverite [38]. A similar interaction might exist in the present case also, which could then explain the complete vanishing of the 3780 cm^{-1} vibration. Furthermore, it would indicate a relation between partially hydrolysed framework aluminium species and Lewis acidity.

Unfortunately, no large differences in the amounts of Lewis acid sites of the H-BEA(1) catalysts, treated at different activation temperatures, could be observed from the interaction with pyridine (1455 cm^{-1}). However, it cannot be excluded that not all types of Lewis acid sites are detected by this method. Another possibility is that some of the Lewis acid sites formed during the high temperature treatment were lost during storage at ambient conditions, before being transported to the IR cell where they were reactivated to 450°C in vacuo. Furthermore, we were unable to determine the distribution of Lewis acid sites with different acid strengths because further dehydroxylation of Brønsted acid sites occurred during heating under vacuum. Zeolite H-BEA(2) appears to have significantly more Lewis-acid sites than H-BEA(1), while a much smaller amount of Lewis acid sites is determined in the case of H-BEA(3).

3.4. Reaction mechanism and origin of stereoselectivity

Based on the catalytic results, in combination with the information obtained by ^{27}Al MAS-NMR and FT-IR, the following reaction mechanism is proposed. The initial step is chemisorption of the secondary alcohol on a Lewis acid aluminium site. This active site consists of a coordinatively unsaturated aluminium, bound to the lattice by one, two, or three remaining bonds.

Chemisorption of the alcohol on a Lewis acid site results in the formation of an surface alkoxide which is considered to be the activated hydrogen donor. The coordinative interaction of the carbonyl of the ketone present, with the same aluminium centre, allows the formation of a six-membered transition state in which hydride transfer can occur (Fig. 7). As the active aluminium site is partially hydrolysed from the framework there will be enough space for both the secondary alcohol and the ketone to have the required interaction with the catalytic site.

The transition states which lead to the *cis*- and *trans*-alcohols differ substantially in size (Fig. 7). That for the *cis*-isomer is more or less linear in form and aligned with the BEA channel while the formation of the *trans*-alcohol requires an axially oriented (bulkier) transition state. Although the latter might still fit in the intersections of BEA it is questionable whether

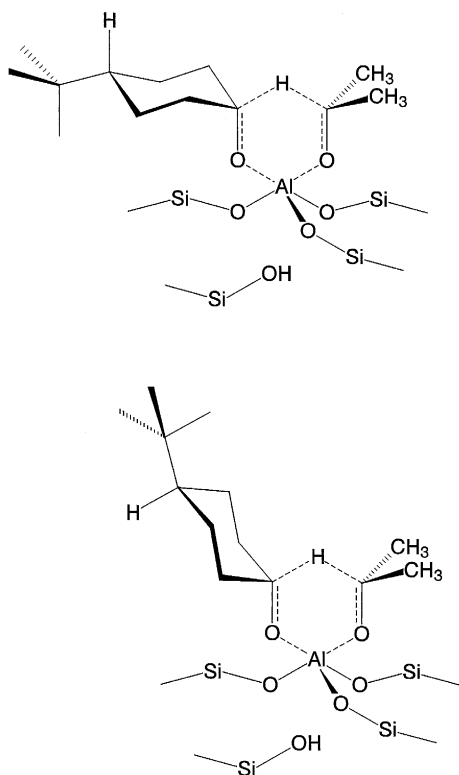


Fig. 7. Transition states for the formation of *cis*-4-*tert*-butylcyclohexanol (top) and *trans*-4-*tert*-butylcyclohexanol (bottom) in the proposed reaction mechanism over zeolite BEA.

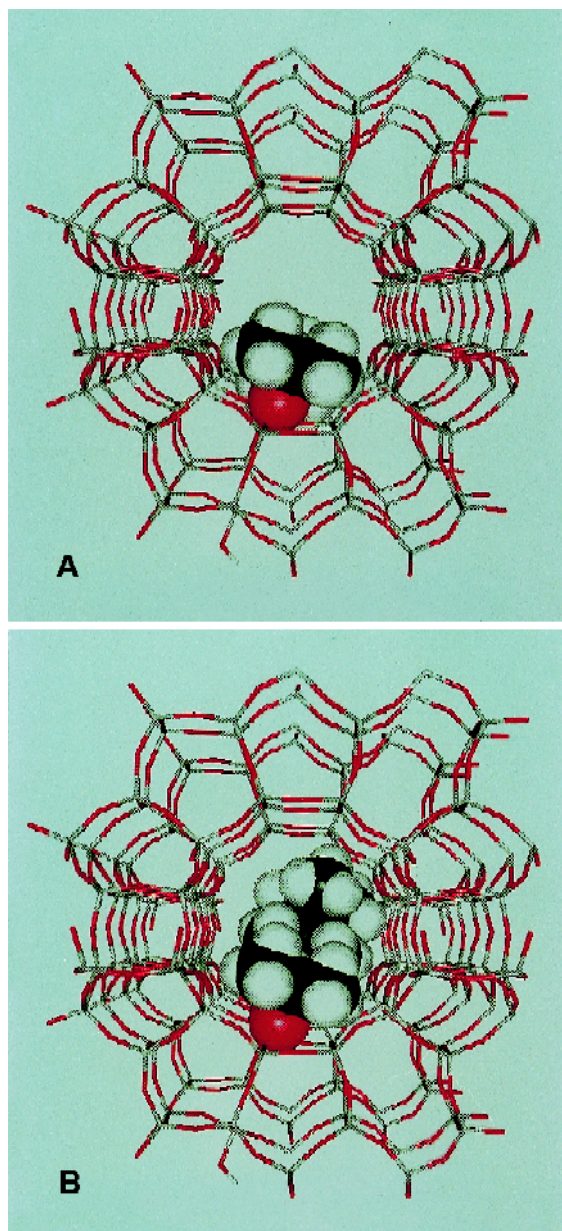


Fig. 8. Transition states, spatial pictures, for the formation of *cis*-4-*tert*-butylcyclohexanol (a) and *trans*-4-*tert*-butylcyclohexanol (b) accommodated in a straight channel of zeolite BEA.

there is an active site available at the required position. More coordination possibilities are available for the *cis*-transition state, which can be easily accommodated within the straight channels of BEA as illustrated in Fig. 8. The observed kinetically determined product distribution in the MPV reduction of 4-*tert*-butyl-

cyclohexanone is thus satisfactorily explained by true transition-state selectivity. Furthermore, the observed stereoselectivity in the Oppenauer oxidation of 4-*tert*-butylcyclohexanol is also in agreement with the proposed mechanism as this reaction requires the same transition state. However, the interaction of the substrates with the zeolite wall can also contribute to the preferential formation of the *cis*-transition state in the zeolite catalysed MPVO reactions.

4. Conclusions

Zeolite BEA is found to be a regenerable, stereoselective catalyst for the Meerwein–Ponndorf–Verley reduction of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol and the complementary Oppenauer oxidation. The active sites consist of Lewis acid aluminium sites which are located in the micropores of the zeolite. Infrared results indicate that these sites consist of aluminium which is only partially connected to the framework. Such aluminium sites are formed during template removal and their number depends on the conditions employed (temperature, deep- or shallow-bed calcination). The mechanism is proposed to involve a six-membered transition state which is formed upon chemisorption of the secondary alcohol on the Lewis acid aluminium site and coordination of the ketone to the same aluminium site. The observed high stereoselectivity to the thermodynamically less stable *cis*-isomer can be explained by transition-state selectivity resulting from the limited space in zeolite BEA.

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