

The hydration and isomerization of α -pinene over zeolite beta. A new coupling reaction between α -pinene and ketones

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Abstract

The catalytic potential of zeolite H-beta in the hydration and isomerization of α -pinene was investigated. In the presence of water the main product is the monocyclic alcohol α -terpineol (48%) though selectivity towards bicyclic terpenes is higher than observed for sulphuric acid (26% vs. 5.5%). When the isomerization is performed in pure acetone, a new compound forms by a novel C–C coupling reaction between α -pinene and acetone. The product is identified as α -terpinyl acetone. This coupling seems to be a general reaction between α -pinene and ketones and is catalyzed exclusively by zeolite beta.

Keywords: Zeolite beta; α -Pinene; Isomerization; Hydration; C–C coupling reaction; α -Terpinyl acetone

1. Introduction

Upon subjecting α -pinene **1** to aqueous mineral acids, complex mixtures are obtained resulting from isomerization and hydration [1]. The main products (see Fig. 1) are the monocyclic terpenes: α -terpineol **12**, limonene **8** and terpinolene **10**. Minor amounts of camphene **4**, α - and γ -terpinene **9**, **7**, α - and β -fenchol **5**, **6**, isoborneol **2**, borneol **3**, γ -terpineol **13** and 1,8-terpine **14** are also formed, as well as 1,4- and 1,8-cineol, *para*-cymene and tricyclene [2,3]. In current industrial practice, e.g. borneol preparation, often two- or three-step processes are applied in which α -pinene is first isomerized to camphene. Much research has been done to develop clean processes which have high selectivity towards one of the products starting directly from α -pinene.

Zeolites, microporous aluminosilicates, may have potential in improving selectivity here. The kinetic size of the α -pinene molecule as well as that of most of the bicyclic products restrict the use of zeolites to the large pore zeolites (i.e. 12-membered rings, access 7–7.5 Å pore diameter) like Y, beta and mordenite. Two publications deal with the use of zeolites in the hydration and/or isomerization of α -pinene. Nomura et al. [4] used various zeolites (Ca-Y, US-Y Na-X, ferrierite) in the hydration of very diluted aqueous solutions of α -pinene to α -terpineol. Highest selectivity to α -terpineol was obtained using ferrierite (yield 69%, 117 h at 90–100°C). Selective hydration of α -pinene to borneol and camphene using a three phase system (water, terpene and an unspecified zeolite) has been reported by Chen et al. [5]. No yields and conversions are given but 90 to 95%

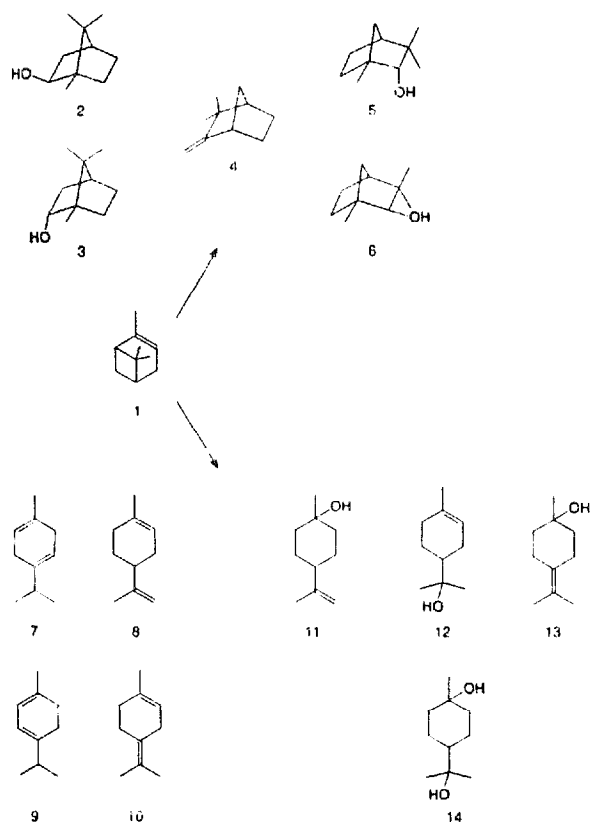


Fig. 1. Acid catalyzed isomerization and hydration of α -pinene. 1 – α -pinene; 2 – isoborneol; 3 – borneol; 4 – camphene; 5 – α -fenchol; 6 – β -fenchol; 7 – γ -terpinene; 8 – limonene; 9 – α -terpinene; 10 – terpinolene; 11 – β -terpineol; 12 – α -terpineol; 13 – γ -terpineol; 14 – 1,8-terpine.

pure borneol is claimed after distillation. However, in both cases relatively long reaction times are necessary for high conversions of α -pinene (> 90 h).

In this work we report on the fast hydration and/or isomerization of α -pinene using zeolite H-beta as the catalyst. Zeolite beta is a high-silica zeolite (Si/Al 10 to ∞) [6,7] with a three-dimensional pore system containing 12-membered ring apertures ($7.4 \times 6.5 \text{ \AA}$) [8], which makes this zeolite very suitable as a regenerable catalyst in organic reactions. Upon performing zeolite beta catalyzed isomerization in pure acetone a new C–C coupling reaction was discovered which is described in this paper and appears to be a general reaction of α -pinene and ketones.

2. Experimental

2.1. Catalyst preparation

Zeolite beta (Si/Al=10) was synthesized according to Wadlinger and Kerr [6]. 11.61 g sodium aluminate (0.1415 mol NaAlO_2 , Riedel-de Haën), 110 g 40% (w/w) tetraethylammonium hydroxide (0.299 mol TEAOH, Aldrich) and 291.57 g silica sol (1.461 mol Ludox LS) were mixed and transferred to a Teflon-lined autoclave. After crystallization (145 h at 150°C), the zeolite was collected by filtration, dried at 115°C and calcined at 500°C to remove the organic template. H-beta is obtained by ion exchange with NH_4NO_3 and subsequent activation at 500°C . Outer surface deactivation of zeolite beta by means of dealumination, as reported earlier by Rigutto et al. [9], was performed by overnight washing of the as-synthesized zeolite with a 0.025 M $\text{Na}_2\text{H}_2\text{EDTA}$ solution (34 ml/g zeolite), followed by thorough washing with distilled water prior to calcination. In the same way, but applying 0.07 or 0.035 mol NaAlO_2 , samples with Si/Al=20 and 40 were prepared and zeolite boron beta (Si/B = 20) was synthesized according to van der Waal et al. [7].

2.2. General procedure for monoterpene hydration or isomerization

The catalyst (0.5 g) was suspended in a solution of 1,3,5-tri-isopropylbenzene (internal standard, 1.65 mmol) in the solvent (90% aqueous acetone, acetone, butanone, cyclohexanone or dioxane) and the mixture was heated up to reaction temperature, 56°C , under N_2 atmosphere. After 30 min the reaction was started by addition of 1.65 mmol of the starting compound (α -pinene, limonene, α -terpineol or borneol; all purchased from Janssen Chimica) to the reaction mixture. Samples were taken at regular intervals and analyzed by GC using a $50 \text{ m} \times 0.53 \text{ mm}$ CP Sil-5 CB capillary column. Peak identification of the products was done by GC–MS analysis.

3. Results

3.1. Hydration and isomerization of α -pinene

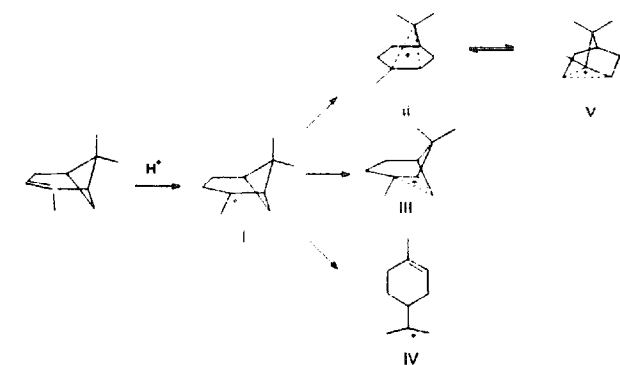
The hydration of α -pinene in 90% (w/w) aqueous acetone in the presence of H-beta (Si/Al = 10) yielded a complex mixture of monoterpenes (both alcohols and hydrocarbons). The

Table 1
Selectivity to product groups and to borneol (**3**) and α -terpineol (**12**) in the isomerization/hydration of α -pinene^a

Catalyst	Water added (g)	Conv. (%)	<i>t</i> (h)	Selectivity (%) to ^b					
				B-T	B-A	3	M-T	M-A	12
H-beta	–	75	1.3	20.05	7.59	3.04	79.95	7.01	4.93
H-beta	2.97	75	2.5	26.23	14.50	5.15	73.77	47.57	42.76
H-Y	–	<5	16	–	–	–	–	–	–
H ₂ SO ₄	–	75	2.8	5.5	–	–	94.5	–	–

^a Using zeolite H-beta (200 mg, Si/Al = 10, outer surface dealuminated); H-Y (200 mg, Si/Al = 3.2); H₂SO₄ (33 mg), in 30 ml acetone at 56°C.

^b B-A = bicyclic alcohols; B-T = bicyclic terpenes; M-A = monocyclic alcohols; M-T = monocyclic terpenes.



Scheme 1.

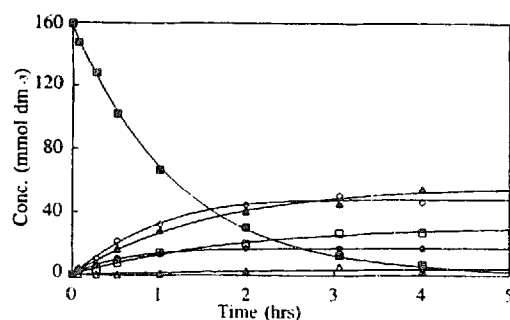
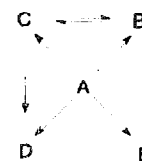


Fig. 2. Hydration and/or isomerization of α -pinene over H-beta (Si/Al = 10, at 56°C) in 90% (w/w) aqueous acetone. Product groups according to Scheme 3: \blacksquare – α -pinene; \square – bicyclic alcohols; \blacklozenge – bicyclic hydrocarbons; \diamond – monocyclic hydrocarbons; \blacktriangle – terpineols; \triangle – 1,8-terpineol.



Scheme 2.

main products (see Table 1) are the monocyclic terpenes, also found by catalysis with mineral acids. H-beta differs from sulphuric acid by yielding a substantially higher amount of bicyclic terpenes, predominantly camphene. The activity of zeolite H-beta in comparison with zeolite H-Y (Si/Al = 3.2) was high, which is probably caused by the higher hydrophilicity of zeolite Y, leading to a very low adsorption of α -pinene.

Our first interest was in the selective hydration of α -pinene to bicyclic alcohols, borneol **3** in particular, however the main alcohol formed is α -terpineol **12** (see Table 1), which is formed via cation **IV** (cf. Scheme 1). Small amounts of borneol **3** are formed over H-beta while isoborneol **2** is initially not formed. The selective formation of borneol over isoborneol, which is thermodynamically more favoured, can only be explained by a direct attack of water on the pinene cation **II** to give borneol before its rearrangement to cation **V** which apparently rather deprotonates to give camphene than hydrates to give isoborneol. This is in agreement with Barkhash [10] who states that isoborneol is formed from cation **V** whereas borneol is formed from cation **II**. Since cation **I** is thought to rearrange fast to either **II**, **III** or **IV**, it is not assumed to be an intermediate on which water can attack [10]. The protonation of α -pinene to give cation **I** is generally accepted to be the slowest (rate determining) step in the acid catalyzed rearrangement.

3.2. Kinetics of α -pinene hydration and isomerization

The kinetic curves for hydration and isomerization in the presence of water can be fitted (see Fig. 2) by a simple pseudo-homogeneous kinetic model assuming first order elementary reaction steps between each group of species as shown in

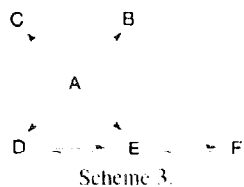


Table 2
Effect of external surface dealumination of H-beta (Si/Al = 10) on the pseudo first order rate constant of α -pinene conversion^a

Zeolite treatment	Rate constant ($10^{-2} \text{ dm}^3 \text{ h}^{-1} \text{ g}_{\text{zeolite}}^{-1}$)
A1 unextracted uncalcined ^b	2.01
A2 unextracted calcined	1.71
B1 extracted uncalcined ^b	0.00
B2 extracted calcined	5.97

^a In 90% w/w aqueous acetone at 56°C.

^b Activated at 250°C overnight.

Table 3
Influence of zeolite beta composition on the pseudo first order rate constant of α -pinene hydration/isomerization^a

Zeolite composition		Rate constant ($10^{-2} \text{ dm}^3 \text{ h}^{-1} \text{ g}_{\text{zeolite}}^{-1}$)
Si/Al	Si/B	
10		5.97
20		10.5
	20	0.65

^a Outer surface dealuminated beta, 90% w/w aqueous acetone at 56°C.

Scheme 2 and Scheme 3. The difference between Scheme 2 and Scheme 3 is the number of curves used to represent different type of pseudo species, as convenient. Since under homogeneous conditions kinetics also can be described by similar models [10], i.e. assuming first order elementary steps, we assume a similar mechanism for zeolite catalyzed reactions. We note however that for a first-order reaction there is no influence of internal diffusion limitations on the apparent order of the reaction rate, so determination of the nature of the rate determining step (kinetic or diffusion) is not possible from our experiments. For zeolite H-beta catalyzed isomerization in pure acetone the kinetics change to Langmuir–Hinshelwood kinetics though the first order in α -pinene remains.

3.3. Influence of the outer surface of zeolite beta

Since the outer surface of a zeolite also contains active acid sites which do not exhibit shape-selectivity due to the absence of a pore structure, removal of such sites could enhance selectivity. This was indeed found by Rigitto et al., in the Fischer-indole synthesis using zeolite beta as the catalyst [9]. The dealumination of the outer-surface of medium or large pore zeolites containing organic templates, can be achieved by treatment of the as-synthesized material with $\text{Na}_2\text{H}_2\text{EDTA}$. The presence of the template protects the internal aluminium sites for removal. The effects of outer-surface dealumination on the pseudo first-order rate constant of α -pinene hydration and isomerization are shown in Table 2. Previous studies on thermogravimetric analysis of tetraethylammonium (TEA^+) degradation in zeolite beta, showed that the decomposition of TEA^+ starts around 300°C [11]. It is therefore assumed that in catalyst A1 and B1 (activated at 250°C, Table 2) all TEA^+ is still present in the zeolite channels and reaction can only proceed via outer-surface aluminium sites. The high reactivity of uncalcined, untreated zeolite beta (catalyst A1, Table 2) suggests that a large amount of outer-surface acid sites is present. The $\text{Na}_2\text{H}_2\text{EDTA}$ treatment effectively removes all outer-surface aluminium as shown by the complete deactivation of catalyst B1. Upon dealumination and subsequent calcination, catalyst activity is greatly improved (catalyst B2) in comparison with the untreated catalyst A2. This enhanced activity may be due to removal of non-crystalline materials from the outer-surface, which blocked pore openings.

3.4. Influence of zeolite composition

Catalyst activity changes dramatically with zeolite composition. Table 3 shows kinetic data for three different zeolites beta. Catalyst activity increases with increasing silicon to aluminium ratio. Three explanations are possible: (i) the hydrophobicity of a zeolite increases with increasing Si/Al ratio. This is due to the acid sites which

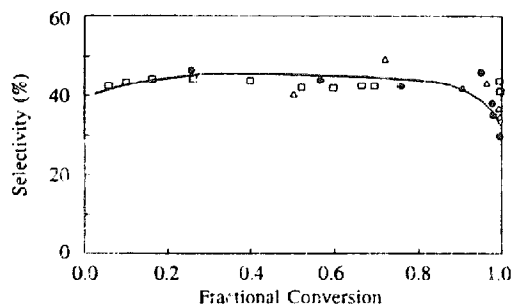


Fig. 3. Effect of zeolite composition on the selectivity to α -terpineol in the hydration/isomerization of α -pinene at 56°C in 90% (w/w) aqueous acetone. ● Si/Al=10; Δ Si/Al=20; \square Si/B=20.

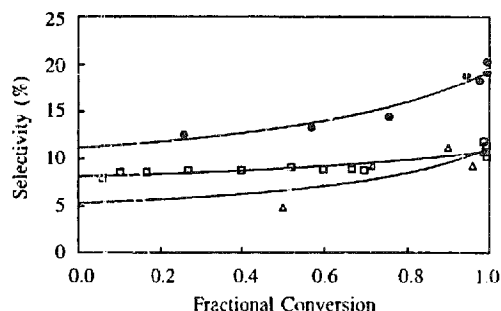


Fig. 4. Effect of zeolite composition on the selectivity to bicyclic terpenes in the hydration/isomerization of α -pinene at 56°C in 90% (w/w) aqueous acetone. ● Si/Al=10; Δ Si/Al=20; \square Si/B=20.

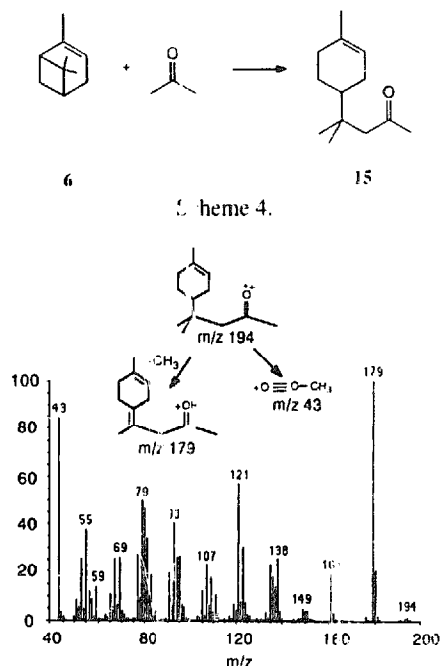


Fig. 5. Mass spectrum of α -terpinyl acetone.

strongly adsorb water and polar solvent molecules. In case of low Si/Al ratios, adsorbed water and solvent molecules could become a barrier hindering the diffusion of α -pinene into the zeolites pore system. This suggests one would find diffu-

sion limitations. Since there is a pseudo first-order rate constant, this can, however, neither be rejected nor supported on the basis of our experiments. (ii) The sorption distribution within a zeolite changes with increasing Si/Al ratio (due to the increasing hydrophobicity). The intrinsic concentration of terpenes in the zeolite pores will become higher thereby increasing reaction rate. It may be noted that (i) and (ii) are in essence closely related. (iii) The acid strength of an aluminium site is dependent on the number of next-neighbour aluminium sites. The higher the number of next-neighbouring aluminium sites the lower the acid strength. A higher Si/Al ratio therefore means stronger acid sites together with a lower number of acid sites per gram of zeolite.

Effect (iii) is perhaps the unlikeliest explanation since the difference between Si/Al=10 and 20 in the absolute number of next-neighbouring aluminium sites is relatively small. The large difference between the aluminium and the boron zeolite beta (Table 3) is explained by the very low acid strength of a proton on a boron site. There is little effect of the zeolite composition on the selectivity towards α -terpineol though the boron zeolite seems to keep a high selectivity towards almost complete conversion (see Fig. 3). Selectivity towards bicyclic alcohols is favoured by a low silicon to aluminium ratio as can be seen in Fig. 4.

3.5. Formation of a new product, α -terpinyl acetone

Upon isomerization of α -pinene in pure acetone (a trace amount of water is assumed to be present in the zeolite or acetone used) a new product is formed. This product is not formed when dioxane is used as the solvent or when other acids (sulphuric acid, zeolite Y, H-MCM-41, amorphous silica-aluminas, and SAPO-5) are applied as the catalyst. Identification by means of mass spectroscopy allowed the new product to be identified as α -terpinyl acetone 15 (Scheme 4 and Fig. 5). This coupling was further confirmed by using acetone- d_6 as the solvent. The mass spectrum of the deuterated α -terpinyl acetone not only showed

Table 4
Effect of ketone structure on the first-order rate constant of α -pinene isomerization and selectivity to α -terpinyl ketone catalyzed by zeolite H-beta^a

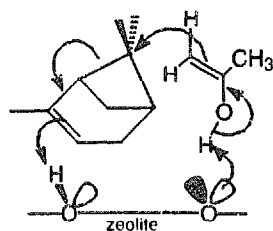
Ketone	Rate constant of α -pinene conversion ($10^{-2} \text{ dm}^3 \text{ h}^{-1} \text{ g}^{-1}$)	Selectivity to α -terpinyl ketone ^b [%]
acetone ^c	10.2	15.1
acetone (90 wt% in water) ^c	6.0	0.0
acetone	81.4	7.7
acetone-d ₆	54.6	8.9
butanone	32.4	10.0
cyclohexanone	1.7	— ^d
pinacolone	1.4	0.0

^a Zeolite H-beta (Si/Al = 40), 30 ml pure ketone at 56°C.

^b At α -pinene conversion of > 99%.

^c Si/Al = 10 used.

^d Selectivity at complete α -pinene conversion could not be determined, but the extrapolated yield is better than for butanone.



Scheme 5.

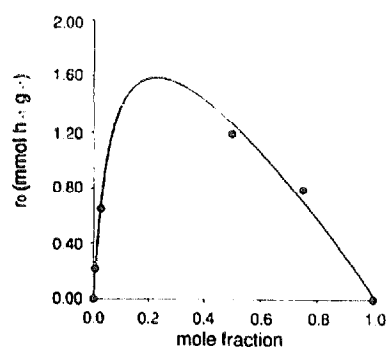


Fig. 6. Initial rate as a function of mole fraction pinene.

evidence of a $-\text{CD}_2-\text{CO}-\text{CD}_3$ moiety but also showed an isotropic deuterium substitution of up to 6 deuterium atoms in the terpinyl moiety, presumably by H/D exchange via the tertiary cation formed at C₁.

We found that butanone and cyclohexanone also entered this new coupling reaction whereas pinacolone (3,3-dimethyl-2-butanone) did not

(see Table 4), which can be explained by steric hindrance of the bulky butyl group. The pseudo first order rate constant for α -pinene conversion is strongly dependent on the nature of ketone used (Table 4) and is found to decrease with increasing kinetic diameter of the ketones: acetone > butanone > cyclohexanone > pinacolone. Kinetic modelling of the experimental data can only be achieved if an intermediate species between α -pinene and acetone is assumed. However, such a species was not detected by GC, suggesting that this effect should be ascribed to internal diffusion limitations of the bulky α -terpinyl acetone. This effect is even more pronounced for the coupling of α -pinene and the other ketones.

3.6. Mechanism of α -terpinyl acetone formation

The use of related terpenes as starting material (limonene, α -terpineol or borneol) which can give the same carbocations II–V did not result in the formation of α -terpinyl acetone. This indicates that α -terpinyl acetone is directly formed by a specific reaction between α -pinene and acetone in a concerted way as shown in Scheme 5 rather than the existence and stabilization of an intermediate carbocation (e.g. cation type I through V) which is subsequently attacked by acetone. We assume that the α -pinene molecule adsorbs on an acid site and that the enolic form of acetone adsorbs on a nearby oxygen atom. Thus, a protic and a neighbouring basic site are required. The enolic acetone could then attack the bridging carbon of the gem-dimethyl group of the α -pinene molecule. This mechanism is supported by the kinetic behaviour of the initial rate of formation of α -terpinyl acetone, which goes through a maximum when the mole fraction of α -pinene changes from 0 to 1 (see Fig. 6). The fitted line represents a Langmuir–Hinshelwood model, assuming a second order reaction between acetone and α -pinene (both first order).

Zeolites are generally thought to be shape-selective catalysts by either reactant selectivity, product selectivity or transition state selectivity

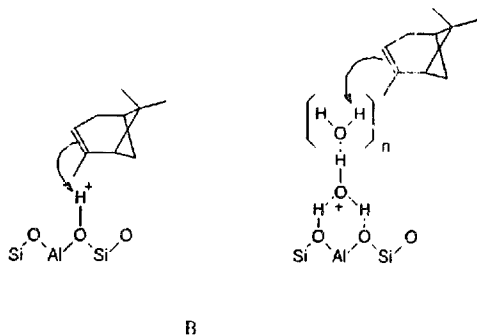


Fig. 7. Protonation of α -pinene in zeolites. A – in absence of water; B – in presence of water.

[12]. Since the terpinyl ketones are only formed using zeolite beta and not with the other acid catalysts tested, the product is apparently formed by transition state selectivity [12]: the specific adsorption and reaction of the α -pinene–ketone couple in the zeolite beta channel or intersection. Molecular mechanics calculations on the transition state show that the distance between the zeolite proton and the enolic proton should be at least 5.2 Å. The average oxygen–oxygen distance in a zeolite is about 3.04–3.14 Å [13], thus ruling out the possibility of the reaction proceeding over a single aluminium site. The fact that only zeolite beta catalyzes this new C–C coupling reaction, indicates that only zeolite beta meets the spatial requirements for this reaction.

The nature of the acid site and subsequent catalysis is dependent on the presence of water. In the absence of water there is a direct interaction between the zeolite proton and C–C double bonds as reported by Kazanski [14] for the adsorption of ethene. In our case an α -pinene molecule or maybe an ion pair involving a cation II–V, will be directly bonded at the aluminium site (Fig. 7A). As a consequence the kinetic behaviour is one of the Langmuir–Hinshelwood type. In the presence of water this alkene–H-zeolite interaction presumably does not exist due to preferentially adsorbed water [15]. The α -pinene molecule is now protonated by the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ present (Fig. 7B) which spatially separates the α -pinene and/or cations from the aluminium site and normal first-order kinetics are observed. This might explain why in the presence of water no α -terpinyl ketones are formed: the spatial require-

ments for the concerted mechanism as proposed in Scheme 5 are not met.

4. Conclusions

The hydration/isomerization of α -pinene catalyzed by zeolite H-beta is fast and leads mainly to monocyclic terpenes and alcohols with α -terpineol as the principal product (up to 48%). The selectivity towards the commercially more interesting bicyclic products is about 26% which is significantly better than observed for H_2SO_4 (about 5%). Upon dealumination of the zeolite's outer surface with $\text{Na}_2\text{H}_2\text{EDTA}$, an enhancement of the reaction rate and an increased selectivity towards α -terpineol is observed. The reaction rate increases with increasing Si/Al ratio, which is possibly due to increased hydrophobicity of the zeolite, the selectivities are however not significantly affected.

Upon isomerization of α -pinene in pure ketones (acetone, butanone or cyclohexanone) a new type of product is formed by a C–C coupling reaction of α -pinene and the ketone. Structure identification, performed by GC–MS, showed these products to be 1-(α -terpinyl)-acetone, 1-(α -terpinyl)-butan-2-one and 2-(α -terpinyl)-cyclohexanone, respectively. The α -terpinyl ketones are not formed when other monoterpenes are used as starting reagents, suggesting that they are formed directly from α -pinene and not by any of the intermediate classical or non-classical carbocations usually postulated to describe the isomerization of terpenes. A concerted mechanism is postulated in which a ketone molecule in the enolic form attacks an α -pinene molecule adsorbed on an acid site. This is supported by the observation that the kinetics is first order in α -pinene as well as in ketone and by the Langmuir–Hinshelwood type of kinetic behaviour. The new reaction appears to be specific for zeolite beta, which indicates shape selectivity due to the specific interaction and stabilization of the transition state by the pore system of zeolite beta.

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