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On the remarkable behaviour of zeolite Beta in acid catalysis

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Abstract

Zeolite Beta is developing into a major catalyst in organic chemicals conversion, contributing to low waste technology. In comparison with other zeolites, zeolite Beta possesses unique acid properties which are related to local defects. These defects are generated when a tertiary building unit (TBU) is rotated 90° around the *c*-direction with respect to the neighbouring TBUs in the same layer. The rotated TBU cannot connect properly with the adjacent layers. This results in *T*-atoms that are not fully coordinated to the framework, thereby creating potential Lewis-acid sites. The high stereoselectivity observed in the Meerwein–Ponndorf–Verley (MPV) reduction of 4-*tert*-butylcyclohexanone to the corresponding *cis*-alcohol and the absence of MPV reduction of the bulky probe molecule 1-(3,5-di-*tert*-butylphenoxy)propan-2-one on the external surface, indicate that Lewis-acid sites are mainly present in the micropore walls. By contrast, Brønsted-acid sites are present on the internal as well as the external surface.

Keywords: Zeolite Beta; Tertiary building unit (TBU); Acid-catalyzed conversion

1. Introduction

The three-dimensional large pore zeolite Beta (BEA) is developing into a major catalyst in organic chemicals conversion, contributing to low waste technology. Examples of successful applications of zeolite Beta include aromatic alkylation [1], aromatic acylation [2,3], indole synthesis [4], aromatic nitration [5] and aliphatic alkylation [6]. The highly stereoselective MPV reduction of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol with zeolite Beta as Lewis-acid catalyst [7] has provoked studies on its structural properties and catalytic performance. A comparison of the physico-chemical data of zeolite Beta with those of zeolite Y, ZSM-5, mordenite, MCM-22 and MCM-41 indicates that unique catalytic properties can be expected. Some structural and chemical details of the aforementioned catalysts are briefly discussed here.

2. Structural and chemical considerations

Zeolite Beta has a three-dimensional intersecting channel system depicted in Fig. 1. Two mutually perpendicular straight channels, each with a cross section of 0.76 × 0.64 nm, run in the *a*- and *b*-directions. A sinusoidal channel of 0.55 × 0.55 nm runs parallel to the *c*-direction. Zeolite Y has a three-dimensional pore system, which is constructed from

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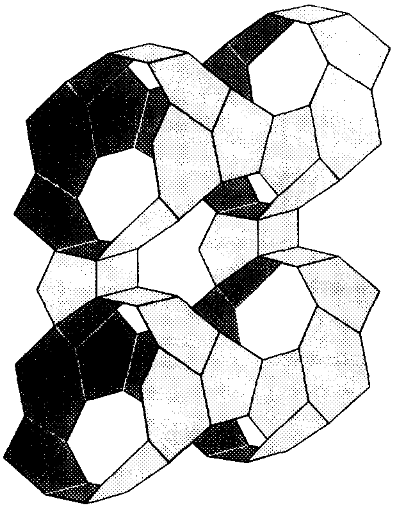


Fig. 1. Schematic presentation of the channel system of zeolite Beta.

large supercages with diameters of 1.20 nm [9] that are connected via apertures of 0.74 nm diameter. Mordenite [9] has a semi-two-dimensional channel system. Parallel straight channels of 0.70 × 0.65 nm perpendicularly intersect smaller channels of 0.57 × 0.26 nm. ZSM-5 [9] has a three-dimensional intersecting channel system. A straight channel of 0.56 × 0.53 nm runs parallel to the *a*-axis and a sinusoidal channel of 0.55 × 0.51 nm runs parallel to the *b*-axis. Molecules can also move in the *c*-direction by alternately using both channels. Although the channels are relatively small in comparison with those of the large-pore zeolites discussed previously, naphthalene molecules with a kinetic diameter of even 0.74 nm can be adsorbed into the pore system. This can be explained by the flexibility of the 10-ring apertures [10]. MCM-22 has two independent pore systems [11]. One is defined by two-dimensional sinusoidal channels which are accessible by 10-ring apertures. The other consists of large elongated supercages of 0.71×1.82 nm. The diameter of the straight parallel channels in the mesoporous material MCM-41 varies from 2 to 8 nm, depending on the template micelle dimensions [12]. The structure shows only crystallographic symmetry perpendicular to the pores. The pore walls are probably composed of poorly crystalline material.

Despite the variation in the pore geometry of the discussed zeolites, all of them may convert substituted benzene or cyclohexane molecules. Furthermore, the Si/Al ratios are also rather comparable, except for Y (Table 1). It can be concluded that zeolite Beta, Y, ZSM-5, mordenite, MCM-22 and MCM-41 are in essence 'comparable' catalysts in liquid-phase reactions. Differences may arise, however, when very polar solvents are applied.

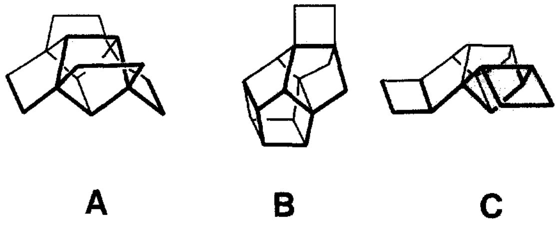
Table 1
Some physico-chemical properties of various zeolites

Zeolite type	Si/Al [b] (bulk)	Pore volume (ml/g)	Crystal size [c] (μm)
Beta [a]	5	0.28	0.05
Y	2	0.34	0.20–1
ZSM-5	10	0.13	0.20–100
Mordenite	5	0.25	0.20–1
MCM-22	10	0.20	0.50
MCM-41	15	0.50	0.50–1

[a] See Ref. [13]a–d.
[b] Minimum value.
[c] From regular synthesis.

3. Stacking faults and local defects in zeolite Beta

Crystallographic faulting is often observed in zeolite structures. Examples are the structures of zeolite analcite, dachiardite, offretite, erionite, gmelinite, mordenite, faujasite, L, ZSM-5, ZSM-11, ZSM-12 and ZSM-20 [15]. In zeolite Beta faulting is also frequently observed [8,14]. Zeolite Beta can be constructed from several tertiary building units (TBUs) [16] given in Scheme 1. The 16 *T*-membered TBU (A) is used in this study. Connection of TBUs after a simple translation over one unit-cell dimension in the *a*- and *b*-directions, produces layers perpendicular to the *c*-direction. Stacking of these layers can be achieved by rotation of a layer over ±90° with respect



Scheme 1. Tertiary building units (TBUs) for zeolite Beta; (A) is used in this study.

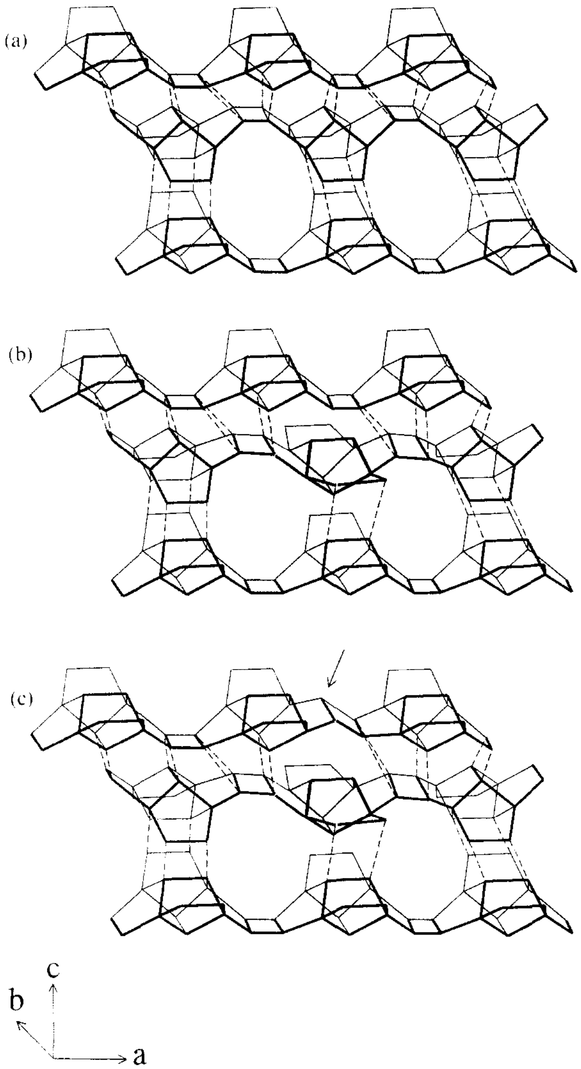


Fig. 2. (a) Stacked layers of ordered TBUs resulting in a perfect framework; (b) local defect, induced by one TBU which has been rotated 90° around the c-direction with respect to the neighbouring TBUs in the same layer (see text); and (c) relief of local strain by inverting T-atoms, indicated by the arrow.

to the preceding layer accompanied by a shift of $1/3(a+b)$ (Fig. 2a). When these 4_3 and 4_1 operations alternate randomly [8], fault planes occur. This disordered stacking of layers does not obstruct the micropores or affect the micropore volume. The unique catalytic properties of zeolite Beta, however, are not ascribed to this disorder.

Local defects are created upon connecting two layers in which one of the layers contains a TBU which is rotated over another 90° around c-direction with respect to the connecting TBUs in the same layer. The rotated TBU can connect reasonably well with its adjoining units in the same layer. The connection with neighbouring TBUs in the adjacent layers, however, is severely obstructed. This results in local unsaturated bonding, depicted in Fig. 2b. The local strain may be relieved by inverting several T-atoms (Fig. 2c), thereby introducing potential Lewis-acid sites. Experimental data that support the presence of these local defects are: (i) the observed hydroxyl IR-absorption bands [17]; and (ii) the excess exchange of cations with respect to the Al-content [18]. In addition, the small pyramids in the c-direction [8], frequently observed in zeolite Beta crystals (Fig. 3), also might be an indication for the presence of local defects in the layers.

The aluminium atoms in zeolite Beta can produce Brønsted as well as Lewis acidity. The first type of acidity is introduced by aluminium atoms that are tetrahedrally coordinated in a locally perfect framework. Al-sites located at the external surface, probably terminated by hydroxyl groups, also require a charge compensating proton, thus producing Brønsted acidity as well. It is concluded that Brønsted acidity is present both on the internal and external surface. As already discussed, local defects comprise partially coordinated aluminium atoms giving rise to Lewis acidity. These aluminium atoms are always located between two neighbouring TBUs (Fig. 2b). Therefore, Lewis sites are predominantly present on the internal surface. The presence of both internal and external Bronsted-acid sites and mainly internal Lewis-acid sites in zeolite Beta is in harmony with catalytic data, as will be discussed below.

The occurrence of the defects described here depends on the specific TBU chosen in this study. Similar defects could not be created with the other TBUs in Scheme 1. This might indicate that TBU (A) is not without significance in crystal growth.

4. Acid catalysed conversions over zeolite Beta

4.1. *Lewis acid catalysed Meerwein–Ponndorf–Verley (MPV) reductions*

Recently, we reported the application of zeolite Beta in the stereoselective (> 95%) MPV reduction

Fig. 3. A relatively large crystal of zeolite Beta; the arrow indicates the small pyramids.

of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol in the liquid phase [7,19]. This zeolite-based catalyst proved to be fully regenerable without loss in activity or stereoselectivity. The *cis*-isomer is the compound of industrial interest, the *trans*-isomer is not. Commercially a 70/30 *cis*/*trans* mixture is achieved and applied. Other active heterogeneous catalysts, including zeolites, invariably gave the thermodynamically more stable *trans*-isomer (Table 2). FT-IR results indicated a relation between the catalytic activity and the amount of aluminium which is only partially bonded to the framework (Lewis-acid sites). As already discussed, such aluminium sites result from local defects. The MPV mechanism was proposed to involve a six-membered transition state which is formed upon chemisorption of a secondary alcohol (the H-donor) on a Lewis-acid aluminium site and coordination of the ketone (to be reduced) to the same site. The transition states which lead to the *cis*- or *trans*-alcohol were shown to differ substantially in spatial requirements; whereas those for the *cis*-isomer were more or less linear in form and aligned with the channel while the formation of the *trans*-alcohol requires an axially oriented (bulkier) transition state. More coordination possibilities are available for the *cis*-transition state, which can easily be accommodated within the straight channels (Fig. 4). The observed kinetically determined product distribution is thus satisfactorily explained by true transition-state selectivity.

The crystallites of zeolite Beta are usually very rough and have a diameter of approx. 50 nm. They possess a large external surface, in particular cases up to 250 m^2/g, which is approx. 35% of its total surface area [20]. The high stereoselectivity of zeolite Beta in the Lewis-acid catalysed MPV reduction of 4-*tert*-butylcyclohexanone to the *cis*-alcohol, however, indicates that the reaction almost exclusively takes place within the micropores of the zeolite. Apparently, Lewis-acid sites are mainly present in the micropores and not on the external surface. This was confirmed by a catalytic test reaction in which the bulky probe

Table 2
MPV reduction of 4-*tert*-butylcyclohexanone with 2-propanol to 4-*tert*-butylcyclohexanol over various heterogeneous catalysts [a].

Catalyst [b]	Si/Al	Conv. (%)	Sel. (%)	*cis:trans*
Na-BEA(1)	12.5	32	> 95	96 : 4
NH_4-BEA(1)	12.5	30	> 95	95 : 5
All-Si BEA	>5000	0	—	—
Na-Y	2.5	0	—	—
NH_4-Y	2.5	0	—	—
USY	2.5 (bulk)	24.4	approx. 85	9 : 91
NH_4-MOR [c]	6.5	0	—	—
Deal-MOR [c]	32	0	—	—
H-MCM-41 [c]	15	10	approx. 80	10 : 90
Na-MCM-41 [c]	15	10	> 95	10 : 90
H-MCM-22	15	33	approx. 25	24 : 76
Silica–alumina	2	19	> 95	9 : 91
γ-Al_2O_3	—	45	> 95	9 : 91

[a] Reaction conditions: 2.5 mmol 4-*tert*-butylcyclohexanone, 25 ml dry 2-propanol, 0.5 g catalyst, under reflux and stirring; reaction time 6 h.
[b] Activation temperature 500°C.
[c] Activation temperature 430°C.

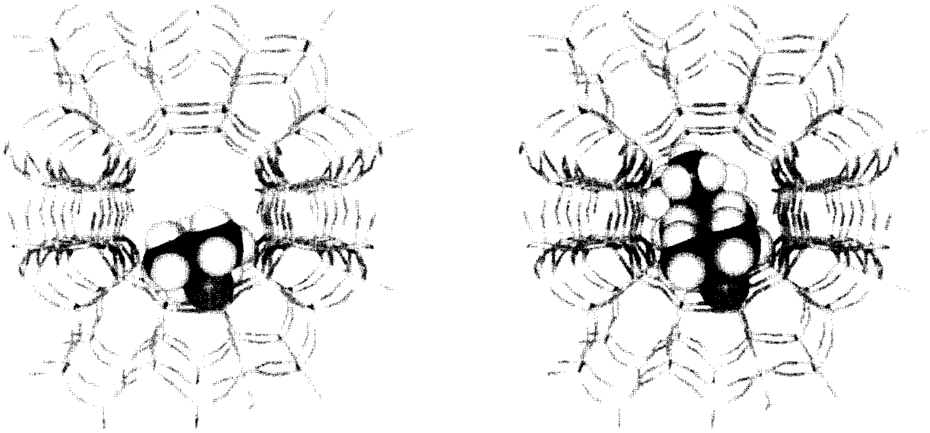
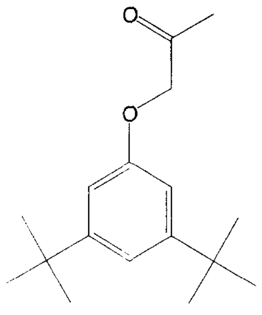


Fig. 4. Transition states, spatial pictures, for the formation of *cis*-4-*tert*-butylcyclohexanol (left), and *trans*-4-*tert*-butylcyclohexanol (right), accommodated in a straight channel of zeolite Beta.

molecule 1-(3,5-di-*tert*-butylphenoxy)propan-2-one



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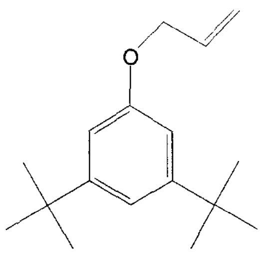
(dimensions: 0.58 × 1.1 × 1.1 nm) was applied. This molecule, which is too large to enter the micropores, could not be reduced with zeolite Beta [7,19]. Other Lewis-acid solid catalysts, however, proved to be active.

4.2. *Brønsted-acid catalysed reactions*

A study on the external surface Brønsted acidity of zeolite H-Beta was carried out with the bulky probe molecule allyl 3,5-di-*tert*-butylphenyl ether



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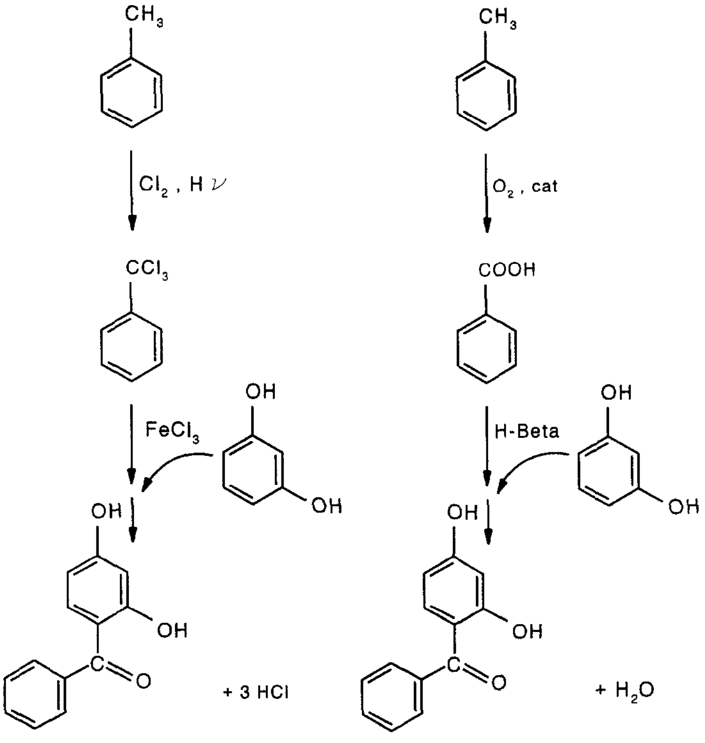
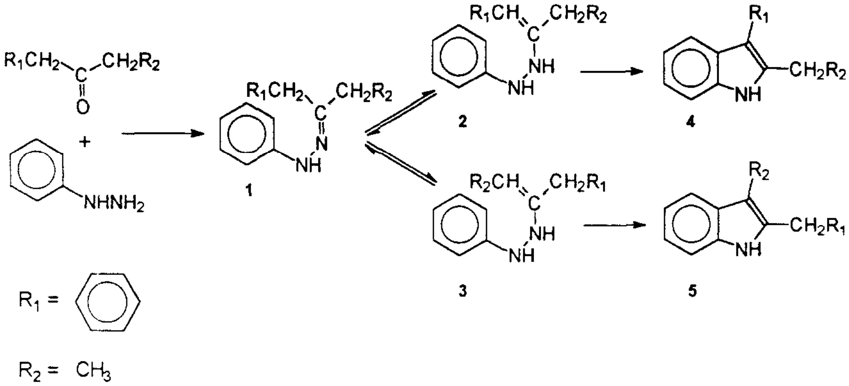
(1.1 × 1.1 × 0.58 nm) which is too large to enter the micropores. The Brønsted-acid catalysed Claisen rearrangement of this molecule, followed by the cyclisation of the primary product to 4,6-di-*tert*-butyl-2-methyldihydrobenzofuran, illustrates the presence of Brønsted-acid sites on the external surface of zeolite Beta [21].

The direct Fries reaction of resorcinol and benzoic acid is another example of the potential of zeolite Beta in fine chemical synthesis [2]. The present industrial process and the zeolite H-Beta catalysed route are depicted in Scheme 2. The industrial route is accompanied by a large amount of inorganic waste, whereas the zeolite H-Beta catalysed synthesis in essence produces no waste. The observed activity of zeolite H-Beta in the reaction between resorcinol and 2,6-dimethylbenzoic acid indicates that Brønsted-acid sites are present on the external surface. The dimensions of the product, 2,4-dihydroxy-2′,6′-dimethylbenzophenone, are 0.75 × 0.85 × 0.9 nm, which exceed the pore dimensions of zeolite H-Beta. This was confirmed by performing an experiment with zeolite H-Beta of which the external surface was dealuminated with EDTA while the zeolite was still loaded with template. Here, the Fries rearrangement did not take place at all [2].

The Fischer indole synthesis of 2-benzyl-3-methylindole from phenylhydrazine and 1-phenyl-2-butanone catalysed by zeolite Beta is an example of shape selectivity [4,22]. As shown in Scheme 3, the use of a non-symmetrical ketone will result in two isomeric indoles 4 and 5. The reaction is believed to involve a fast [3,3]-sigmatropic rearrangement of the enehydrazine tautomers 2 and 3 which, in turn, are formed from



Scheme 2. Industrial (left) and H-Beta catalysed route (right) to 2,4-dihydroxybenzophenone.



Scheme 3. Reaction scheme for the Fischer indole synthesis.

the hydrazone 1. The formation of 2 and 3 from 1, catalysed by both Lewis and Brønsted acids, is probably rate-determining.

An approx. 75 : 25 ratio of the 4 : 5 isomers was observed for the catalytic experiments when the reaction was catalysed by organic acids. The use of silica–alumina or acidic Filtrol clay results in only minor selectivity changes in favour of the isomer 5 (approx. 70 : 30). The use of (H,Na)-Y or H-mordenite further increased the selectivity for the 5 isomer, but the effect was negligible (approx. 65 : 35). Zeolite Beta, however, was found to be selective for the formation of the 5 isomer (31 : 69). A further improvement was obtained after minimisation of the outer-surface Brønsted acidity by selective dealumination of the as-synthesised zeolite with EDTA. This catalyst produced isomer 5 with a high selectivity of 82% at full conversion.

Adsorption experiments performed at reaction temperature, employing isomers 4 and 5, showed that zeolite Beta is fully selective in sorbing the smaller isomer 5, whereas zeolite Y also sorbs the larger isomer 4. These data and molecular dimensions indicate that the formation of both enehydrazines 2 and 3 inside the micropores of zeolite Beta should be possible. Isomer 2, however, is probably severely hindered in adopting the conformation required for indolization. This conformation is even bulkier than the indole isomer 4 which is formed from it. The shape-selective Fischer synthesis of 2-benzyl-3-methylindole 5 catalysed by zeolite Beta is, therefore, another example of transition-state selectivity.

5. Conclusions

Zeolite Beta has Brønsted-acid sites in the micropores and on the relatively large external surface. Lewis-acid sites, however, are predominantly present at the internal surface. They are related to local defects. These defects occur when a TBU is rotated 90° around the *c*-direction with respect to the neighbouring TBUs in the same layer. The rotated TBU cannot connect properly with the adjacent layers. This results in *T*-atoms which are not fully connected to the framework. The unique combination of optimal pore dimensions and Lewis-acid sites in the micropores of zeolite Beta results in the remarkably high stereoselectivity of zeolite Beta in the MPV reduction of 4-*tert*-butylcyclohexanone to the *cis*-alcohol. This result demonstrates the potential of zeolite Beta as Lewis-acid catalyst in shape-selective organic conversions.

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