# Hydrolytic cleavage of epoxy ring during the epoxidation of alkenes over boron modified titanium silicalites of MFI topology

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Boron incorporated bifunctional microporous titanium silicalites of MFI topology, which contained both oxidizing and acidic sites, can effectively catalyse the selective epoxidation of $\alpha$-olefins, followed by ring opening of the epoxide through hydrolysis reactions. Data are presented that correlate the oxidative and acidic functions of these catalysts. The rate of hydrolysis is seen to depend on the phases generated by incorporation of the boron atoms.

**Keywords:** titanium silicalites, titanium boralites, hydrolytic cleavage, alkenes epoxidation, $H_2O_2$, diols

## 1. Introduction

The possibility to use heterogeneous catalysts in the liquid phase offers a number of advantages compared with their homogeneous counterparts, e.g. recycling, ease of recovery, and enhanced stability [1]. The recent advances in the application of microporous titanium silicalites (TS-1) represented that TS-1 is an effective epoxidation catalyst for selective oxidation reactions with aqueous hydrogen peroxide [2], since water is detrimental to conventional titania-based catalysts and no environmentally undesirable side products are formed from hydrogen peroxide reaction. Recently, Camblor and Corma et al. [3,4] have shown the influence of the alkene structure, as well as of the type of oxidant used ($H_2O_2$ or *t*-butyl hydroperoxide) in the oxidation of olefins on a Ti-substituted beta zeolite. In a more recent report [5] they have disclosed that mesoporous Ti-MCM-41 can accommodate bulkier molecules for the selective epoxidation reaction. Hutchings et al. [6,7] have reported the control of product selectivity in the epoxidation of allyl alcohol by variation of the acidity of the titanium silicalites (TS-1) catalyst. The further cleavage of the epoxide group by hydrolysis, which may lead to additional products, has received little attention. Therefore, there is an increasing interest in such bifunctional catalysts because the epoxide group may be readily opened to produce 1,2 functionality in a stereospecific manner [8]. Jacobs et al. [9] have also shown that the epoxidation of cyclohexenes can be achieved using zeolites-encapsulated Mn(II) complexes, followed by acid catalysed ring opening and carbon–carbon bond cleavage. The simultaneous incorporation of a trivalent metal ion, e.g. $B^{3+}$, $Al^{3+}$, $Ga^{3+}$ and $Fe^{3+}$, along with $Ti^{4+}$ has been reported for the zeolitic [10,11] and amorphous silica materials [12]. These modified silica materials are shown to be active in oxidation as well as acid catalysed reactions [13]. In a recent report [14], we have demonstrated that the epoxidation of $\alpha$-pinene and subsequent secondary ring opening reaction through hydrolysis, toward the formation of corresponding diols, can be achieved by simultanous incorporation of titanium and a trivalent ion ($B^{3+}$, $Al^{3+}$ and $Fe^{3+}$). Since both the oxidation and the acid functions depend on whether the ions are in framework or extraframework positions, we have performed a more detailed study of the effect of boron incorporation on the catalytic activity, as well as the solvent effect in the epoxidation reaction. The reactions involve epoxidation of an $\alpha$-olefin by $H_2O_2$ followed by hydrolytic cleavage of the epoxy ring yielding the corresponding 1,2 diols. In this work, we compare the reactivity of titanium silicalite (TS-1), titanium boralite (TBS-1) and titanium silicalites treated with boric acid or borax, in the presence of and without a solvent, for the epoxidation of hex-1-ene and oct-1-ene with hydrogen peroxide.

## 2. Experimental

The synthesis of titanium silicalite ($Ti/Si = 0.015$) and titanium boralites ($Ti/Si = 0.014$, $B/Si = 0.027$) catalysts were carried out using gels of the following gel compositions: 0.40 TPAOH-0.015 $TiO_2$-$xB_2O_3$-$SiO_2$-35 $H_2O$ (where $x = 0.0$ or 0.05). The gels were charged in teflon-lined autoclave and maintained in hydrothermal conditions for five days at 488 K. The solids were filtered, washed, dried and then calcined under a continuous flow of dry oxygen gas at 823 K. The typical synthesis procedure is described elsewhere [11,15]. For comparison, TS-1 treated with boric acid and TS-1 treated with borax ($Na_2B_2O_7 \cdot 10H_2O$) were also prepared. This treatment is performed at room temperature by

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directly dispersing the catalyst into the well stirred clear solution of boric acid or borax (~ 2.7 wt% boron). Stirring is maintained for 1 h, the solid is then filtered and dried at 403 K in vacuum for 10 h.

The X-ray diffraction (XRD) patterns of these materials were measured using a Rigaku D-Max.II VC X-ray diffractometer using nickel filtered Cu K$\alpha$ ($\lambda = 1.5406$ Å) radiation. The unit cell volumes were calculated from XRD using silicon as an internal standard. Infrared (FTIR) spectra were recorded for catalyst powder tabletted with KBr on a Bomen 102 FTIR spectrometer. Diffuse reflectance UV-spectra were obtained using a Perkin-Elmer Lambda 5 spectrophotometer using MgO as a standard. The catalysts were also characterized by $^{11}$B-MAS-NMR. The spectra were recorded on a Bruker CXP-300 spectrometer by a one-cycle type measurement. The details are already described elsewhere [15].

The peroxide oxidation reaction, namely the epoxidation followed by hydrolysis, is carried out to demonstrate the exceptional efficiency of these catalysts. These materials have been used as catalysts in the epoxidation of hex-1-ene and oct-1-ene. The kinetic experiments were conducted under identical conditions with continuous stirring in a glass batch reactor with reflux without any loss of products through evaporation during the reaction. At 328 K using 0.25 g catalyst, 0.116 mol of hex-1-ene or 0.089 mol of oct-1-ene was mixed with 0.044 mol of aqueous $H_2O_2$. For comparison, the reactions were carried out in the presence of a solvent (0.109 mol of ethanol) and without solvent. Product aliquots were taken at selected reaction times for analysis in a gas chromatograph (HP 5890) equipped with a 30 m capillary (DB-Wax) column using a FID detector. The conversions are given as mol% of the substrate consumed at a given time and limited by the initial substrate to $H_2O_2$ ratio in the reaction mixture.

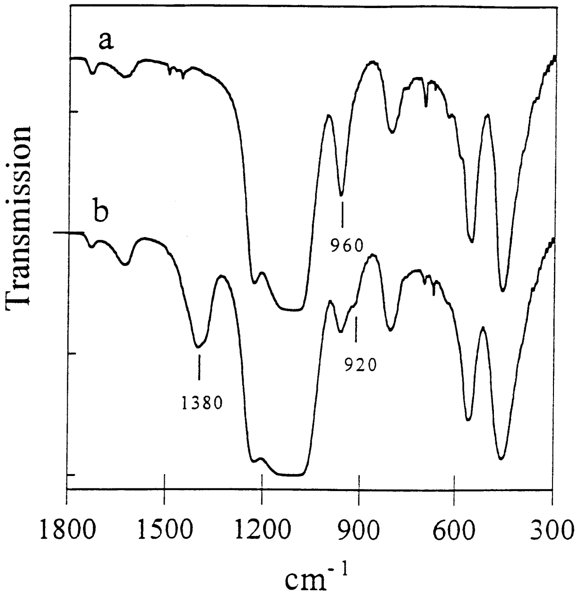

Fig. 1. FTIR spectra of (a) titanium silicalite (1.5 wt% Ti) TS-1 and (b) titanium boralite (1.5 wt% Ti–2.7 wt% B) TBS-1, calcined at 823 K in air for 6 h.

## 3. Results and discussion

The X-ray diffraction patterns of these materials revealed a pnma-orthorhombic symmetry from which the indexation was performed. The unit cell volume was estimated using the different reflections in the XRD pattern with the absolute accuracy of about 10 Å$^3$. The addition of boron leads to a decrease of the unit cell volume from 5375 Å$^3$ (TS-1) to 5325 Å$^3$ (TBS-1), consistently with literature data [16], which supports the incorporation of titanium and boron in the framework lattice.

The isomorphous substitution of Si by Ti and/or B in both catalysts was assessed by FTIR characterization (fig. 1). The band which appears at ca. 960 cm$^{-1}$ in the IR spectrum of TS-1 corresponds to Si–O–(Ti) groups in the framework of TS-1 [17], whereas the bands at ca. 920 cm$^{-1}$ and 1380 cm$^{-1}$ in TBS-1 are assigned to tetra- and trigonal co-ordinated framework boron respectively [11,15]. The UV–Vis absorption between 270 and 400 nm exhibits a broad peak assigned to $TiO_2$ anatase, while below 270 nm, an intense peak is assigned to isolated titanium species incorporated in the framework [18]. The UV–Vis spectra of TS-1 and TBS-1 are quite similar (fig. 2). They exhibited an intense band at 210 nm clearly showing that titanium is in framework position [15]. The UV–Vis spectra of TBS-1 show an extraframework band along with the framework titanium band at 210 nm, thus indicating that extraframework titanium species are systematically generated in the presence of boron. The $^{11}$B-

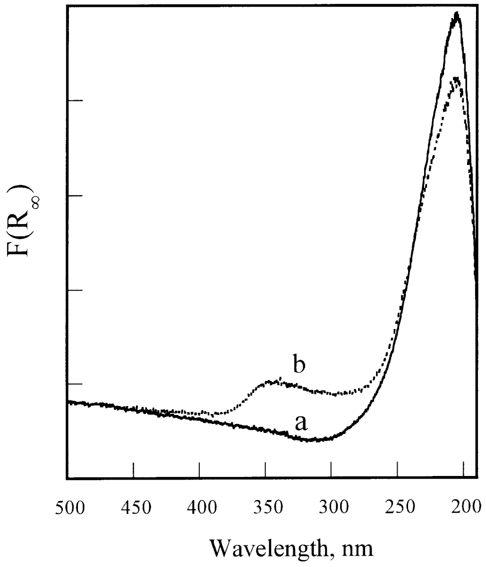

Fig. 2. UV–Visible diffuse reflectance spectra of (a) titanium silicalite (1.5 wt% Ti) TS-1 and (b) titanium boralite (1.5 wt% Ti–2.7 wt% B) TBS-1, calcined at 823 K in air for 6 h.

MAS-NMR spectrum showed a signal at ca. −3.7 ppm indicating that boron atoms had been incorporated into tetrahedral sites in the MFI structure.

The catalytic activity of these Ti-silicalites is expressed in terms of alkenes and $H_2O_2$ conversions, $H_2O_2$ selectivity to epoxidation products and product distribution under one set of reaction conditions. The catalytic results are summarised in tables 1 and 2 respectively. The proposed reaction scheme is given in fig. 3. The results (table 1) indicate that in the epoxidation of hex-1-ene with $H_2O_2$ over TS-1, in the presence of ethanol as a solvent, a maximum 8.0% conversion can be achieved with 100% selectivity to epoxides after 5 h of reaction. The incorporation of boron in the framework of a zeolite known to introduce mild acidic bridging (Brønsted acidic) sites leads to the cleavage of the epoxide group and the formation of diols, the products of secondary reaction namely hydrolysis. As the reaction time is increased the hex-1-ene conversion increases, whereas the epoxide selectivity decreases while diols formation increases. The 6.1% hex-1-ene conversion was reached after 5 h reaction with 52.4% selectivity to epoxide and 46.6% selectivity to diols (21.2 and 26.4% selectivity to 1,2-hexanediol (12HxDOL) and 2-ethoxyhexane-1-ol (2EHx1OL) respectively). For comparison, we have included the results obtained on the catalytic activity of the TS-1 and TBS-1 in the absence of ethanol solvent (table 1). Under the same reaction conditions, the hex-1-ene conversion is slightly lower; however, a significant difference in the product distribution is noticed. Selectivity for diol over TBS-1 is higher (74.0%) in absence of the solvent. In the presence of the solvent (ethanol) over TS-1, there is nevertheless a fair conversion of $H_2O_2$ (27.0% after 5 h) showing a little $H_2O_2$ decomposition with $H_2O_2$ selectivity over 77.9%, quite higher than the one observed with TBS-1 (67.7%). The $H_2O_2$ selectivity and conversion are not much affected in the absence of the solvent and are in a similar range.

Concerning the epoxidation activity of oct-1-ene, table 2 compares our results on the epoxidation of oct-1-ene over these Ti-silicalites. The performance of the catalysts appear to be similar to those observed with hex-1-

Table 1
Epoxidation of hex-1-ene over TBS-1 and various boron containing TS-1

| Catalyst | *t* (h) | Hex-1-ene conversion (mol%) | $H_2O_2$ [c] | | Product selectivity (mol%) | | |
|---|---|---|---|---|---|---|---|
| | | | conversion (mol%) | selectivity (mol%) | epoxide | diols | |
| | | | | | | 12HxDOL [d] | 2EHx1OL [e] |
| *with solvent ( ethanol)* | | | | | | | |
| TS-1 | 1 | 2.9 | 9.1 | 84.1 | 100 | 0 | 0 |
| | 3 | 5.0 | 16.6 | 79.3 | 100 | 0 | 0 |
| | 5 | 8.0 | 27.0 | 77.9 | 100 | 0 | 0 |
| TBS-1 | 1 | 1.7 | 6.2 | 73.7 | 64.5 | 12.2 | 23.3 |
| | 3 | 4.4 | 16.4 | 70.1 | 54.6 | 20.3 | 25.1 |
| | 5 | 6.1 | 23.6 | 67.7 | 52.4 | 21.2 | 26.4 |
| TS-1 [a] | 1 | 0.7 | 5.9 | 32.7 | 100 | 0 | 0 |
| | 3 | 0.9 | 12.2 | 20.0 | 100 | 0 | 0 |
| | 5 | 1.1 | 19.0 | 15.0 | 100 | 0 | 0 |
| TS-1 [b] | 1 | 1.5 | 6.8 | 59.7 | 97.9 | 0.9 | 1.2 |
| | 3 | 3.8 | 17.9 | 58.3 | 97.4 | 1.1 | 1.4 |
| | 5 | 5.4 | 26.9 | 52.8 | 97.2 | 1.1 | 1.7 |
| *without solvent* | | | | | | | |
| TS-1 | 1 | 2.8 | 9.3 | 78.6 | 100 | 0 | 0 |
| | 3 | 4.5 | 15.2 | 77.4 | 100 | 0 | 0 |
| | 5 | 7.0 | 24.5 | 75.6 | 100 | 0 | 0 |
| TBS-1 | 1 | 1.5 | 6.1 | 64.2 | 72.5 | 27.5 | 0 |
| | 3 | 3.8 | 14.7 | 67.9 | 60.1 | 39.9 | 0 |
| | 5 | 5.7 | 22.1 | 68.0 | 26.0 | 74.0 | 0 |
| TS-1 [a] | 1 | 0.3 | 4.7 | 29.8 | 100 | 0 | 0 |
| | 3 | 0.5 | 11.3 | 21.6 | 100 | 0 | 0 |
| | 5 | 0.9 | 16.5 | 19.8 | 100 | 0 | 0 |
| TS-1 [b] | 1 | 1.1 | 6.3 | 48.0 | 95.7 | 4.4 | 0 |
| | 3 | 3.4 | 15.6 | 57.1 | 91.4 | 8.6 | 0 |
| | 5 | 4.9 | 21.4 | 60.2 | 87.8 | 12.2 | 0 |

Reaction conditions: catalyst (g) = 0.25; hex-1-ene (mol) = 0.1163; $H_2O_2$ (30% aqueous solution) = 5 g; reaction temperature (K) = 328; reaction duration = 5 h; solvent[ethanol (5 g)]; [a] treated with borax, [b] treated with boric acid, [c] $H_2O_2$ selectivity: $H_2O_2$ utilization in the formation of oxy-functionalization products. [d] 12HxDOL: 1,2-hexanediol, [e] 2EHx1OL: 2-ethoxyhexane-1-ol.

Table 2
Epoxidation of oct-1-ene over TBS-1 and various boron containing TS-1

| Catalyst | *t* (h) | Oct-1-ene conversion (mol%) | $H_2O_2$ [c] | | Product slectivity (mol%) | | |
|---|---|---|---|---|---|---|---|
| | | | conversion (mol%) | selectivity (mol%) | epoxide | diols | |
| | | | | | | 12OcDOL[d] | 2EOc1OL[e] |
| *with solvent (ethanol)* | | | | | | | |
| TS-1 | 1 | 1.8 | 7.9 | 79.4 | 100 | 0 | 0 |
| | 3 | 3.4 | 13.3 | 78.1 | 100 | 0 | 0 |
| | 5 | 6.3 | 24.2 | 75.4 | 100 | 0 | 0 |
| TBS-1 | 1 | 1.6 | 5.8 | 56.0 | 63.1 | 28.7 | 8.2 |
| | 3 | 3.0 | 11.6 | 51.4 | 52.8 | 35.3 | 11.9 |
| | 5 | 5.4 | 18.8 | 57.7 | 45.6 | 33.4 | 21.0 |
| TS-1[a] | 1 | 0.2 | 5.3 | 24.6 | 100 | 0 | 0 |
| | 3 | 0.5 | 10.9 | 18.1 | 100 | 0 | 0 |
| | 5 | 0.8 | 16.8 | 12.2 | 100 | 0 | 0 |
| TS-1[b] | 1 | 1.1 | 5.4 | 46.8 | 78.9 | 17.7 | 3.4 |
| | 3 | 2.6 | 12.6 | 43.9 | 72.2 | 14.3 | 13.5 |
| | 5 | 4.2 | 21.9 | 40.7 | 70.1 | 9.1 | 20.8 |
| *without solvent* | | | | | | | |
| TS-1 | 1 | 1.7 | 6.6 | 67.0 | 100 | 0 | 0 |
| | 3 | 3.1 | 11.5 | 73.1 | 100 | 0 | 0 |
| | 5 | 5.7 | 20.1 | 74.7 | 100 | 0 | 0 |
| TBS-1 | 1 | 1.1 | 5.3 | 55.2 | 57.5 | 42.5 | 0 |
| | 3 | 2.3 | 10.5 | 58.5 | 53.3 | 46.7 | 0 |
| | 5 | 5.0 | 19.1 | 68.7 | 31.7 | 68.3 | 0 |
| TS-1[a] | 1 | 0.2 | 4.2 | 10.9 | 100 | 0 | 0 |
| | 3 | 0.5 | 8.3 | 15.1 | 100 | 0 | 0 |
| | 5 | 0.7 | 10.4 | 17.8 | 100 | 0 | 0 |
| TS-1[b] | 1 | 0.9 | 5.3 | 45.6 | 77.0 | 23.0 | 0 |
| | 3 | 2.5 | 12.7 | 51.4 | 69.8 | 30.2 | 0 |
| | 5 | 3.9 | 18.5 | 54.9 | 63.3 | 36.7 | 0 |

Reaction conditions: catalyst (g) = 0.25; oct-1-ene (mol) = 0.089; $H_2O_2$ (30% aqueous solution) = 5 g; reaction temperature (K) = 328; reaction duration = up to 5 h; solvent[ethanol (5 g)];[a] treated with borax,[b] treated with boric acid,[c] $H_2O_2$ selectivity: $H_2O_2$ utilization in the formation of oxyfunctionalization products.[d] 12OcDOL: 1,2-octanediol,[e] 2EOc1OL: 2-ethoxyoctane-1-ol.

ene. The conversions are slightly lower with oct-1-ene than with hex-1-ene, both in the presence and even in the absence of the solvent. The $H_2O_2$ conversion and selectivity are also lowered. The very interesting observation is the product distribution, quite similar with both substrates, formation of the 2-ethoxyalkane-1-ol (2EOc1OL), only in the presence of ethanol as a solvent. With increasing reaction time (upto 5 h), a comparatively lower selectivity of epoxides (45.6%) and increased formation (33.4%) of 1,2-octanediols (12OcDOL) and solvolysis products 2EOc1OL (21.0%), clearly indicate that framework incorporation of boron presents the milder acidic bridging sites and positively favours the hydrolysis and solvolysis reactions. Even though the epoxidation of oct-1-ene over TBS-1 in absence of a solvent is also taking place, the selectivity to diols are very impressive (68.3%). No heavier elimination products such as ethers of 1,2-hexanediol or 1,2-octanediol or other similar diols solvolysis products are observed. Therefore, it is quite clear that the solvent may also be involved in the secondary ethanolysis reaction.

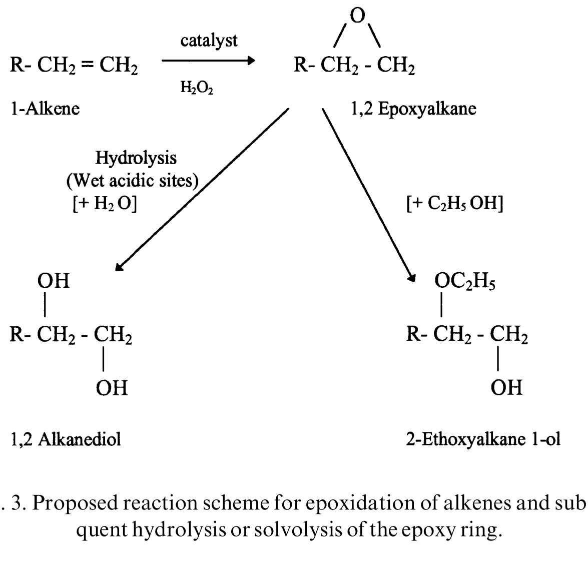

Fig. 3. Proposed reaction scheme for epoxidation of alkenes and subsequent hydrolysis or solvolysis of the epoxy ring.

Further experiments were carried out in which TS-1 was treated with boric acid or borax (~ 2.7 wt% boron).

For both substrates with solvent, compared to TS-1 and TBS-1, the boric acid treated TS-1 shows lower conversions 5.4 and 4.2% for hex-1-ene and oct-1-ene respectively. In the case of hex-1-ene, 97.2% selectivity to epoxide, 1.1 and 1.7% selectivity to 12HxDOL and 2EHx1OL respectively were observed, while comparatively higher selectivities for 12OcDOL (9.1%) and 2EOc1OL (20.8%) are noticed with oct-1-ene. Interestingly, these boric acid treated TS-1 catalysts show comparatively fair activity in secondary ring opening reaction in the absence of the solvent. The selectivity for diols reached 12.2 and 36.7% for hex-1-ene and oct-1-ene respectively. The lower $H_2O_2$ selectivity with TBS-1 as compared to TS-1 can be explained by the effect of boron on $H_2O_2$ decomposition. Hence, the TBS-1 contains additional mild Brønsted acidic sites that are the hydroxyl groups adjacent to the framework boron and which favour the $H_2O_2$ decomposition [12] simultaneously with epoxide ring opening, resulting in a loss of epoxidation activity. Treatment of TS-1 with borax solution (~ 2.7 wt% boron) resulted in a net loss of catalytic activity, although the only product is epoxide for both substrates. The conversions are quite lower, only 1.1 and 0.8 mol% for hex-1-ene and oct-1-ene respectively after 5 h. This clearly suggests that the epoxidation sites of TS-1 can be poisoned by sodium. Moreover, this further confirms that sodium has a significant effect on the reaction rate of alkenes epoxidation and strictly hinders the secondary ring opening reactions, whereas the activity for secondary ring opening reaction follows the order: TBS-1 > TS-1 treated with boric acid > TS-1 treated with borax.

The function of TBS-1 and boric acid treated TS-1 catalysts are quite similar except their performance in the catalytic activity. The significant difference was noticed in the catalytic activity for secondary ring opening reactions (hydrolysis). Moreover, the comparison between the activities of TBS-1 and boric acid treated TS-1 catalysts should be based on whether the boron occupies framework or extraframework position rather than on mere boron content. The observed difference in $H_2O_2$ selectivity is entirely explained by the higher $H_2O_2$ decompositon rate associated with the different species of boron present in TBS-1 and boric acid treated TS-1 catalysts.

## 4. Conclusion

This catalytic oxidation work shows the importance of bifunctional acidic oxidation catalysts which promote epoxidation of alkenes by $H_2O_2$ followed by hydrolytic cleavage of the epoxy ring yielding the corresponding 1,2 diols. The presence of ethanol as a solvent results in the decrease of diols formation and leads to the solvolysis reaction. The Ti provides the epoxidation site, whereas the mild acidity associated with the BOH site allows selective hydrolysis of the epoxide ring while avoiding the side reaction of olefins which is known to take place with more strongly acidic sites. Thus, the results of this study clearly show that the presence of mild acid sites promotes the hydrolysis reaction and their strength is low enough to prevent secondary oxidation and selectively permits the solvolysis reaction in the presence of solvent in epoxidation. Detailed kinetic studies are in progress to optimise the catalytic performance.

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