Zeolite titanium beta: a selective and water resistant catalyst in Meerwein–Ponndorf–Verley–Oppenauer reactions

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Aluminium-free zeolite titanium beta was found to be a selective and water stable catalyst in the Meerwein–Ponndorf–Verley reduction of alkylcyclohexanones and the Oppenauer oxidation of alkylcyclohexanol. 4-*t*-butyl- and 4-methylcyclohexanone were reduced with $> 98\%$ selectivity to the cis-alcohol. The high stereoselectivity is explained by transition-state selectivity.

Keywords: zeolite Ti-beta; Meerwein–Ponndorf–Verley reduction; Oppenauer oxidation; transition-state selectivity; 4-*t*-butylcyclohexanone; 4-*t*-butylcyclohexanol; methylcyclohexanones

1. Introduction

Zeolite beta is the only high-silica zeolite with a three-dimensional pore system containing large 12-membered ring apertures [1], which makes it very suitable as a regenerable catalyst in organic reactions. The synthesis of zeolite beta has been systematically studied since the material was discovered by Wadlinger and Kerr [2]. Despite its early discovery in 1967 [2], research reports concerning the application of zeolite beta in organic conversions long remained relatively scarce in the literature. In recent years, because of its structural characteristics, zeolite beta was successfully used in Friedel–Crafts type reactions of benzene and functionalized aromatics [3–5] and in the hydration and isomerization of bulky olefins, e.g. α-pinene [6]. Upon incorporation of titanium in the zeolite beta framework Camblor et al. [7] found zeolite titanium aluminium beta to be a promising catalyst in various oxygenations using hydrogen peroxide. The synthesis of aluminium-free analogues of zeolite beta is possible by using more selective templates [8]. Recently we reported the synthesis of an aluminium-free titanium zeolite beta [9] by further improvement of the template.

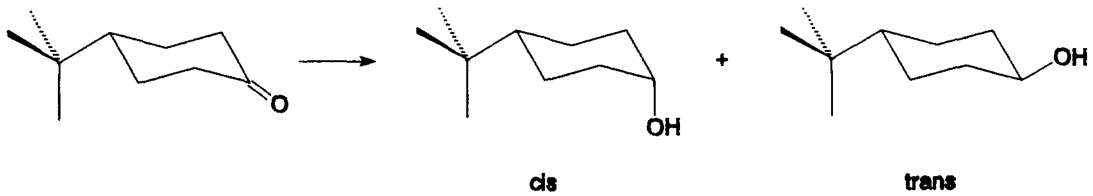
The Meerwein–Ponndorf–Verley reduction of carbonyl compounds and the Oppenauer oxidation of alcohols, together denoted as MPVO reactions, are considered to be highly selective reactions. For instance, C–C double bonds are not attacked. In MPV reductions a secondary alcohol is the reductant whereas in Oppenauer oxidations a ketone is the oxidant. It is generally accepted that MPVO reactions proceed via a complex in which both the carbonyl and the alcohol are coordinated to a Lewis acid metal ion after which a hydride transfer from the alcohol to the carbonyl group occurs [10]. Usually metal alkoxides derived from secondary alcohols are used as homogeneous catalyst in reductions and metal *t*-butoxides in oxidations. As has been reported by Bourgeat-Lami et al. [11], the aluminium in the framework of zeolite beta can exist in the normal zeolitic four-coordination as well as in partially or fully hydrolyzed forms. So, part of the aluminium in beta exhibits Lewis acidic properties. Accordingly, Creyghton et al. [12] recently reported the use of zeolite beta in the MPV reduction of 4-*t*-butylcyclohexanone. The high selectivity towards the thermodynamically less favored cis-alcohol is explained by a restricted transition state around a Lewis acidic aluminium in the zeolite pores [12].

The use of Lewis acid titanium complexes was reported by Li et al. [13], i.e. $Ti(OR)_4$ (R = Et, iPr, nBu), $TiCl_4$ and $Cp_2Ti(OPh)_2$ were used as catalysts for homogeneous MPVO reactions. $Ti(OiPr)_4$ was found to give the best catalytic activity, but it was also observed that catalytic amounts of $Ti(OiPr)_4$ did not reduce cycloalkanones. When using an aluminium free zeolite titanium beta (Ti-β) in the epoxidation of olefins, we have shown that Ti-β has acidic properties when alcoholic solvents were employed [9]. This indicated that the titanium site in beta can act as a Lewis acid. In the present work Ti-β is tested and compared with Al-β in MPVO reactions of alkylcyclohexanones and is found to be an excellent catalyst with a tolerance for water and low by-product formation.

2. Experimental

2.1. Materials

Samples of zeolite aluminium beta (Al-β) with Si : Al ratios greater than 10 were synthesized according to



Scheme 1.

Wadlinger and Kerr [2]. In a typical preparation 12.2 g sodium aluminate ($NaAlO_2$) was dissolved in 110 g tetraethylammonium hydroxide (40% w/w, TEAOH). To the clear solution 291.6 g Ludox LS (30% w/w colloidal silica) was added and the resulting gel was hydrothermally crystallized at 423 K for 6 days. After cooling the zeolite was washed, dried and calcined at 813 K. Titanium beta (Si : Ti = 76) was synthesized according to van der Waal et al. [9] using di(cyclohexylmethyl)dimethylammonium hydroxide as the template and activated at 540°C. The catalysts were characterized using XRD and AES/ICP. UV–Vis spectra (DREAS) were recorded on a Varian Cary-1 spectrophotometer using barium sulfate as a reference.

2.2. Catalytic reactions

The reductions of ketones were performed under stirring in refluxing isopropanol (25 ml, 358 K) using 2.5 mmol of the appropriate ketone (e.g. 4-*t*-butylcyclohexanone, methylcyclohexanone or cyclopentanone) and 1,3,5-tri-*t*-butylbenzene as internal standard. As the catalyst either 0.5 g zeolite, activated at 540°C, or 0.25 mmol metal alkoxide, $Al(OiPr)_3$ or $Ti(OiPr)_4$, were used.

The oxidations of 4-*t*-butylcyclohexanol were performed under stirring in butanone (25 ml, 358 K) using 2.5 mmol of a 1 : 1 cis : trans mixture of the alcohol and 1,3,5-tri-*t*-butylbenzene as internal standard. As the catalyst either 0.5 g zeolite, activated at 540°C, or 0.25 mmol metal alkoxide were used. Samples were taken at regular intervals and analyzed by GC and GC-MS.

3. Results and discussion

3.1. Catalyst characterization

As we reported earlier, Ti-β exhibits Brønsted acidic properties in the epoxidation of olefins using aqueous hydrogen peroxide when alcoholic solvents were employed [9]. This was explained on the basis of Lewis acidic properties of the tetrahedrally coordinated titanium atom, which on coordination with alcohols gives moderate to weak Brønsted acid sites. Some direct information on the state of the titanium can be obtained from the diffuse reflectance UV–Vis charge-transfer spectra (DREAS) of calcined Ti-β and from the effects of the adsorption of water and isopropanol. The presence of a strong absorption maximum at 47 000–50 000 cm^1 (see van der Waal et al. [9]) confirms that in the calcined material all titanium is incorporated in tetrahedral positions. Upon adsorption of either water or isopropanol a shift to lower wavenumbers occurs, which indicates a higher coordination number around the titanium atom, most probably five [9,14].

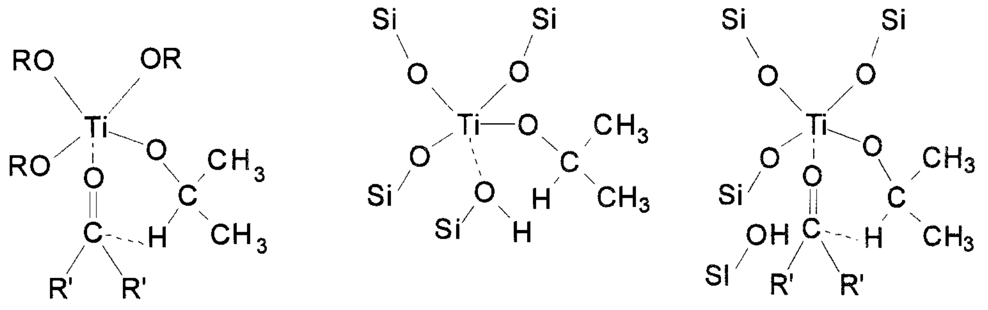
3.2. Titanium catalyzed Meerwein–Ponndorf–Verley reduction

Since the MPVO reactions are in general catalyzed by Lewis acids, Ti-β and various other titanium containing materials were tested in the reduction of 4-*t*-butylcyclohexanone (scheme 1). As can be seen from table 1 only Ti-β is able to catalyze the MPV reduction, although with a lower TOF than observed for Al-β. Other heterogeneous titanium containing materials, i.e. rutile (TiO_2) and TiO_2 on silica [15], were found to be inactive in the MPV reduction. The high selectivity towards the thermodynamically less favorable cis-alcohol, which is the isomer of industrial relevance, and the non-reactivity of homogeneous titanium isopropoxide, indicate that the reaction takes place over framework titanium and not over leached titanium species. This further confirms our belief that in the case of Ti-β the titanium site has considerable Lewis acidic properties.

Table 1
MPV reduction of 4-*t*-butylcyclohexanone over various titanium containing catalysts in refluxing isopropanol (2.5 mmol ketone, 0.5 g catalyst, 25 ml solvent, 1,3,5-tri-*t*-butylbenzene as internal standard)

Catalyst	TOF [d] (h^{-1})	Conversion [e] (%)	Selectivity [e] cis : trans
Ti-β(76) [a]	2.26	64.9	98 : 2
$Ti(OiPr)_4$ [b]		0.0	
Ti-MCM-41 (66) [a]		0.0	
Al-β(10) [a]	> 12	100.0	95 : 5
Si-β [c]		0.0	

[a] Values in parentheses indicate either Si : Ti or Si : Al ratios.
[b] 0.25 mmol catalyst used.
[c] All-silica zeolite beta prepared according to van der Waal et al. [6].
[d] Initial turn-over-frequency in mol ketone per mol titanium or aluminium per hour.
[e] Conversion and selectivity after 6 h reaction.



1 **2** **3**

Fig. 1. Catalytic sites for titanium catalyzed MPVO reactions.

3.3. *Catalytic site*

In the homogeneous system using titanium alkoxides, Li et al. [13] proposed that the reaction proceeds via a five-coordinated titanium transition state **1** (fig. 1). The DREAS spectra and the catalytic behavior of Ti-β in the epoxidation of olefins [9] indicate that alcohols can adsorb on the Ti site to give a five-coordinated species **2**. On replacement of the silanol group by a carbonyl group a transition state **3** similar to the homogeneous system, is obtained. Creyghton et al. [12] also propose that the formation of an aluminum alkoxide group is necessary for MPVO reactions to take place. We therefore suggest that the five-coordinated titanium species **2** and **3** are the active intermediates in the Ti-β catalyzed MPVO reactions.

The extremely high selectivity in the 4-*t*-butylcyclohexanone reduction towards the thermodynamically less favored cis-alcohol catalyzed by Al-β, is explained by Creyghton et al. [12] on the basis of transition-state selectivity. It can be seen in fig. 2, in an analogous way for Ti-β, that the transition states leading to the cis- and trans-alcohol differ substantially in spatial requirements. The transition state leading to the cis-isomer is aligned with the zeolite channel while that leading to the trans-alcohol occupies a much more axial position. Even with smaller alkyl groups than *t*-butyl or on other positions selectivity to the axial alcohol product prevails. Thus in the reduction of 4-, 3- and 2-methylcyclohexanone the thermodynamically less favored products, the cis-, trans- and cis-alcohol, respectively, were the major products (table 2). It is therefore assumed that the cycloalkane ring itself is already a structure directing group, favoring an equatorial attack of the hydride to give an axial alcohol group. When a 4-alkyl group is present, the selectivity is further enhanced towards > 98 cis-alcohol formation. In the case of 2-methylcyclohexanone a cis : trans ratio of 60 : 40 was observed. This is probably due to the close proximity of the methyl group to the catalytic site, which distorts the favorable cis transition state (fig. 2 left), leading to a lower selectivity and activity. The even more bulky 2-*t*-butylcyclohexanone could not be reduced at all under the present conditions.

3.4. *Poisoning tests*

The commonly used MPVO catalysts consist of metal alkoxides which are easily hydrolyzed to inactive oxides in the presence of water. The use of hydrophobic heterogeneous materials, high silica zeolites in particular, could be favorable. As shown in table 3, Ti-β hardly loses activity in the presence of 1 vol% water, while for both aluminium containing catalysts the activity drops significantly. The low decrease of the activity in the case of Ti-β can be explained by the hydrophobic interior of the nearly all-silica zeolite. As we reported earlier the sorption capacity for water of all-silica beta at 50°C is very

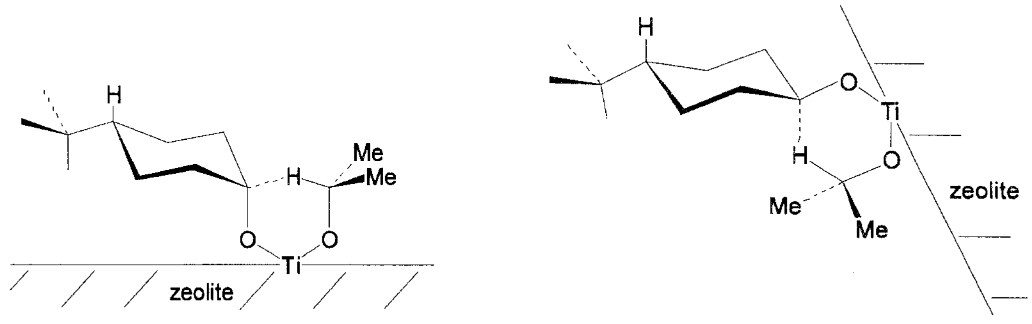


Fig. 2. Transition states for the formation of cis-4-*t*-butylcyclohexanol (left) and trans-4-*t*-butylcyclohexanol (right).

Table 2
MPV reduction of alkylcyclohexanones over Ti-β[a]

Substrate	TOF[b] (h^{-1})	Conversion[c] (%)	Selectivity[c] cis : trans
2-methylcyclohexanone	0.28	8.8	60 : 40
3-methylcyclohexanone	0.74	25.8	30 : 70
4-methylcyclohexanone	1.04	33.7	99 : 1
2-*t*-butylcyclohexanone		0.0	
4-*t*-butylcyclohexanone	2.26	64.9	98 : 2

[a] For reaction conditions see table 1.
[b] Initial turn-over-frequency in mol ketone per mol titanium per hour.
[c] Conversion and selectivity after 6 h reaction.

low (about 8 mg water $\mathrm{g}_{\text{zeolite}}^{-1}$ compared to 74 mg $\mathrm{g}_{\text{zeolite}}^{-1}$ for Al-β) [8]. It is therefore expected that hardly any water, hindering the formation of the water sensitive titanium alkoxide group, enters the zeolite. The acid aluminium site in Al-β is much more inclined to adsorb water on the H^+ site, though the zeolite still has a considerable hydrophobic character. The catalytic MPV site, as proposed by Creyghton et al. [12], consists of an aluminium alkoxide intermediate, similar to the titanium isopropoxide in our transition states **2** and **3**, which is also water sensitive. The higher amount of water in Al-β reduces the amount of the catalytic active aluminium sites apparently much more than in the case of Ti-β.

Upon addition of a strong Lewis base (pyridine) the activity of both Al-β and Ti-β is reduced to zero. In the case of Al-β this can be explained by the formation of a pyridinium cation by protonation of pyridine or the coordination of the amine directly onto Lewis acid sites. In principle the same reasoning applies to Ti-β. The amine can either add directly to the titanium atom or deprotonate the silanol group of **2**. The deprotonation of the Brønsted acidic silanol group is most likely. From the DREAS spectra it could be concluded that alcohols coordinate to the Lewis acid titanium site to give higher coordinated species e.g. **2** [9]. Furthermore titanium is a hard Lewis acid, preferring hard Lewis bases (oxygen containing bases) over pyridine, which is a intermediate Lewis base.

Table 3
Influence of water and pyridine on the catalytic activity of Ti-β, Al-β and $\mathrm{Al(OiPr)_3}$ in the MPV reduction of 4-*t*-butylcyclohexanone[a]

	Initial TOF[b] (h^{-1})		
	no addition	water	pyridine
Ti-β	2.26	1.86 (1.89)[c]	0.0
Al-β	> 12	1.17 (0.68)[c]	0.0
$\mathrm{Al(OiPr)_3}$	> 12	0.0	0.15

[a] For reaction conditions see table 1, 0.25 ml water or pyridine was added to the reaction mixture.
[b] Initial turn-over-frequency in mol ketone per mol titanium or aluminium per hour.
[c] 0.50 ml water was added to the reaction mixture.

3.5. By-product formation

The most important side reactions in heterogeneously catalyzed MPVO reactions are the acid catalyzed aldol condensation and acetalization. Ketones are less prone than aldehydes to give acetals, and the reaction usually requires relatively strong Brønsted acids. Aldol products are usually formed during the Oppenauer oxidation when surplus ketone or aldehyde is used as oxidizing agent as well as solvent. In the zeolite beta catalyzed Oppenauer oxidation (see table 4) of a 1 : 1 mixture of cis- and trans-4-*t*-butylcyclohexanol both Ti-β and Al-β selectively convert the cis-alcohol, which is probably due to spatial restrictions of the transition state in the zeolite channel in analogy with the reduction of the corresponding ketone. In this way MPVO reduction and oxidation are in harmony as to the high transition-state selectivity. The low amount of by-products formed when Ti-β is used as a catalyst clearly shows another advantage of the titanium system over Al-β. This is probably caused by the much weaker Brønsted acidity of the solvated titanium site **2**, compared with the strong H^+-acidity of the aluminium site in Al-β.

3.6. Comparison with other titanium containing silicates

The possibility of using titanium containing zeolites as Lewis-acid catalysts was further tested by the MPV reduction of cyclopentanone over Ti-β as well as over the medium pore titanium containing zeolite TS-1. Ti-β was found to be active (11.0% conversion after 6 h) while no reduction products could be detected for TS-1 even after 24 h. Likewise Ti-MCM-41, a mesoporous silicious material with 40 Å pores, and $\mathrm{TiO_2}$ on $\mathrm{SiO_2}$ [15] were found not to be able to catalyse the reduction of 4-*t*-butylcyclohexanone (see table 1). It therefore seems that the Lewis acidic nature of the titanium site and the coordination of ligands towards higher coordination numbers is unique for zeolite beta. An analogy may be seen with the reversible interconversion of framework tetrahedral and octahedral aluminium species as recently

Table 4
Oppenauer oxidation of 4-*t*-butylcyclohexanol with butanone as the oxidant. (2.5 mmol alcohol 1 : 1 mixture of cis and trans, 85°C, 25 ml butanone, 0.5 g zeolite or 0.25 mmol metal alkoxide as catalyst)

Catalyst	Conversion[a] of cis-alcohol(%)	Conversion[a] of trans-alcohol (%)	By-products[b] (mg)
Ti-β	52.1	4.6	22.4
Al-β	98.6	47.3	317.3
	49.4[c]	5.7[c]	63.8[c]
$\mathrm{Ti(OiPr)_4}$	6.1	12.9	22.7
$\mathrm{Al(OiPr)_3}$	5.3	7.4	56.5

[a] After 6 h reaction time.
[b] Total amount of by-products formed after 6 h, predominantly aldol condensates.
[c] After 15 min reaction time.

reported by Bougeat-Lami et al. [11] for zeolite beta, which strongly suggests that the properties of the titanium site are related to the framework topology of zeolite beta.

4. Conclusion

Ti-β was found to be active in the Meerwein–Ponndorf–Verley reduction of 4-*t*-butylcyclohexanone and the Oppenauer oxidation of the corresponding alcohols. High stereoselectivity is observed in both reactions. The catalytic potential of Ti-β compared to Al-β and metal alkoxides is shown by its high tolerance towards water. Furthermore, the lower acidity of Ti-β makes it a more suitable catalyst for the Oppenauer oxidation due to the reduced formation of aldol products from ketone solvents. Neither TS-1 nor Ti-MCM-41 were found to be able to reduce ketones, which restricts the MPV reaction over titanium containing zeolites to Ti-β, so far. The Lewis acidic properties of titanium sites in zeolite beta show analogy with the remarkable dynamic behavior of aluminium in zeolite beta and seem to be caused by the framework topology of zeolite beta. The Lewis-acidic and moderate to weak Brønsted acidic properties of the large pore Ti-β make it a potentially interesting catalyst for various Lewis-acid catalyzed reactions.

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