Journal of Catalysis **196,** 339–344 (2000)
doi:10.1006/jcat.2000.3043, available online at http://www.idealibrary.com on IDEAL®

Titanium-Catalyzed Heterogeneous Oxidations of Silanes, Chiral Allylic Alcohols, 3-Alkylcyclohexanes, and Thianthrene 5-Oxide: A Comparison of the Reactivities and Selectivities for the Large-Pore Zeolite Ti-β, the Mesoporous Ti-MCM-41, and the Layered Alumosilicate Ti-ITQ-2

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Received April 28, 2000; revised August 21, 2000; accepted August 21, 2000

A comparative study of silane oxidation, olefin epoxidation, and thianthrene 5-oxide sulfoxidation with the oxidants Ti-β/H_2O_2, Ti-MCM-41/*t*-BuOOH, and Ti-ITQ-2/*t*-BuOOH provides the catalytic reactivity order Ti-β > Ti-MCM-41 > Ti-ITQ-2. The steric constraints of the narrow channels make the Ti-β zeolite the most selective. For the more open structures of the Ti-MCM-41 and Ti-ITQ-2 hosts, such steric constraints are less pronounced and, therefore, a lower selectivity is exhibited by these heterogeneous catalysts. Both activate *t*-BuOOH for oxygen transfer through a transition structure analogous to the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH oxidant. © 2000 Academic Press

Key Words: **zeolites; heterogeneous oxidation; silanes; allylic alcohols; thianthrene 5-oxide.**

INTRODUCTION

The application of metal-doped zeolites in organic synthesis has received increased attention during the past decade (1). The structural variety of metal-doped zeolites has made possible manipulations of their surface characteristics and tuning of their acid/base properties, such that these materials have become powerful synthetic tools. Since the sites responsible for the oxidation activity are located within highly uniform channels and cavities, the zeolite oxidants offer the opportunity to conduct shape-selective catalysis (2). The most prominent example is the titanium silicalite TS-1 (channel diameter 5.5 Å); however, only relatively small organic molecules penetrate to reach the active sites of this useful catalyst (3). To circumvent these limitations, titanium-doped micro- and mesoporous materials with larger channel diameters, e.g., Ti-β (6.4 × 7.5 Å) (4) or Ti-MCM-41 (35 Å) (5), have been developed, which are capable of oxidizing large organic substrates. Recently, a new layered alumosilicate has been prepared, which has no channels or cavities, but consists of a layer of 25-Å-thick sheets (6). This material has been grafted with titanium atoms and, therefore, exhibits catalytic oxidation activity (7). These active Ti atoms are predominantly located at the rims of the open cups of the ITQ-2 structure and are not significantly shielded by the zeolite framework.

While Ti-β-catalyzed oxidations are well studied (4, 8), only a few reports for Ti-MCM-41 (9) and Ti-ITQ-2 exist (6, 7). Furthermore, no efforts have been made so far to assess the reactivity and selectivity of these heterogeneous catalysts and compare them with those of the heterogeneous Ti-β/H_2O_2 (4) and the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH (10) oxidants. Herewith we fill this gap by reporting our recent results for the catalytic oxidation of phenyldimethylsilane, the epoxidation of 3-alkylcyclohexanes and chiral allylic alcohols, as well as the sulfoxidation of thianthrene 5-oxide with Ti-β/H_2O_2, Ti-MCM-41/*t*-BuOOH, and Ti-ITQ-2/*t*-BuOOH.

METHODS

Preparation of Ti-ITQ-2. The titanium grafting was carried out by pouring a solution of titanocene dichloride in 60 ml of $CHCl_3$ onto 10 g of thermally dehydrated ITQ-2 (6), heated at 300°C under 10^{-3} Torr for 2 h. The suspension was stirred at room temperature (20°C) under an atmosphere of N_2 gas for 1 h. Subsequently, a solution of triethylamine in 7 ml of $CHCl_3$ (1 : 1 ratio of NEt_3 and $TiCp_2Cl_2$) was added. The suspension changed from red to yellow-orange, an indication of Ti coordination. The solid was collected by filtration, exhaustively washed with CH_2Cl_2, and calcined at 540°C in a nitrogen gas stream for 1 h and then in air for an additional 6 h.

General oxidation procedure. To 150 μmol of the substrate in 0.3 ml of the appropriate solvent was added

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0021-9517/00 $35.00

1.1 equiv of the oxygen donor (85% H_2O_2 or 8.0 M *t*-BuOOH in CH_2Cl_2), followed by 15 mg of the catalyst. The mixture was stirred for 24 h at the stated temperature, and the zeolite was removed by means of a membrane filter (0.45 μm pore size), washed with 0.4 ml of MeOH (d_4-MeOH in the case of the allylic alcohols and cyclohexene derivatives to enable direct NMR analysis of the reaction mixture), and two times with 0.4 ml of the solvent in which the reaction was carried out. The product analysis was conducted after workup as follows: the *silane oxidation* was performed in CH_2Cl_2 (CH_3CN for Ti-β) at ambient (ca. 20°C) temperature and the product composition determined by GC analysis {HP-5 column (5% diphenylpolysiloxane and 95% dimethylpolysiloxane), 80(5 min) → [30°C/min] → 130(1 min) → [30°C/min] → 240(2 min), N_2 pressure $= 1.5\ \mathrm{kg/cm^{-2}}$}, with *n*-hexadecane as internal standard; the *allylic alcohols* were epoxidized in $CDCl_3$ (CD_3CN for Ti-β) at ambient (ca. 20°C) temperature and the product composition was determined by ^{1}H NMR spectroscopy, with naphthalene as internal standard; the *cyclohexene derivatives* (11) were epoxidized in $CDCl_3$ (CD_3CN for Ti-β) at 40°C in sealed ampoules and the product composition was determined as stated for the allylic alcohols; the sulfoxidation of thianthrene 5-oxide (**SSO**) was performed as described previously (12). The use of an internal standard allowed the conversions (%) and mass balances (mb, %) to be assessed quantitatively. The lower mb values (<80%) in Tables 1 and 2 are due to incomplete product recovery from the zeolite in the extraction process, presumably due to covalent grafting of the sensitive epoxides.

RESULTS

Reactivity

We demonstrated previously that Ti-β efficiently catalyzes the selective oxidation of silanes to silanols with H_2O_2; the condensation of the silanol product to its disiloxane is prevented due to space limitations (8d). This oxidation process has been used herein to assess the reactivity and selectivity of the heterogeneous catalysts Ti-ITQ-2 and Ti-MCM-41 (Table 1). As oxidant, *t*-BuOOH was used with Ti-MCM-41 and Ti-ITQ-2, since these catalysts do not exhibit sufficient oxidation activity with H_2O_2. This is in contrast to Ti-β, which poorly activates *t*-BuOOH (data not shown). While with Ti-β/H_2O_2 complete silane conversion was reached within 24 h (entry 1) (8d), Ti-ITQ-2 and Ti-MCM-41 displayed substantially lower conversions (entries 2 and 3), as indicated in the drop of the percent conversion for Ti-MCM-41 and Ti-ITQ-2. Additionally, small amounts of the disiloxane were also formed in the case of Ti-ITQ-2 and Ti-MCM-41. These results contrast those of Ti(O*i*-Pr)$_4$/*t*-BuOOH, for which a low conversion was found (entry 4) (8d). The reactivity, therefore, follows the order Ti-β/H_2O_2 > Ti-MCM-41/*t*-BuOOH > Ti-ITQ-2/*t*-BuOOH > Ti(O*i*-Pr)$_4$/*t*-BuOOH.

TABLE 1

Mass Balances, Conversions, and Product Selectivities for the Heterogeneous Oxidation of Phenyldimethylsilane[a]

$$\mathrm{PhMe_2SiH} \xrightarrow[\text{solvent},\,20^\circ\text{C},\,24\,\text{h}]{\text{catalyst}} \underset{(\mathrm{SiOH})}{\mathrm{PhMe_2SiOH}} + \underset{(\mathrm{Si_2O})}{[\mathrm{PhMe_2Si}]_2\mathrm{O}}$$

Catalyst	Solvent	mb (%)	convn (%)	Selectivity [SiOH] : [Si_2O]
Ti-β/H_2O_2[b]	CH_3CN	89	99	>99 : 1
Ti-MCM-41/*t*-BuOOH	CH_2Cl_2	80	48	90 : 10
Ti-ITQ-2/*t*-BuOOH	CH_2Cl_2	>99	29	95 : 5
Ti(O*i*-Pr)$_4$/*t*-BuOOH[b]	CH_2Cl_2	74	38	39 : 61

[a] Mass balances, conversions, and chemoselectivities were determined by gas chromatography after workup, with *n*-hexadecane as internal standard.

[b] See Ref. (8d).

Chemoselectivity

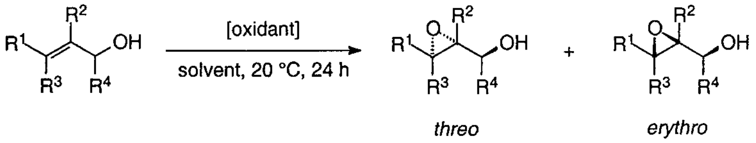
In addition to the reactivity, the silane oxidation offers also the possibility to test for chemoselectivity (i.e., silanol versus disiloxane formation) of these oxidants. For Ti-β/H_2O_2, we have previously found exclusively the silanol product (8d). Despite their more open structure, Ti-MCM-41/*t*-BuOOH and Ti-ITQ-2/*t*-BuOOH still display a high chemoselectivity for the silanol. This is in stark contrast to the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH, for which the disiloxane product dominates. For the silane oxidation with Ti-β/H_2O_2, we have postulated that steric constraints inside the 7-Å-wide channel of Ti-β prevents the silanol condensation (8d). However, this does not apply to the 35-Å-wide channels of the mesoporous Ti-MCM-41 or on the surface of the layered alumosilicate Ti-ITQ-2. We have shown recently (12) that even inside the mesoporous Ti-MCM-41, the metal is sufficiently shielded from coordination. It is likely, therefore, that the good silanol selectivities for Ti-MCM-41 are due to the inhibition of the simultaneous coordination of two silanol molecules at the same Ti center. For Ti-ITQ-2, the product selectivity may be rationalized by its low acidity compared to that of Ti-β, as supported by the lack of acid-catalyzed ring-opening products in the former case (6). The chemoselectivity, therefore, parallels essentially the reactivity order.

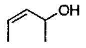
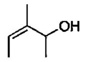
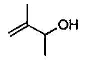
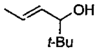
Diastereoselectivity

By use of the concept of allylic strain (13), we recently have refined the assumed transition structure for the Ti-β-catalyzed epoxidation (8c, 14). This mechanistic probe is now to be applied to the alcohols **1a–d**, which were chosen

TABLE 2

Comparison of the Diastereoselectivities (*threo*/*erythro*) for the Epoxidation of Allylic Alcohols 1 with Various Heterogeneous and Homogeneous Titanium-Based Oxidants



Substrate	Ti-ITQ-2/*t*-BuOOH (in $CDCl_3$)[a]			Ti-MCM-41/*t*-BuOOH (in $CDCl_3$)[a]			Ti-β/85% H_2O_2 (in CD_3CN),[a,b]	Ti(O*i*-Pr)$_4$/*t*-BuOOH (in $CDCl_3$),[c]
	mb (%)	convn (%)	dr	mb (%)	convn (%)	dr	dr	dr
 **1a**	80	65	95 : 05	>95	31	86 : 16	91 : 09	91 : 09
 **1b**	93	75	95 : 05	82	78	83 : 17	89 : 11	83 : 17
 **1c**	82	34	35 : 65	72	50	31 : 69	56 : 44	22 : 78
 **1d**	80	60	78 : 22	72	63	78 : 22	70 : 30	57 : 43

[a] Heterogeneous reaction; mass balances, conversions, and *threo*/*erythro* diastereoselectivities (dr) determined by ^1H NMR spectroscopy after workup; error ±5% of the given value.

[b] See Ref. (8d).

[c] Homogeneous reaction, see Ref. (8d).

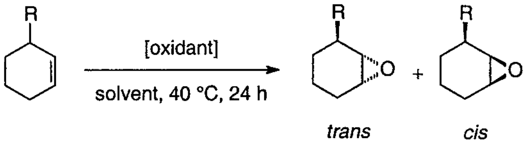
since they display the largest differences in diastereoselectivity between heterogeneous (Ti-β/H_2O_2) and homogeneous [Ti(O*i*-Pr)$_4$/*t*-BuOOH)] oxidations. The epoxidation of these chiral allylic alcohols with Ti-ITQ-2/*t*-BuOOH and Ti-MCM-41/*t*-BuOOH afforded exclusively the corresponding epoxides in moderate to good yields (Table 2). The diastereomeric ratios (dr) follow a similar trend for these catalysts; in fact, for the allylic substrates **1c,d** the dr values are within the error limits. For the alcohols **1a,b** (entries 1 and 2) with a *cis*-methyl group (1,3-allylic strain present), the *threo* epoxide is preferentially formed with all oxidants, even when a *gem*-methyl group (1,2-allylic strain present) is also present. In contrast, for substrate **1c** (entry 3) without a *cis*-methyl group (1,3-allylic strain absent), the *erythro* epoxide prevails for Ti-ITQ-2, Ti-MCM-41, and Ti(O*i*-Pr)$_4$, while an almost 1 : 1 mixture of the *threo*/*erythro* epoxides is found for Ti-β. For the *tert*-butyl substrate **1d** (entry 4), without 1,3- and 1,2-allylic strain, the *threo* epoxide is obtained for all heterogeneous oxidants examined herein, while the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH yields a nearly 1 : 1 mixture of both diastereomers. Except for the substrate **1d**, the diastereoselectivities for the heterogeneous Ti-MCM-41/*t*-BuOOH and Ti-ITQ-2/*t*-BuOOH oxidants match those for the homogeneous one Ti(O*i*-Pr)$_4$/*t*-BuOOH, a mechanistically pertinent result.

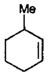
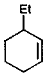
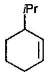
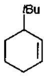
Steric Constraints

The epoxidation of the 3-alkyl-substituted cyclohexene derivatives **3a–d** (Table 3) was conducted to probe for purely steric effects, in the absence of electronic and coordination effects between the substrate and metal catalyst, which usually operate in the case of the allylic alcohols **3**. With increasing bulk of the 3-alkyl substituent, the *trans* selectivity increases. Again, no significant difference in the *cis*/*trans* selectivity was observed for the mesoporous Ti-MCM-41 and the layered alumosilicate Ti-ITQ-2. In contrast, with the large-pore zeolite Ti-β (7 Å diameter), the *trans* epoxide was found in large excess over the *cis* one, even for the sterically more exposed methyl derivate **3a**. The other sterically more encumbered cyclohexenes **3b–d** afforded the *trans* epoxide exclusively. A semilogarithmic plot of the diastereomeric ratios against Taft's steric parameter E_S afforded a good linear correlation for Ti-MCM-41 and Ti-ITQ-2 (Fig. 1); however, such a plot is not feasible for the Ti-β case due to the essentially exclusive formation of the *trans* epoxide already for the methyl derivative **3a**,

TABLE 3

Diastereoselectivities (*trans*/*cis*) of the Heterogeneous Oxidation of 3-Alkyl-Substituted Cyclohexenes by Ti-ITQ-2/*t*-BuOOH, Ti-MCM-41/*t*-BuOOH, and Ti-β/H_2O_2



	Ti-ITQ-2/*t*-BuOOH (in $CDCl_3$)[a]			Ti-MCM-41/*t*-BuOOH (in $CDCl_3$)[a]			Ti-β/H_2O_2 (in CD_3CN)[a]		
Substrate	mb (%)	convn (%)	dr	mb (%)	convn (%)	dr	mb (%)	convn (%)	dr
 **3a**	75	68	61 : 39	76	71	58 : 42	79	47	92 : 08
 **3b**	80	79	63 : 37	86	82	61 : 39	80	52	>95 : 05
 **3c**	81	31	71 : 29	84	70	69 : 31	83	55	>95 : 05
 **3d**	79	54	>95 : 05	82	43	92 : 08	89	73	>95 : 05

[a] Mass balances, conversions, and *trans*/*cis* diastereoselectivities (dr) determined by ^{1}H NMR spectroscopy after workup; error ±5% of the given value.

such that the steric effects between the substrate and catalytic site are not sensed for this catalyst. Nevertheless, the constraint-controlled selectivity, i.e., Ti-β > Ti-MCM-41 $\approx$ Ti-ITQ-2, follows the expected order of steric effects, which are most pronounced for Ti-β.

Electronic Nature

We have recently assessed the electrophilic character of the heterogeneous oxidants Ti-β/H_2O_2 and Ti-MCM-41/*t*-BuOOH by employing the thianthrene 5-oxide (**SSO**) probe for electronic effects (12). Since we had observed for these heterogeneous oxidants significant differences in the X_{SO} parameter [a quantitative measure of sulfone (**SSO₂**) versus sulfoxide (**SOSO**) formation] (15) when compared to the homogeneous oxidant Ti(O*i*-Pr)$_4$/*t*-BuOOH, it was mechanistically relevant to determine also the electronic nature of the Ti-ITQ-2/*t*-BuOOH oxidant (Scheme 1). As for the heterogeneous oxidations described above, the results for Ti-ITQ-2/*t*-BuOOH ($X_{SO} = 0.12$) parallel those for Ti-MCM-41/*t*-BuOOH ($X_{SO} = 0.18$) and Ti-β/H_2O_2 ($X_{SO} = 0.07$), but contrast those for the homogeneous oxidant Ti(O*i*-Pr)$_4$/*t*-BuOOH ($X_{SO} = 0.59$) (12). Therefore, the heterogeneous Ti-ITQ-2/*t*-BuOOH oxidant displays the expected electrophilic oxidizing properties, as previously found for the Ti-MCM-41/*t*-BuOOH and Ti-β/H_2O_2 cases.

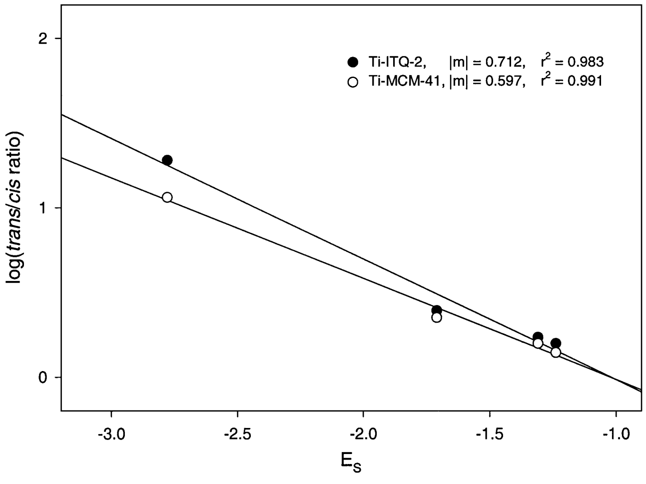
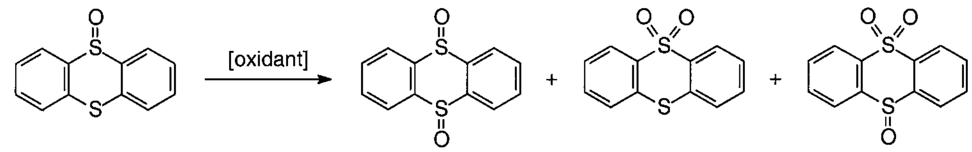


FIG. 1. Diastereoselectivity (*trans*/*cis*) for the epoxidation of the chiral 3-alkylcyclohexenes **3a–d** as a function of Taft's steric parameter E_s.

MECHANISTIC DISCUSSION

Unquestionably, the overall catalytic activity of the three porous titanosilicates (H_2O_2 or *t*-BuOOH as oxygen sources) is primarily governed by the zeolite pore size and by their relative hydrophilicity/hydrophobicity (1); however, mechanistic information on the transition structures may be gained by means of stereochemical probes (13). For this purpose, a detailed comparison of the herein acquired stereochemical data of the Ti-ITQ-2/*t*-BuOOH and



SSO *trans,cis*-**SOSO** **SSO$_2$** **SOSO$_2$**

Oxidant	*trans,cis*-SOSO	SSO$_2$	SOSO$_2$	X_{SO}
Ti-ITQ-2/*t*-BuOOH	87	7	6	0.12
Ti-MCM-41/*t*-BuOOH (Ref 12)	80	12	8	0.18
Ti-beta/H$_2$O$_2$ (Ref 12)	93	0	7	0.07
Ti(O*i*-Pr)$_4$/*t*-BuOOH (Ref 12)	46	46	8	0.50

SCHEME 1. Chemoselectivities for the sulfoxidation of thianthrene 5-oxide (**SSO**) with various heterogeneous and homogeneous titanium-mediated oxidants.

Ti-MCM-41/*t*-BuOOH systems with those of the previously reported Ti-β/H$_2$O$_2$ (8c) and Ti(O*i*-Pr)$_4$/*t*-BuOOH (8c) shall now be made, which allows us to propose a detailed mechanism for the oxygen transfer by these oxidants. Allylic strain in the chiral allylic alcohols **1a–c**, i.e., the steric interactions between the two geminal groups at a double bond (1,2-allylic strain, ^{1,2}A) or between the *cis* substituents (1,3-allylic strain, ^{1,3}A), leads to a preferred conformation of the substrate–oxidant complex with the hydroxy group favorably disposed for interaction with the oxidant. Consequently, the two π faces in the allylic substrate are appropriately differentiated for the oxygen transfer and characteristic diastereoselectivities are observed (*hydroxy group directivity*) (13).

In the case of Ti(O*i*-Pr)$_4$/*t*-BuOOH, the substrate is fixed by a metal–alcoholate bond (Fig. 2, structure **A**) (16), which requires a more acute dihedral angle α (C=C–C–O) of ca. 70° to 90° in the oxygen transfer, such that a pronounced influence of ^{1,2}A strain operates in the control of the diastereoselectivity, as observed for substrates **1a,c** (Table 2, entries 1 and 3). In contrast, hydrogen bonding between the metal-based oxidizing species and the allylic alcohol substrate is involved in the case of Ti-β/H$_2$O$_2$, which leads to a more obtuse dihedral angle α of ca. 120° (Figure 2, **B**) (8c). Consequently, ^{1,3}A strain dominates for this oxidant and *threo* diastereoselectivity is observed for substrates **1a** and **1b** (Table 2, entry 1 and 2); the latter stereochemical probe (17) clearly demonstrates that ^{1,2}A strain is negligible.

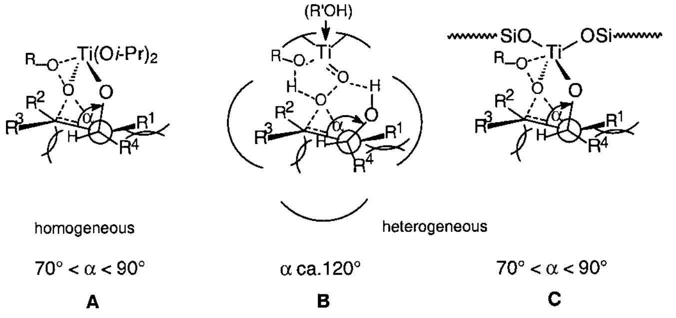
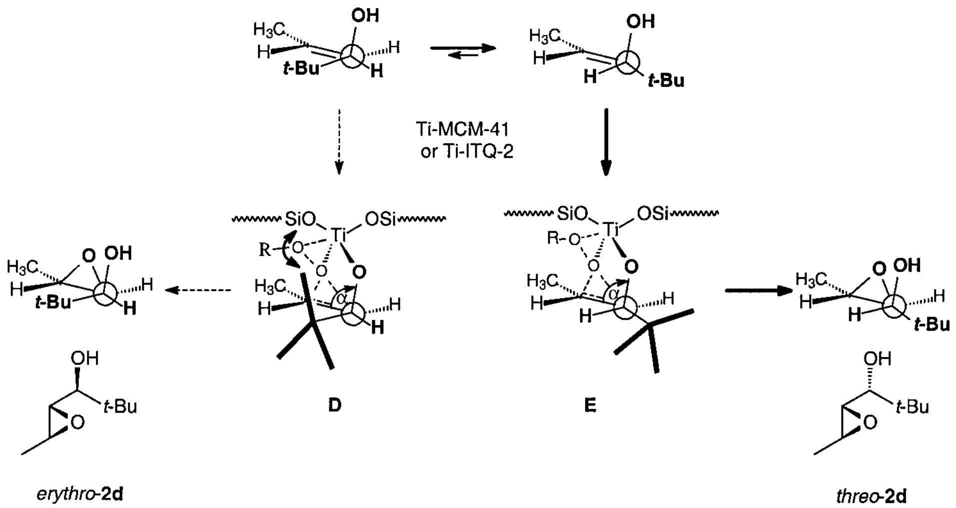


FIG. 2. Transition structures for the oxygen transfer by the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH (**A**) and the heterogeneous Ti-β/H$_2$O$_2$ (**B**), Ti-ITQ-2/*t*-BuOOH (**C**), and Ti-MCM-41/*t*-BuOOH (**C**) oxidants. Note the difference between the oxygen sources in the activated complexes **B** (H$_2$O$_2$) and **C** (*t*-BuOOH).

A comparison of the stereochemical results for the oxidation of the chiral allylic alcohols **1a–c** by Ti-ITQ-2/*t*-BuOOH and Ti-MCM-41/*t*-BuOOH (Table 2) with the known data for Ti(O*i*-Pr)$_4$/*t*-BuOOH (8c) and Ti-β/H$_2$O$_2$ (8c) reveals better correspondence with the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH oxidant (metal–alcoholate bonding) than the heterogeneous one Ti-β/H$_2$O$_2$ (hydrogen bonding). Therefore, we propose that the transition structure for the oxidation by the heterogeneous catalysts Ti-ITQ-2 and Ti-MCM-41 is more akin to the one for Ti(O*i*-Pr)$_4$/*t*-BuOOH, i.e., the substrate is fixed by a metal–alcoholate bond (Figure 2, **C**) and a dihedral angle of $70° < \alpha < 90°$ applies in this oxygen-transfer process.

The appreciable *threo* selectivity for the epoxidation of the *tert*-butyl derivative **1d** with the heterogeneous oxidation systems Ti-ITQ-2/*t*-BuOOH, Ti-MCM-41/*t*-BuOOH, and Ti-β/H$_2$O$_2$ (Table 2, entry 4) seems to contradict the proposed transition-structure model in Fig. 2. If at all, an *erythro* preference would be expected in the diastereoselectivity since metal–alcoholate bonding operates and the substrate does not possess allylic strain (13). However, for such sterically encumbered chiral allylic substrates as the *tert*-butyl derivative **1d**, additional repulsions come into play, which are divulged in Scheme 2. Thus, in the *erythro* transition structure **D**, the steric interactions of the large *t*-Bu group with the zeolite lattice disfavor this arrangement, while such interactions are absent in the *threo* transition structure **E**. In the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH oxidant no such steric constraints are present and, consequently, a ca. 1 : 1 *erythro*/*threo* mixture of epoxides is obtained. In this respect, it is mechanistically relevant to note that for the epoxidation of the alcohol **1d** by *m*-CPBA, for



SCHEME 2. Transition structures *erythro* (**D**) and *threo* (**E**) for the epoxidation of the chiral *tert*-butyl-substituted allylic alcohol **1d** with the heterogeneous Ti-ITQ-2/*t*-BuOOH and Ti-MCM-41/*t*-BuOOH oxidants.

which the transition structure analogous to that of Ti-β was postulated (8c), also a ca. 1 : 1 *erythro*/*threo* mixture of epoxides was found. All these results taken together substantiate that the preferred *threo* selectivity for the oxidation of alcohol **1d** by Ti-ITQ-2/*t*-BuOOH, Ti-MCM-41/*t*-BuOOH, and Ti-β/H_2O_2 derives from steric constraints at the zeolite surface of these solid-supported titanium-based catalysts.

CONCLUSION

It was demonstrated that the heterogeneous oxidants Ti-ITQ-2/*t*-BuOOH and Ti-MCM-41/*t*-BuOOH exhibit similar reactivity and chemoselectivity due to their quite open structure. A transition structure analogous to the one for the homogeneous Ti(O*i*-Pr)$_4$/*t*-BuOOH oxidant applies, in which the substrate is fixed by metal–alcoholate bonding and with a dihedral angle of $70° < \alpha < 90°$ for the oxygen transfer. The importance of allylic strain is evident for the chiral allylic alcohols **1a–c**, but additionally interactions with the inorganic framework influence the transition-state geometry for the sterically encumbered substrate **1d**.

ACKNOWLEDGMENTS

We thank the Deutsche Forschungsgemeinschaft (SFB 347 “Selektive Reaktionen Metall-aktivierter Moleküle”) and the Fonds der Chemischen Industrie for generous financial assistance. O.W. thanks the Fonds “Hochschule International” for a research fellowship at the Instituto de Tecnología Química, Valencia.

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