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Quantitative Sorption Experiments on Ti-Zeolites and Relation with α-Olefin Oxidation by H_2O_2

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A tracer chromatographic method is used to study liquid-phase adsorption on TS-1, Ti-β, and Ti-MCM-41. Partition coefficients for alkenes, alkanes, epoxides, and other polar products are strongly dependent on the carrier solvent. Linear α-olefins are concentrated inside the TS-1 micropores, particularly when methanol is the solvent. This agrees well with the superior initial rates of olefin epoxidation with TS-1 in methanol. Sorption also governs the relative reactivities of olefin substrates, especially in competitive experiments. Thus, under truly initial conditions, 1-hexene is less reactive than 1-octene or 1-nonene. For the latter substrates, however, deactivation is fast, especially in methanol. This process is related to the strong adsorption of higher 1,2-epoxyalkanes in TS-1 in methanol. Deactivation due to competitive epoxide adsorption is slower in acetone, making this a more suitable solvent than methanol for 1-nonene epoxidation with TS-1. Overall, physisorption effects play a dominant role in the small pore TS-1 catalyst, due to the close interaction of substrates such as alkenes with the pore wall. Wider-pore catalysts such as Ti-β and especially Ti-MCM-41 do not adsorb olefins as selectively and hence intraporous olefin concentrations are much lower.

Key Words: **physisorption; titanium; TS-1; epoxidation; α-olefins.**

INTRODUCTION

The rising demand for epoxides of propylene, and α-olefins in general, urges industry to replace existing peracid and homogeneous catalytic technology by clean, heterogeneous catalytic reactions. Ti-substituted zeolites (titanium silicalite-1, Ti-β) are truly heterogeneous catalysts, and they can use H_2O_2 as the oxidant (1, 2). Several industrial groups have reported on the synthesis of propylene oxide with TS-1 (3, 4). As TS-1 barely decomposes any H_2O_2, yields on peroxide basis are usually excellent. This has qualitatively been ascribed to the hydrophobic nature of TS-1, disfavoring peroxide accumulation in the intraporous volume. A second important characteristic of TS-1 epoxidations is that they are generally fastest in methanol. This preference has been explained by a model in which methanol coordinates on the active Ti sites (5, 6). The possible link between physisorption and solvent effects in olefin epoxidation, however, has not extensively been studied. In the case of alcohol oxidation with TS-1, reaction kinetics have been modeled based on chemisorption at the active site, rather than in terms of physisorption in the zeolite pores (7).

This paper quantitatively studies liquid-phase adsorption of a broad series of compounds on heterogeneous Ti oxidation catalysts. Partition coefficients are determined from tracer liquid chromatographic experiments on TS-1 and Ti, Al-β zeolites and on the mesoporous molecular sieve Ti-MCM-41. These data are then used to gain insight in the effects of solvents on the rate of Ti-zeolite-catalyzed epoxidations and in the relative reactivities of α-olefins in competitive or separate reactions. Special attention is devoted to the deactivation process for different solvents and olefins. It is demonstrated that in many cases, adsorption data correctly predict the observed catalytic behavior.

MATERIALS AND METHODS

Materials. *n*-Octane (99+%), *n*-nonane (99%), *n*-decane (99+%), *n*-dodecane (99+%), 1-hexene (97%), 1-heptene (97%), 1-octene (98%), 1-nonene (98%), 1-decene (94%), 1-dodecene (95%), 2-heptanol (98%), 2-octanol (97%), 2-nonanol (99%), 1,2-epoxyhexane (97%), 1,2-epoxyoctane (96%), 1,2-epoxydecane (95%), 1,2-hexanediol (98%), and hydrogen peroxide (35 wt% in water) were obtained from Aldrich. *n*-Hexane (95%), *n*-heptane (99%), methanol (99.9+%), ethanol (99.5%), 1- propanol (99.5%), 2-propanol (99.5%), acetone (99.9+%), and acetonitrile (99.9+%) were purchased from Sigma Aldrich (HPLC grade). 2-Hexanol (99%) was obtained from Janssen Chimica.

Catalyst preparation. TS-1 was prepared according to a literature procedure (8). After 4 days of crystallization at 448 K, the zeolite was isolated and finally calcined at 823 K (Si/Ti = 34). The X-ray diffractogram was typical of phase-pure TS-1 (e.g., peaks at 22.6, 23.6, 24.0, 28.8, 29.5, 44.7, and 45.1° 2θ). SEM pictures revealed a remarkably narrow crystal size distribution, with a typical dimension of 150 nm. UV-Vis diffuse reflectance spectroscopy showed

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that the material was nonabsorbing above 250 nm. N_2 sorption experiments were performed with a Coulter Omnisorp 100 apparatus at 77 K. The micropore volume of the TS-1 material is 0.175 ml/g, as determined by *t*-plot analysis. The microporosity remains intact after the HPLC sorption measurements, indicating that no pore blockage occurs.

Al containing Ti-β-zeolite was synthesized by the following procedure (9). Four milliliters of tetraethyl orthotitanate (Aldrich) was mixed with 84 ml water and cooled to 278 K. Subsequently, 34 ml precooled H_2O_2 (35% in water, Akros) was added and stirring was continued for 1 h (solution 1). Solution 2 was prepared by suspending 0.1268 g Al powder (UCB) in 120 ml tetraethyl ammonium hydroxide (40% in water, Alfa) and heating at 353 K for 1 h. After Al dissolution, 60 ml water was added and the resulting solution was cooled at 278 K. Solutions 1 and 2 were then combined and stirred for 30 min at 278 K. Twenty grams of Aerosil (200 $m^2\ g^{-1}$, UCB) was added. The gel was crystallized under dynamic conditions at 408 K for 10 days. The crystals were isolated and calcined at 823 K. XRD shows a typical *BEA diffractogram (broad reflection at 22.5° 2θ; other peaks at 7.6, 21.5, 25.3, 27.1, and 29.6° 2θ) (10). Elementary ratios were $Si/Ti = 17$ and $Si/Al = 72$. The micropore volume, determined by the *t*-plot method, was 0.251 ml/g.

Ti-MCM-41 was obtained by grafting titanocene dichloride on a preformed mesoporous MCM-41 molecular sieve ($Si/Ti = 10$), following the procedure of Maschmeyer *et al.* (11). The material was calcined at 823 K before use.

Liquid-phase chromatographic sorption experiments. Measurements were performed with a Hewlett Packard 1100 HPLC and 1037A RI detector. A 1/4-in. stainless-steel column with a length between 26 and 50 mm was used. Pure compounds (0.5–3 μl) were injected into a liquid solvent carrier (flow rate 0.1–0.5 ml/min). Water was used as a model compound for H_2O_2, as injection of H_2O_2 results both in physisorption and (irreversible) chemisorption. Peaks due to reaction of the products (e.g., epoxides) on the column were not observed. Retention times were corrected for the system's dead volume. The partition coefficients K are defined as $K = (q/C)$, with q and C the intraporous and extraporous concentrations of the tracer, respectively (12–15). K values can be derived by injection of a tracer compound into a single component carrier:

$$\mu = \frac{L}{\nu_f}(\varepsilon_{\text{ext}} + (1 - \varepsilon_{\text{ext}})K), \qquad [1]$$

with μ the retention time, L the column length, ν_f the superficial velocity, and ε_{ext} the external packed bed porosity. Even for longer molecules such as nonane, K values were independent of the flow through the column. This indicates that for all reported data, the K values reflect equilibrium adsorption and are not affected by transport limitations, as expected for the relatively small flow rates (13–15).

Catalytic reactions. Catalytic reactions were conducted in 6-ml septum flasks. To 15 mg catalyst was added 0.2–3.6 mmol of olefin, and the volume was made up to 4 ml with a solvent. Next the suspension was immersed in an oil bath with accurate temperature control. The reaction was started by injection of 0.2–1.0 mmol of 35% aqueous H_2O_2, diluted with the solvent to 1 ml, into the well-stirred suspension (700 rpm). Oxidant injection altered the temperature by less than 1°C. In all cases, there was only a single liquid phase. Samples were withdrawn through the septum and immediately injected into a GC with a 10 m CP-Sil 5 column (oven temperature program 0.5 min at 343, 363 or 393 K; subsequent heating at 10 K min^{-1}) or a 50-m column (7 min at 413 K; heating at 10 K min^{-1} up to 563 K). The injection port was at 473 K and was cleaned at least after every 10th injection. Reference injections of reaction mixtures at zero time or containing no catalyst did not show product formation. H_2O_2 consumption was regularly checked by cerimetry. For TS-1 reactions, H_2O_2 consumption was found to equal olefin conversion within 5%.

Initial rates (expressed as mmol olefin converted per g catalyst and per h) were determined by calculating the slope of the tangent to the conversion–time plots at time zero (see, e.g., curves in Fig. 5b). While a constant rate as a function of time is expected for zero order in olefin and peroxide, TS-1 olefin epoxidations have been reported to be first order in peroxide (4) and between zero and first order in olefin (see below, Fig. 6). Thus rates are expected to decrease gradually as the reaction proceeds, even with a nondeactivating catalyst. In order to determine whether catalyst activity is stable over a series of successive data points, following function Y was plotted as a function of time:

$$Y = \ln\left(\frac{x_{\text{olefin}}}{x_{\text{olefin}} - s}\right) + \ln(1 - s) = kst, \qquad [2]$$

with $x_{\text{olefin}} = c_{\text{olefin}}/c_{\text{olefin,initial}}$; $x_{H_2O_2} = c_{H_2O_2}/c_{H_2O_2,\text{initial}}$; $s = (c_{\text{olefin,initial}} - c_{H_2O_2,\text{initial}})/c_{\text{olefin,initial}}$; k the rate constant (time^{-1}). Equation [2] is the solution of the differential equation $dx_{\text{olefin}}/dt = -kx_{\text{olefin}}x_{H_2O_2}$ (except for $c_{\text{olefin,initial}} = c_{H_2O_2,\text{initial}}$). For first order in olefin and in peroxide, and for a constant activity of the catalyst, a plot of Y (or $-Y$, for $s < 0$) according to Eq. [2] should give a straight line through the origin. Downward deviation of this plot ($d^2Y/dt^2 < 0$) means that the rate decreases even faster than predicted by first order dependence on olefin and peroxide. Therefore, a plot according to Eq. [2] is a sensitive method for detecting a decreasing catalyst activity. The use of this equation does not imply that the reaction is first order in olefin and peroxide; in view of the strong adsorption phenomena, orders between 0 and 1 (as previously proposed in literature) are more probable (4).

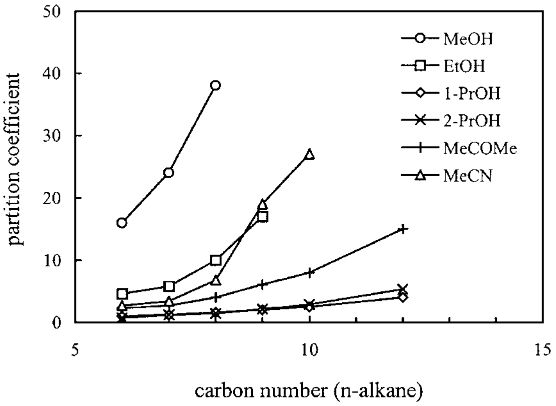


FIG. 1. Partition coefficients K for adsorption of linear alkanes on TS-1 in different solvents (308 K). Plots of K vs carbon number.

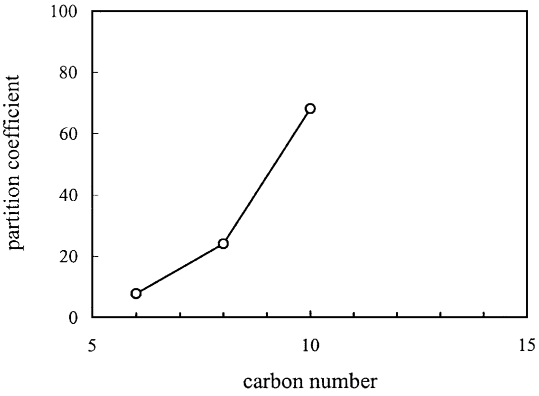


FIG. 3. K values for 1,2-epoxide adsorption on TS-1 (methanol, 308 K).

RESULTS

Adsorption on TS-1

Data for adsorption of alkanes, alkenes, and other compounds are gathered in Figs. 1 to 3 and in Table 1. For linear alkanes, partition coefficients in a series of solvents increase exponentially with increasing carbon number (Fig. 1). For a given alkane, partition coefficients decrease with decreasing polarity of the alcohol solvent (e.g., $K_{\text{methanol}} > K_{\text{ethanol}} > K_{\text{1-propanol}}$). This agrees with the known organophilic nature of TS-1. Similar trends are observed with alkenes (Table 1). Thus, 1-octene is concentrated more inside the TS-1 micropores than 1-hexene, and the sorption is much stronger in a methanol carrier than in a less polar alcohol (1-propanol) or in an aprotic solvent (e.g., acetonitrile). For the 2-alkanols, the partition coefficients are smaller than for alkanes or alkenes, but the general trends are the same.

Only water displays an anomalous behavior. With decreasing solvent polarity, it is slightly more strongly adsorbed in TS-1. This adsorption is probably related to the specific interaction of water with the hydrophilic Ti site. This hypothesis is supported by the experiments with Ti-free silicalite, for which K_{H_2O} varies little with the solvent nature (Table 1, bottom row). This confirms that the presence of Ti sites has an impact on the K_{H_2O} values measured for TS- 1.

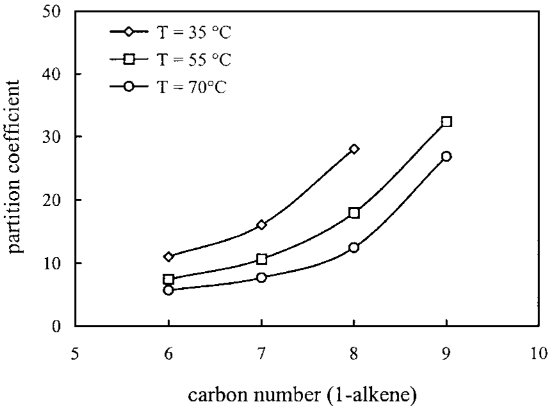


FIG. 2. Effect of temperature on partition coefficients K for adsorption of α-olefins on TS-1 in methanol.

Temperature has the expected effect on the sorption: K values are lower when the temperature is raised from 308 to 343 K (Fig. 2). Of special interest are the data for epoxides and vicinal diols. Even if epoxidation seemingly would increase the polarity of an olefin compound, the partition coefficients for epoxides are high, particularly in methanol (Fig. 3), and are even superior to those of the corresponding olefins. Again an exponential increase of K with carbon number is observed, in going from 1,2-epoxyhexane over 1,2-epoxyoctane to 1,2-epoxydecane. In the same methanol background, the K value for 1,2-hexanediol is much lower than for the corresponding 1,2-epoxyhexane (Table 1).

TABLE 1

Partition Coefficients for Adsorption of α-Alkenes, 2-Alkanols, Epoxides, and Polar Products on TS-1 at 308 K

	MeOH	EtOH	1-PrOH	Acetone	Acetonitrile
1-Hexene	11	3.1	0.7	1.8	2.0
1-Heptene	16	4.3	1.1	2.0	2.8
1-Octene	28	6.2	1.5	2.7	3.6
1-Nonene	—	13	1.8	3.9	8.4
1-Decene	—	21	2.9	5.1	15
1-Dodecene	—	—	3.4	8.6	—
2-Propanol	0.7	0.3	0.5	1.4	—
2-Hexanol	4.2	1.0	0.6	3.3	5.6
2-Heptanol	9.5	1.6	0.8	3.1	6.0
2-Octanol	18	3.2	1.0	4.3	7.9
2-Nonanol	37	6.6	1.4	6.5	19.0
1,2-Epoxyhexane	24	11	4.6	2.7	1.9
1,2-Hexanediol	9.3	2.2	1.3	3.9	2.5
Water, TS-1	0.7	0.9	1.6	1	0.4
Water, silicalite	0.6	0.8	0.5		

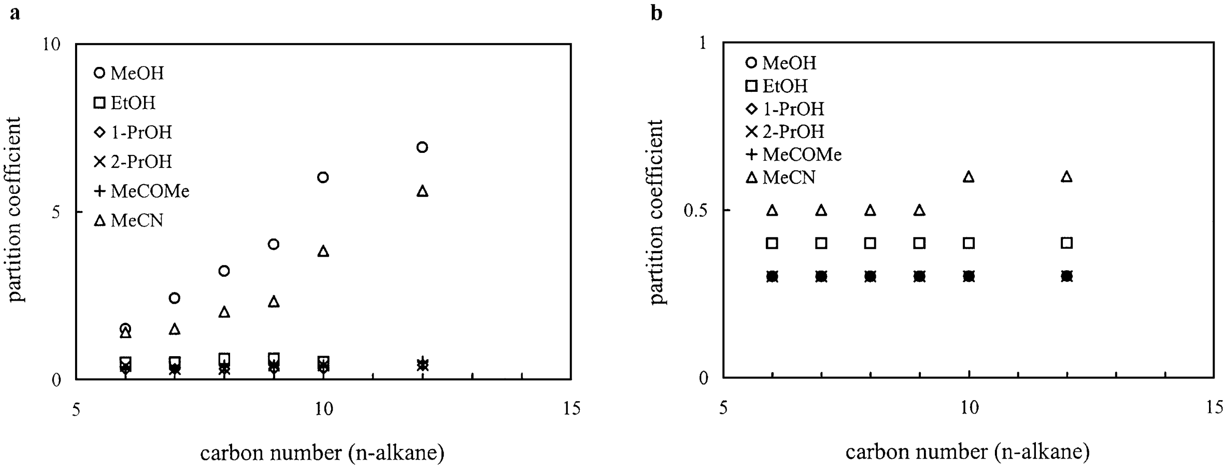


FIG. 4. Partition coefficients *K* for adsorption of linear alkanes on (a) Ti,Al-β and (b) Ti-MCM-41 in different solvents (308 K).

Adsorption on Ti,Al-β and Ti-MCM-41

The data for adsorption in these molecular sieves are remarkably different from those for TS-1. Ti,Al-β and Ti-MCM-41 clearly have a much lower affinity for the *n*-alkanes, as reflected in much lower *K* values (Fig. 4). With α-olefins and Ti,Al-β, a significant enrichment of the tracer is only observed in methanol ($K_{\text{1-octene,MeOH}} = 3.8$ for Ti,Al-β, vs 28 for TS- 1) (Table 2). Particularly for Ti-MCM-41, *K* values of potential olefin substrates and hence intraporous concentrations are low (Table 3).

Note that for Ti,Al-β and Ti-MCM-41, 2-alkanols have a significantly increased *K* if the experiment is run in a nonprotic solvent such as acetone or CH_3CN (Tables 2 and 3). Thus sorption of 2-alkanols on these catalysts seems governed by interaction of -OH groups with the polar channel walls and only to a lesser extent by the hydrocarbon part of the molecule. Nonprotic solvents cannot compete with the alcohol group of the injected tracer compound, and this results in a high *K* value. The specific behavior of water is probably related to its affinity for polar sites, such as terminal silanol groups or the Ti site itself. A similar trend was observed for water adsorption on TS-1 (Table 1).

Finally, the combined effects of catalyst polarity and solvent on *K* are particularly well illustrated in Table 4, with data for 1,2-epoxyhexane. In methanol, 1,2-epoxyhexane behaves as an apolar molecule, e.g., an olefin, and therefore *K* decreases in the series TS-1 > Ti,Al-β > Ti-MCM-41. However, this trend is reversed in *n*-hexane. In this solvent, epoxyhexane behaves as a polar molecule due to its oxirane ring. Accordingly, in hexane, Ti-MCM-41 has a stronger affinity for the epoxide than TS-1.

TABLE 2

Partition Coefficients for Adsorption of α-Alkenes, 2-Alkanols, Epoxides, and Polar Products on Ti,Al-β at 308 K

	MeOH	EtOH	1-PrOH	2-PrOH	Acetone	Acetonitrile
1-Hexene	2.0	0.6	0.3	0.5	0.3	1.2
1-Heptene	2.7	0.7	0.3	0.4	0.4	1.4
1-Octene	3.8	0.7	0.3	0.4	0.4	1.9
1-Nonene	5.2	0.7	0.3	0.4	0.4	2.3
1-Decene	7.2	0.7	0.3	0.4	0.4	3.0
1-Dodecene	14	0.7	0.3	0.4	0.4	4.4
2-Hexanol	1.7	0.5	0.6	0.5	1.9	2.6
2-Heptanol	2.6	0.5	0.6	0.5	2.0	2.9
2-Octanol	3.2	0.5	0.6	0.6	2.4	3.1
2-Nonanol	4.1	0.5	0.6	0.6	2.8	3.7
1,2-Epoxyhexane	2.6	1.3	0.8	1.3	1.2	1.8
1,2-Hexanediol	3	2.7	1	2	1.6	2.3
Water	0.6	1.2	1.9	2.5	1.6	1.4

TABLE 3

Partition Coefficients for Adsorption of α-Alkenes, 2-Alkanols, Epoxides, and Polar Products on Ti-MCM-41 at 308 K

	MeOH	EtOH	1-PrOH	2-PrOH	Acetone	Acetonitrile
1-Hexene	0.4	0.4	0.3	0.3	0.3	0.4
1-Heptene	0.3	0.4	0.3	0.3	0.3	0.4
1-Octene	0.3	0.4	0.3	0.3	0.3	0.5
1-Nonene	0.3	0.4	0.3	0.3	0.3	0.5
1-Decene	0.3	0.4	0.3	0.3	0.3	0.5
1-Dodecene	0.3	0.4	0.3	0.3	0.3	0.6
2-Hexanol	0.4	0.4	0.4	0.4	0.8	1.4
2-Heptanol	0.4	0.4	0.4	0.4	0.8	1.3
2-Octanol	0.4	0.4	0.4	0.4	0.9	1.4
2-Nonanol	0.4	0.4	0.4	0.4	0.9	1.5
1,2-Epoxyhexane	0.5	0.6	0.6	0.6	0.4	0.6
1,2-Hexanediol	0.6	0.8	1.3	1.5	—	1.9
Water	0.6	0.9	1.8	1.4	0.9	1.3

Catalytic Epoxidation of α-Olefins: Effect of Solvent on Rate

Figure 5a shows olefin conversions for the epoxidation of 1-hexene with TS-1 in different solvents (240 mmol hexene, 67 mmol H_2O_2 per g of catalyst). In all cases epoxide selectivity was over 90%. In methanol, the reaction is two to three times faster than in acetone; other solvents give an even slower reaction. Remark that for alcohol solvents, the rate follows the same order as the K values for 1-hexene (MeOH > EtOH > 1-PrOH). However, catalyst activity in Fig. 5a is not constant. If the data for 1-hexene (0.72 M) epoxidation in methanol are plotted as $Y = \{\ln(x_{\text{olefin}}/(x_{\text{olefin}} - s) + \ln(1 - s)\}$ vs time (see Eq. [2]), a strong downward deviation from linearity is observed (Fig. 5c). Note that a constant activity should lead to a linear plot for first order in olefin and in peroxide, or, for lower orders, even to an upward deviation ($d^2Y/dt^2 > 0$). Similarly, in the case of 1-nonene, it is clear that the curve does not follow a linear course through the origin, as would be expected if the catalytic activity were constant (Fig. 5c).

Because of the unusually rapid rate decrease, truly initial epoxidation rates (mmol g^{-1} h^{-1}) are hard to obtain. The problem is particularly acute in methanol and with long alkenes (from 1-octene upward). The literature contains numerous experiments with clear deactivation (see for instance (16), Fig. 3). The few reported TS-1 reactions with a constant activity rather use small olefins, e.g., C_3 or C_4 olefins (4, 6). For C_6–C_9 olefins, problems of deactivation can be overcome by keeping the amount of alkene converted low with respect to the amount of catalyst, i.e., typically 6 less mmol/g of catalyst. This may necessitate (i) lowering the concentrations of alkene and/or peroxide, (ii) limiting reaction temperature (308 K or less), and (iii) rapid sampling, i.e., every 180 s. Examples of reactions with a constant activity are given in Fig. 5b, for 1-hexene (0.088–0.1 M) in methanol (0.04 M H_2O_2) and in acetone (0.2 M H_2O_2). For these reactions, logarithmic plots following Eq. [2] display satisfactory linearity (Figs. 5c and 5d). Under initial conditions, the rate of 1-hexene epoxidation in MeOH is 14 times larger than in acetone, even if the peroxide concentration in MeOH was deliberately set lower in order to avoid deactivation.

TABLE 4

***K* Values for Adsorption of 1,2-Epoxyhexane on TS-1, Ti,Al-β, and Ti-MCM-41 in Methanol or *n*-Hexane Carrier Solvents**

Solvent	TS-1	Ti,Al-β	Ti-MCM-41
n-Hexane	2.7	3.4	6.6
Methanol	24	2.6	0.5

Effect of Solvent on Reaction Order in Alkene

Figure 6 plots initial epoxidation rates as a function of 1-hexene concentration. Initial peroxide concentrations were 0.2 M for acetone and 0.04 M for methanol. In the case of acetone, a Langmuir–Hinshelwood-type transition from first to zero order in alkene is clearly observed at an olefin concentration larger than 0.3 M. In MeOH, the order in alkene is close to 1 at very low alkene concentrations, but it decreases gradually to zero starting at an alkene concentration of 0.08 M.

Solvent Effect on Apparent E_A

Knowing the effect of temperature on rates may be helpful to determine whether a reaction is under chemical or diffusional control. Figure 7 shows that in acetone, the 1-hexene epoxidation rate triples for each 10 K temperature increase between 298 and 318 K (0.07 M 1-hexene,

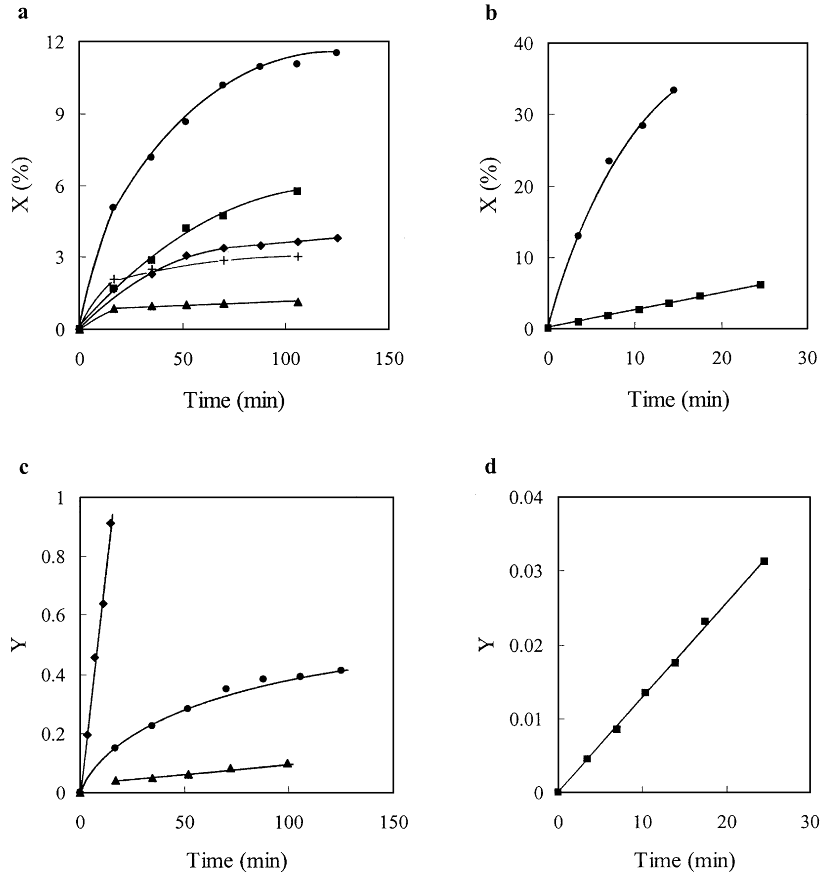


FIG. 5. (a, b) Epoxidation of 1-hexene with TS-1 at 308 K in different solvents. (●) MeOH; (■) acetone; (◆) EtOH; (+) CH_3CN; (▲) 1-PrOH. (a) 15 mg catalyst, 0.72 M olefin, 0.2 M H_2O_2, 5 ml. (b) 15 mg catalyst, 0.088 M olefin, 0.04 M H_2O_2 (in MeOH) or 0.1 M olefin, 0.2 M H_2O_2 in 5 ml acetone. Olefin conversion (X) vs time. (c, d) Plots of $Y = \{\ln(x_{\text{olefin}}/(x_{\text{olefin}} - s) + \ln(1 - s)\}$ vs time (see Eq. [2]) for reactions with 15 mg TS-1 in 5 ml at 308 K. (c) (●) 0.72 M 1-hexene, 0.2 M H_2O_2, MeOH; (▲) same, but with 1-nonene; (◆) 0.088 M 1-hexene, 0.04 M H_2O_2, MeOH. (d) (■) 0.1 M 1-hexene, 0.2 M H_2O_2, acetone.

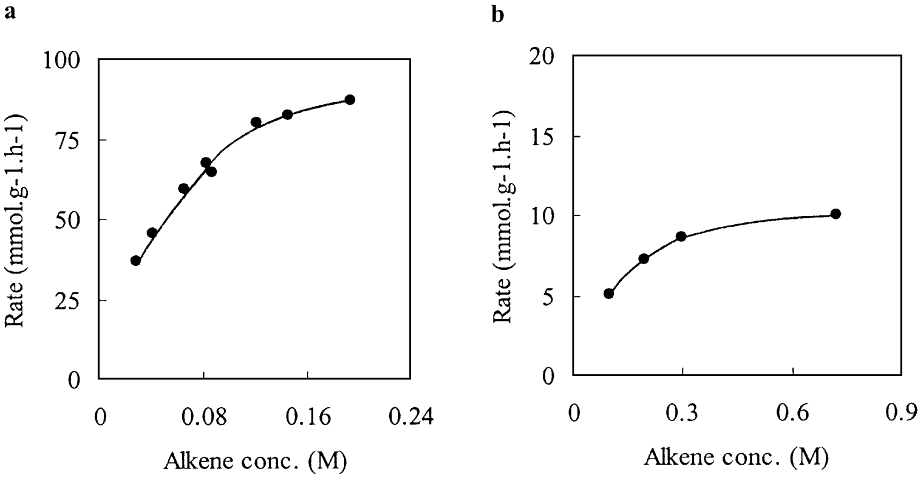


FIG. 6. 1-Hexene epoxidation rates (mmol epoxide g^{-1} catalyst h^{-1}) as a function of alkene concentration in (a) MeOH (0.04 M H_2O_2) or (b) acetone (0.2 M H_2O_2). 5 ml total volume, 15 mg catalyst, 308 K.

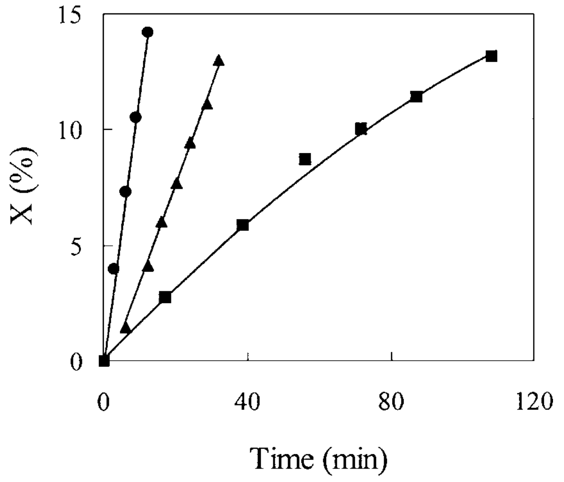


FIG. 7. Effect of reaction temperature on 1-hexene epoxidation in acetone; 15 mg catalyst, 0.2 M H_2O_2, 0.07 M alkene, 5 ml volume. Olefin conversion (X) vs time at 298 K (■), 308 K (▲), or 318 K (●).

0.2 M H_2O_2). This results in an apparent activation energy of 86 ± 6 kJ mol^{-1}, well in the range of a chemically controlled reaction. In methanol, the rate increase with temperature is less pronounced ($E_A = 65 \pm 6$ kJ mol^{-1}).

Relative Reactivities of Homologous α-Olefins

Reactivity ratios may be evaluated in single component experiments (e.g., 1-hexene vs 1-octene) or in competitive experiments (1-hexene vs 1-nonene). Moreover, experiments were performed in methanol or in acetone and under initial conditions or with a catalyst subject to deactivation.

Single component reactions. In acetone, the initial rate of 1-octene epoxidation is twice as high as the rate for 1-hexene. In MeOH, the initial reactivity order curiously depends on the H_2O_2 concentration. With an excess olefin (0.08 M vs 0.04 M H_2O_2), 1-hexene is more reactive, while in excess H_2O_2 (0.08 M vs 0.04 M olefin), 1-octene initially reacts faster than 1-hexene (Figs. 8a–8c).

Alternatively, 1-alkenes were epoxidized under "deactivating" conditions, i.e., with enough reagents to form 67 mmol of epoxide per gram of catalyst, and in MeOH (Fig. 9). Under such conditions, the reactivity order is as reported in the literature, i.e., 1-hexene > 1-heptene > 1-octene > 1-nonene (6). The conversion curves display an initial deactivation "step," especially for 1-nonene (Fig. 9a). However, in acetone, differences between the alkenes are less pronounced (Fig. 9b). 1-Heptene seems the most reactive alkene, and even for 1-nonene, the reaction rate is still

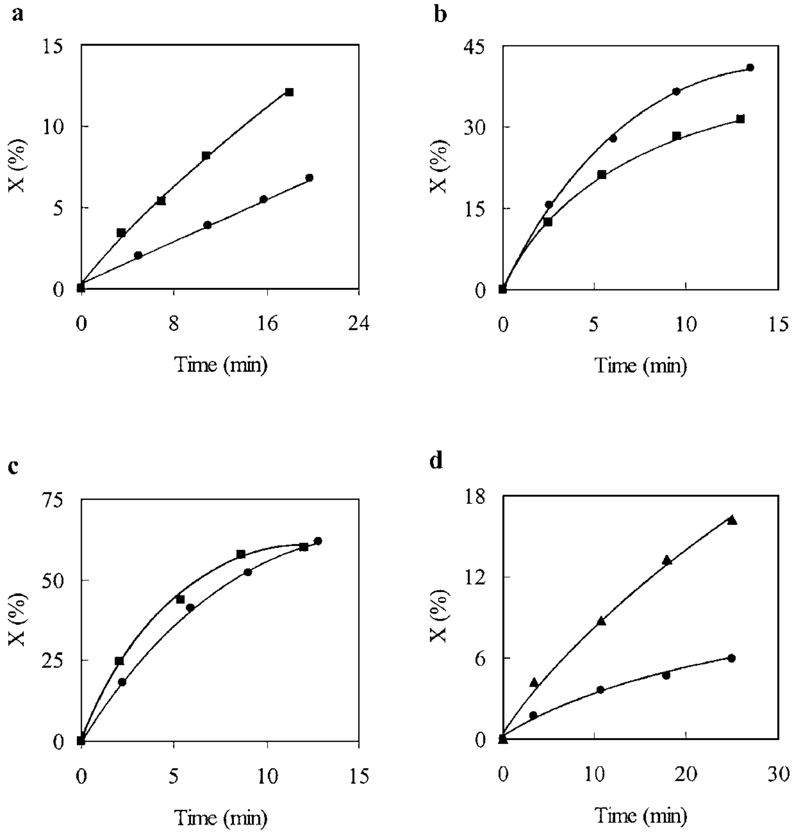


FIG. 8. Relative reactivities of olefins in initial conditions (15 mg catalyst, 308 K, 5 ml volume). Single component experiments with 1-hexene (●) and 1-octene (■): (a) acetone, 0.08 M olefin, 0.2 M H_2O_2; (b) MeOH, 0.08 M olefin, 0.04 M H_2O_2; (c) MeOH, 0.04 M olefin, 0.08 M H_2O_2. (d) Competitive experiment with 1-hexene (●) and 1- nonene (▲): 0.04 M of each olefin, 0.2 M H_2O_2. Olefin conversion (X) vs time.

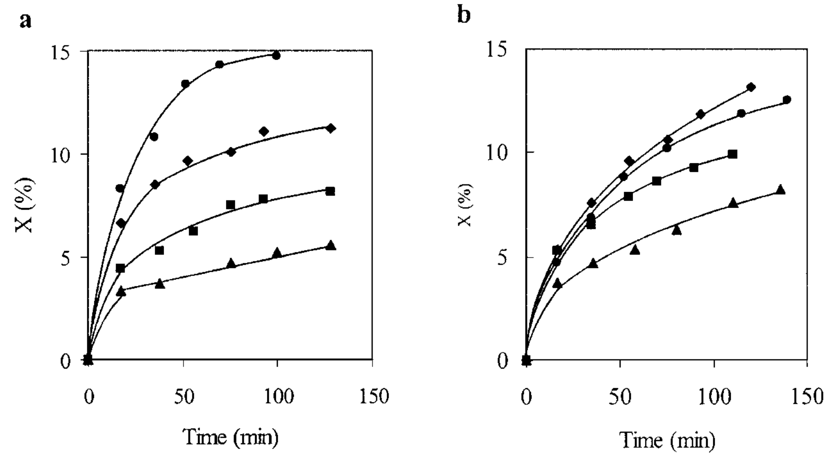


FIG. 9. Epoxidation with TS-1 at 343 K in (a) MeOH or (b) acetone. (●) 1-Hexene; (◆) 1-heptene; (■) 1-octene; (▲) 1-nonene. 15 mg catalyst, 0.72 M olefin, 0.2 M H_2O_2, 5 ml. Olefin conversion (X) vs time.

appreciable after 1 h. As a matter of fact, the reaction of 1-nonene in acetone ultimately yields more epoxynonane than the same reaction in methanol.

Competitive reactions. In all reactions with TS-1, competitive epoxidation of 1-nonene and 1-hexene produces much more epoxynonane than epoxyhexane. An example is shown in Fig. 8d, for a reaction in acetone. A similar result is observed in MeOH. Table 5 displays reactivity ratios from competitive experiments. With TS-1, the preference for nonene over hexene is stronger in methanol than in acetone, and increases with decreasing temperature (entries 1–5). These trends exactly parallel the evolution of the *K* values with solvent and temperature.

Such a preference for nonene is not at all observed on a Ti-β catalyst (Table 5, entries 6 and 7). In MeOH as well as in acetone, slightly more hexene is converted than nonene. As expected, epoxide ring opening products dominate in both solvents (10). In methanol, ethers are found, namely, 1-methoxy-2-hydroxy and 1-hydroxy-2-methoxy alkanes; the dioxolane is observed in acetone.

TABLE 5

Relative Reactivities of 1-Nonene ($C_9^=$) and 1-Hexene ($C_6^=$) in Competitive Experiments

	Catalyst	Solvent	T (K)	C9 epoxide/C6 epoxide	Time (min)
1	TS-1	MeOH	308	2.92	3.5
2	TS-1	Acetone	308	2.57	3.5
3	TS-1	MeOH	308	2.45	58
4	TS-1	MeOH	343	2.05	70
5	TS-1	Acetone	343	1.60	70
6	Ti,Al-β	MeOH	328	0.88	600
7	Ti,Al-β	Acetone	328	0.8	600

Note. Conditions: 15 mg catalyst, 5 ml total volume; (entry 1) 0.2 mmol $C_6^=$, 0.2 mmol $C_9^=$, 0.2 mmol H_2O_2; (entry 2) as in (1), but with 1 mmol H_2O_2; (entries 3–5) 1.8 mmol $C_6^=$, 1.8 mmol $C_9^=$, 1.0 mmol H_2O_2; (entries 6 and 7) 0.5 mmol $C_6^=$, 0.5 mmol $C_9^=$, 1.0 mmol H_2O_2. With Ti,Al-β, most epoxide is solvolyzed (see text).

Effect of Epoxide Chain Length on TS-1 Deactivation

TS-1 was first aged in a solution of H_2O_2 and C_6, C_8, or C_{10} epoxide. Next an epoxidation was started by injection of 1-heptene (Fig. 10). It is clear that preincubation with an epoxide deactivates the TS-1 catalyst. Deactivation is most pronounced for long epoxides.

DISCUSSION

This work presents a large set of liquid-phase adsorption data for TS-1, Ti,Al-β, and Ti-MCM-41 materials (Figs. 1–4, Tables 1–4). Such data can be used to determine in a quantitative way the organophilic or hydrophilic properties of

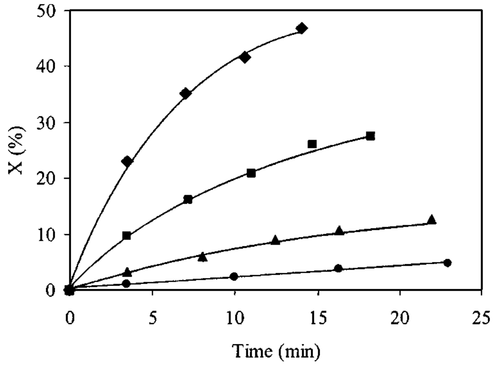


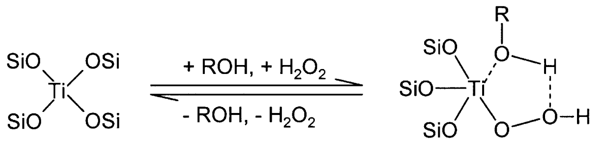
FIG. 10. Effect of epoxide presorption on activity of TS-1 in heptene epoxidation. 15 mg catalyst was incubated for 20 min with 0.2 mmol H_2O_2 and 0.1 mmol 1,2-epoxyhexane (■), 1,2-epoxyoctane (▲), or 1,2-epoxydecane (●) in MeOH (total volume 5 ml); next 1-heptene (0.08 M) was added. (◆) No preincubation. 1-Heptene conversion (X) vs time.

different catalysts. An adsorption approach has also been applied by Weitkamp *et al.* in defining a hydrophobicity index (HI). The latter is determined from the competitive gas phase adsorption of water and a hydrocarbon on a zeolite (17, 18). Application of this concept to TS-1 zeolites has for instance shown that hydrophilicity increases with Ti content (19). While the HI is a highly valuable concept, particularly to understand gas-phase catalytic processes, the present liquid-phase chromatographic data more closely reflect sorption effects in a liquid-phase catalytic reaction. For a given catalyst, the partition coefficients K are not only sensitive to temperature, but also to the solvent in which the reaction is conducted. The latter point is an important advantage over the HI. Remark that the K values essentially result from a competitive adsorption, as adsorption of the tracer implies displacement of the solvent from the catalyst.

In a given solvent, the affinity for a hydrophobic compound, e.g., 1-octene, increases in the series Ti-MCM-41 $<$ Ti,Al-β $<$ TS-1 (Tables 1–3). This order of increasing organophilicity can be expected based on the decreasing Ti content (19) and is consistent with earlier observations, based, e.g., on evaluation of the intensity of the $\nu_{\text{O-H}}$ vibration of physisorbed water (20, 21). The organophilic behavior of TS-1 is in line with the absence of Al, the small number of defect sites, and with the small pore diameter, which imposes a large area of contact between the zeolite walls and the adsorbed molecule (22).

On the other hand, the chromatographic pulse method also reveals the critical effect of a solvent on the partition of a compound and hence on the intraporous concentrations of the different compounds of the reaction mixture. When methanol is used as a solvent, alkanes, olefins, and their epoxides are much more easily absorbed by the organophilic TS-1 structure. The methanol in the bulk solution outside the pores then functions as a polar, hydrogen-bonded network. In order to minimize disturbance of this network, apolar molecules are driven inside the pores of TS-1. With a less polar alcohol or an aprotic solvent as a carrier, apolar molecules are more favorably solvated in the external solution, and the K values are smaller (Table 1).

For TS-1, methanol is not only an exceptional solvent in adsorption, but also in catalysis. In order to account for the exceptionally high activity of TS-1 in MeOH (Figs. 5a and 5b), Bellussi *et al.* (5) propose following active species:



The literature contains indeed strong evidence that a Ti-hydroperoxo species is formed by reaction of H_2O_2 with the Ti site. A Ti(OOH) species explains the acidity of peroxide-activated TS-1, for instance in epoxide solvolysis, and the effects of acids and bases on the epoxidation activity (1, 4, 5, 23). In the hypothesis of Bellussi, a coordinated methanol ligand increases the electrophilicity of the distal peroxide oxygen, via formation of a hydrogen bond. However, coordination of a CH_3OH ligand on the Ti(OOH) complex has not been proven by direct observation in a spectrum.

Based on the sorption data, an alternative explanation for the high rates with TS-1 in methanol is that due to the high intraporous alkene concentration, epoxidation by the Ti(OOH) complex is faster in a methanol medium. With 1-PrOH as a solvent, the K values indicate that the 1-hexene concentration in the TS-1 pores is lower (Table 1), and consequently, epoxidation is much slower. d^0 Epoxidation catalysts (Ti, Mo, . . . , with W as an exception) are generally even inhibited by alcohol solvents (24), and the fact that the intraporous methanol concentration is low in TS-1 may even favor the epoxidation. Summarizing, while methanol coordination is a possible event, there is no need to invoke such a coordination as the reason for the observed rate differences between different solvents (Fig. 5).

The literature data and our own experiments show that for epoxidation of a small olefin such as 1-hexene with H_2O_2, the catalyst activity decreases in the series TS-1 $>$ Ti,Al-β $>$ Ti-MCM-41 (20). Sorption data indicate that the intraporous 1-hexene concentration decreases in the same order. Moreover, it has been noticed during our experiments and in a previous study (20) that the peroxide disproportionation is more pronounced for Ti-MCM-41 than for TS-1. Again this is in line with the stronger sorption of H_2O_2 on the more hydrophilic Ti-MCM-41 structure. While these sorption effects probably contribute to the observed activity differences, it is important to underline that differences between the active sites presumably play an even more decisive role.

While initial rates with TS-1 are highest in methanol, the advantage of using this solvent is partially offset by a fast deactivation. As demonstrated in Fig. 10, particularly long epoxides cause a strong deactivation of TS-1 in the presence of H_2O_2. This may be due to oligomerization or other secondary reactions of the epoxides and pore blocking by the resulting products (4). On the other hand, sorption data indicate that 1,2-epoxydecane is most likely to form such oligomers, as it is much more strongly adsorbed in the micropores than 1,2-epoxyhexane. This holds especially for processes in methanol, where the differences between the K values are largest (Fig. 3). Thus, both pore blocking by secondary products and strong adsorption of high molecular weight epoxides explain the low rates for a catalyst preincubated with 1,2-epoxydecane.

Finally, sorption gives insight in the relative reactivity of homologous olefins. The literature holds that epoxidation of higher α-olefins in TS-1 is slower because of their decreased diffusivity in the micropores; hence $\nu_{\text{1-hexene}} > \nu_{\text{1-nonene}}$ (ν is the reaction rate) (6). The latter order is indeed observed in conditions where the TS-1 catalyst is already deactivated (Fig. 9a). However, a close look under truly initial conditions reveals that, for instance, in acetone, 1-octene clearly reacts faster than 1-hexene (Fig. 8a). This is in agreement with the partition coefficients K, which predict a higher intraporous concentration, and hence a higher reaction rate for the longer alkene (Table 1). Even if diffusion of the longer alkene should be slower, this apparently does not affect its epoxidation.

The fact that diffusion in TS-1 is not necessarily a rate-determining factor is also apparent from Fig. 7: the apparent activation energy E_A for 1-hexene epoxidation in acetone (86.5 kJ mol^{-1}) is well inside the range of a chemically controlled reaction. For the reaction in methanol, the rate increase with temperature is smaller. Sorption predicts that intraporous concentrations decrease with temperature; hence the rates should increase less with temperature than based on thermal activation of the reaction alone. On the other hand, one may not exclude that for the fastest reactions in methanol (up to 85 mmol g^{-1} h^{-1}), intraporous diffusion of peroxide or alkene may become rate determining.

In methanol, initial rates are comparable for 1-hexene and 1-octene (Figs. 8b and 8c). An explanation is that, due to the high K values, intraporous alkene concentrations are very high for both alkenes; hence, the nature of the alkene barely affects the reaction rate. This idea is confirmed by Fig. 6, which shows rate dependences on total alkene concentration. In methanol, the transition from first to zero order in alkene sets in at clearly lower concentrations (0.08 M) than in acetone (0.3 M). Only when the alkene concentration is lowered (e.g., to 0.04 M in Fig. 8c), differences in intraporous alkene concentration become important again, and 1-octene is more reactive than 1-hexene.

In all competitive experiments, the longer, more strongly adsorbed alkene is epoxidized by TS-1 at a clearly higher rate than the shorter substrate (Fig. 8d, Table 5). Even in cases where fast catalyst deactivation cannot be avoided, e.g., for a reaction with 1-nonene in methanol, epoxidation of 1-nonene still largely dominates over the 1-hexene reaction. Thus, in spite of its lower diffusivity, especially in a partially plugged catalyst, nonene is preferred by TS-1 over hexene, proving that such order is determined by sorption phenomena rather than by diffusion. This hypothesis is validated by the competitive reactions over Ti,Al-β; with this catalyst, differences between hexene and nonene are minor. This agrees well with the much smaller differences between the K values on Ti,Al-β.

As an exemplary implication of these findings, one may observe that methanol is not always be the best solvent to work in. With methanol, the initial reaction as well as deactivation are fast. Consequently, for 1-nonene epoxidation, it is more advisable to use a solvent which causes less epoxide adsorption, and consequently less deactivation, such as acetone (compare Figs. 9a and 9b).

CONCLUSION

Summarizing, it has been demonstrated that based on the partition coefficients K for partition between TS-1 and a solvent, one can successfully account for (i) the superior rates of TS-1 epoxidations in methanol, (ii) the deactivating effects of especially long epoxides, and (iii) the relative reactivities of α-olefins in different solvents, in single component and in competitive experiments. These insights are complementary to existing models for olefin epoxidation with TS-1 that are based on the chemistry in the primary coordination sphere of Ti. Sorption data are valuable to understand the behavior of the Ti site in its larger context of a crystalline lattice.

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