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Zeolite screening for the racemization of 1-phenylethanol

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Abstract

To select a suitable system for the racemization of 1-phenylethanol, a commercially relevant chiral alcohol, four acid zeolites and five solvents were screened. Results show that the zeolite/solvent combination influences not only the reaction rate but also the product yield because of their influence on side reactions. As a general rule we can say that the higher the racemization rate, the lower the product yield. The choice of solvent is also important for avoiding catalyst deactivation over time, especially when recycling of the catalyst is envisaged. Kinetic modeling of the results was performed in order to allow a better comparison of the different reaction systems and a more complete analysis of the phenomena underlying their behavior. Of the 20 combinations tested, zeolite H-Beta Si:Al = 75 in ethyl acetate and zeolite H-Beta Si:Al = 12.5 in isooctane, water and vinyl acetate showed the most promising results.

Keywords: Zeolite; Racemization; 1-Phenylethanol; Kinetic modeling

1. Introduction

In organic synthesis, racemization is often an undesirable phenomenon. However, the increasing demand for enantiomerically pure compounds led to the development of processes involving the kinetic resolution (KR) of a racemate [1]. In order to circumvent the 50% conversion limitation in a standard KR, it is useful to introduce, *in situ*, a step involving the racemization (or equilibration) of the substrate, thus creating a dynamic kinetic resolution (DKR) process with a theoretical conversion of 100% [2,3].

Enantiopure 1-phenylethanol (1-PE) is a chiral building block in the fine chemical and pharmaceutical industries and has applications as an ophthalmic preservative, a solvatochromic dye, an inhibitor of cholesterol intestinal absorption and a mild floral fragrance [4].

Depending on their nature, different substrates may be racemized in distinct ways [5–7]. For secondary alcohols such as 1-PE, a variety of racemization methods are available. Some of the most popular exploit the reversible oxidation to the corresponding ketone with iridium-, rhodium- or ruthenium-based catalysts [6]. Their use has been reported both in homogeneous conditions [8] and supported on hydroxyapatite [9] or alumina [10]. For a limited number of *sec*-alcohols and conditions, biocatalytic racemization with mandelate racemase is also possible [11]. Basic catalysis can be used when the substrate presents an acidity-improving substituent adjacent to the chiral center [11].

The racemization of *sec*-alcohols can also be accomplished by acid catalysis. After protonation and water elimination, the chiral identity of the substrate is lost as a result of the reversible formation of a planar carbocation [12]. In the case of 1-PE, the loss of a proton at this stage will yield a styrene molecule as a side product. When using catalysts such as zeolite Beta, the racemization can also occur *via* a redox mechanism [13] (similar to the Meerwein-Ponndorf-Verley reduction and Oppenauer oxidation reactions) with acetophenone as the intermediate (Fig. 1).

Zeolites are extremely versatile heterogeneous catalysts and have a vast number of academic and industrial applications in acid catalysis [14,15]. They have previously been shown to surpass the performance of homogeneous and other heterogeneous acid catalysts in a screen involving the racemization of 1-PE and other benzylic alcohols in aqueous conditions. Wuyts et al. [12] have studied the influence of the zeolite framework type, the zeolite Si:Al ratio, the reaction temperature and the

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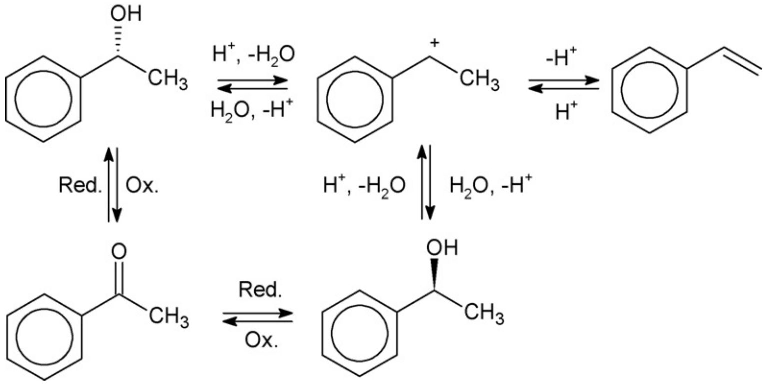

Fig. 1. Two different mechanisms of racemization of 1-phenylethanol catalyzed by zeolite H-Beta [13].

substrate concentration on the reaction rate, but only for racemization occurring in an aqueous medium.

The occurrence of side reactions involving the substrate, the solvent or both can severely impair the development of an adequate system to perform this reaction, as it lowers the product yield. The choice of solvent plays a key role in the analysis of this aspect and it is difficult to theoretically predict the system behavior solely based on the properties of both solvent and zeolite. Therefore, in this work, several acid zeolites were screened in the racemization of 1-PE using aqueous and four organic media.

2. Experimental

Materials. Zeolites Beta CP814E (Si:Al molar ratio = 12.5), Beta CP811E-150 (Si:Al = 75) and HY CBV 720 (Si:Al = 15, %Na_2O = 0.03) were from Zeolyst, zeolite LZY-82 (Si:Al = 4.5) was from UOP and zeolite NH_4Y (Si:Al = 2.5, %Na = 1.6) was from Sigma–Aldrich. All zeolites were calcined at 500 °C for 8 h under 0.5 $L_{dry\ air}\,g_{zeo}{}^{-1}\,h^{-1}$ prior to use. Zeolite NaHY (Si:Al = 15, molar %Na = 76) was obtained from calcined HY CBV 720 after two cycles of ion exchange with $NaNO_3$ 2 M at 100 °C, washing with distilled water and calcination.

(*R*)-(+)-1-phenylethanol 99% (ee 97+%) was from Alfa Aesar, ethyl acetate (EA) 99.5+% was from Sigma–Aldrich, *tert*-butyl methyl ether (TBME) 98% was from Sigma–Aldrich, isooctane *p.a.* was from Merck and vinyl acetate (VA) 99+% was from Sigma–Aldrich.

Instrumentation. Samples were analyzed by gas chromatography on a HP 5890A equipped with a Varian CP-Chirasil-Dex CB (25 m) chiral column and using FID detection. Concentrations were determined using external standards.

Racemization reactions. Standard reactions were carried out in closed 10 mL glass reactors containing 2 mL of solvent and 50 mg of zeolite. Reactions started with the addition of 30 mg of (*R*)-1-PE and took place in an incubator at 30 °C with orbital shaking at 250 rpm.

Catalyst recycling. After the first racemization cycle, the reaction mixture was centrifuged, the liquid phase was discarded and the zeolite was washed twice with 2 mL of fresh solvent before being air-dried overnight and reused. Due to minor losses of catalyst in sampling, the amounts of fresh solvent and reactant were proportionally adjusted.

3. Results and discussion

In order to find a suitable system for the racemization of 1-PE, four zeolites – H-Beta Si:Al = 12.5 and 75, HY Si:Al = 15 and ultra stable H-LZY-82 Si:Al = 4.5 – were tested in different media: water and four organic solvents.

Table 1 compares the enantiomeric excess (ee) of the alcohol obtained at 24 h of reaction and at other relevant times for the slowest and quickest reactions. The MB parameter represents the fraction of the initial mass of 1-PE that has disappeared from solution. Ideally, MB should be close to 0% but in some cases it reached 100% (no 1-PE detected), due to the extent of the side reactions. The GC chromatograms did not show an accumulation of acetophenone (a possible intermediate according to Fig. 1) but a peak attributable to styrene was detected in 11 of the 22 experiments, although it represented only negligible amounts and could not explain the reduction in total 1-PE concentration. However, styrene may polymerize in the presence of zeolites [13] and thus elude detection. Other side reactions may breakdown 1-PE, producing compounds that exit the GC column overlapped by the solvent peak, or promote the adsorption of the substrate onto the acid sites, in a process similar to coking, and prevent its detection. Negative MB values mean that no significant transformation occurred *via* side reactions and that solvent evaporation during the experiment (due to the high volatility of some of the solvents used and because the reactor was opened to collect samples) caused an increase in the total concentration of 1-PE.

Zeolite HY showed the poorer results, as it only managed to racemize a small amount of the substrate in TBME and vinyl acetate. Despite having a lower Si:Al ratio, the performance of the ultra stable H-LZY is equal or better than that of HY in every solvent. In isooctane, H-LZY racemizes 1-PE very quickly but its global concentration also decreases very significantly; this decrease in concentration can be due either to secondary reactions that consume the reactant or to 1-PE molecules remaining strongly adsorbed to the zeolite, as a result of the formation of very stable carbocations, which is likely to happen

Table 1
Performance of several zeolites in the racemization of 1-phenylethanol in five solvents

Zeolite	Solvent[a]	Time (h)	ee[b] (%)	MB[c] (%)
H-Beta 12.5	EA	24	100	9.0
	EA	72	77	1.7
H-Beta 75	EA	24	86	−6.1
HY	EA	24	100	−2.8
H-LZY-82	EA	24	100	−0.8
	EA	72	96	−0.3
H-Beta 12.5	Isooctane	24	78	3.4
H-Beta 75	Isooctane	24	11	32
HY	Isooctane	24	100	25
H-LZY-82	Isooctane	24	–	100
	Isooctane	1	18	63
H-Beta 12.5	TBME	24	100	−19
	TBME	168	97	−26
H-Beta 75	TBME	24	93	−6.2
HY	TBME	24	100	5.3
	TBME	264	95	−19
H-LZY-82	TBME	24	80	22
H-Beta 12.5	VA	24	20	7.7
H-Beta 75	VA	24	–	100
	VA	4	100	95
HY	VA	24	–	100
	VA	4	77	18
NaHY 1.6	VA	24	61	69
NaHY 76	VA	24	100	6.7
H-LZY-82	VA	24	67	67
H-Beta 12.5	Water	24	71	−5.3
H-Beta 75	Water	24	65	36
HY	Water	24	100	7.0
H-LZY-82	Water	24	100	7.3

[a] EA, ethyl acetate; TBME, *tert*-butyl methyl ether; VA, vinyl acetate.

[b] ee = (R-PE − S-PE)/(R-PE + S-PE).

[c] $MB_t = (PE_0 - PE_t)/PE_0$; PE_t, total mass concentration of (RS)-1-PE at reaction time t.

even by interaction of the solvent with the zeolite. The generation of carbenium ions by acid zeolites with 4-methoxystyrenes and isooctane has been described [16].

Zeolite H-Beta Si:Al = 12.5 racemizes the substrate faster than HY with a similar Si:Al ratio. Whereas H-Beta has been reported to perform this reaction by two separate pathways (acid catalysis and oxidation/reduction) [13], the same has not been shown for HY. Zeolite H-Beta Si:Al = 12.5 displayed the best overall performance for this reaction, especially in isooctane, water and vinyl acetate, simultaneously catalyzing the racemization at a satisfactory rate (Fig. 2) and with little or no losses in substrate.

For zeolite H-Beta Si:Al = 75, with fewer active sites than H-Beta Si:Al = 12.5, the racemization is faster in all the tested solvents, in accordance with the expected higher acid strength of the H-Beta Si:Al = 75 sites. However, in isooctane, water and specially vinyl acetate, high MB values indicate a much more significant occurrence of side reactions, casting aside the possibility of using any of these three combinations for the desired purpose.

Examining the performance of each zeolite in different solvents, it can be said that, in general, water and especially isooctane and vinyl acetate offer the best conditions for a fast racemization. Unfortunately, these solvents also favor side reactions significantly.

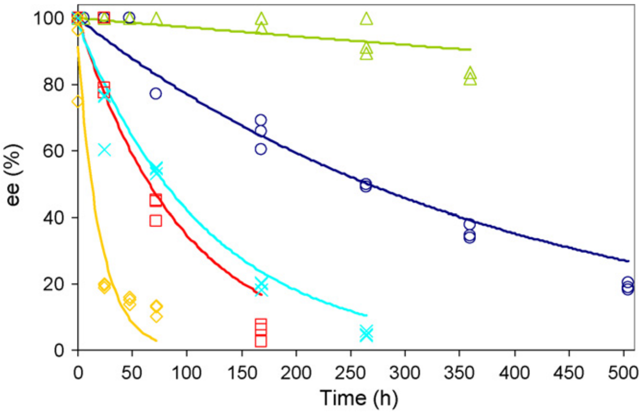

Fig. 2. Racemization of 1-phenylethanol with zeolite H-Beta Si:Al = 12.5 in ethyl acetate (○), TBME (△), isooctane (□), water (×) and vinyl acetate (◇). The lines are the result of kinetic modeling for each reaction.

For vinyl acetate, in addition to zeolite HY, zeolites NaHY with a small (1.6%) and high (76%) sodium content were also tested in the racemization. Results showed that HY caused the complete loss of 1-PE from the reaction mixture. NaHY 1.6 catalyzed the racemization at a good rate but severe losses of reactant also occurred. As for NaHY 76, although some reactant loss was observed, it did not racemize 1-PE at all, as it would be expected from its weak acidity.

Kinetic modeling of the studied systems was performed with the purpose of allowing a more quantitative assessment of the activity of the catalysts for the racemization itself, while taking into account all the relevant phenomena, such as the formation of secondary products and solvent evaporation, which was relevant for the more volatile solvents. The material balance for (R)-1-PE in the reactor yields Eq. (1), where m_{rPE} is the mass of (R)-1-PE in the reaction mixture, rPE and sPE are, respectively, the concentrations (in mg mL^{-1}) of (R)-1-PE and (S)-1-PE, V is the reaction mixture volume (in mL), t is the reaction time (in h), k_1 is the kinetic constant of the racemization reaction (in h^{-1} mg$_{\mathrm{zeo}}{}^{-1}$), assumed to be identical in both reaction directions, and k_2 is the kinetic constant of a generic reaction that consumes (R)-1-PE and (S)-1-PE and leads to the formation of non-discriminated by-products (in h^{-1} mg$_{\mathrm{zeo}}{}^{-1}$).

$$\frac{\mathrm{d}m_{\mathrm{rPE}}}{\mathrm{d}t} = V\frac{\mathrm{drPE}}{\mathrm{d}t} + \mathrm{rPE}\frac{\mathrm{d}V}{\mathrm{d}t} = -k_1\mathrm{rPE}V + k_1\mathrm{sPE}V - k_2\mathrm{rPE}V \tag{1}$$

The reactions were assumed to have first order kinetics. The variation of reaction volume over time, due to evaporation, was considered to be constant throughout the experiment and its rate was denoted by α (in mL h^{-1}). A similar equation was written for (S)-1-PE. The model describing the reaction system is represented as:

$$\frac{\mathrm{drPE}}{\mathrm{d}t} = -k_1(\mathrm{rPE} - \mathrm{sPE}) - k_2\mathrm{rPE} + \frac{\alpha}{V}\mathrm{rPE} \tag{2}$$

$$\frac{\mathrm{dsPE}}{\mathrm{d}t} = k_1(\mathrm{rPE} - \mathrm{sPE}) - k_2\mathrm{sPE} + \frac{\alpha}{V}\mathrm{sPE} \tag{3}$$

Table 2
Optimized kinetic modeling parameters for the racemization of 1-phenylethanol

Zeolite	Solvent[a]	rPE_0 (mg mL^{-1})	sPE_0 (mg mL^{-1})	k_1 (h^{-1} $mg_{zeo}{}^{-1}$)	k_2 (h^{-1} $mg_{zeo}{}^{-1}$)	α (mL h^{-1})	σ (mg mL^{-1})
H-Beta 12.5	EA	7.0	0.0	2.60E−05	0.00E+00	8.13E−04	0.10
H-Beta 75	EA	6.1	0.0	3.48E−05	2.20E−05	1.00E−03	0.09
HY	EA	7.0	0.0	0.00E+00	0.00E+00	1.05E−03	0.07
H-LZY-82	EA	8.4	0.0	6.06E−06	0.00E+00	9.50E−04	0.13
H-Beta 12.5	Isooctane	5.5	0.0	1.05E−04	2.72E−05	7.73E−04	0.11
H-Beta 75	Isooctane	6.4	0.0	7.20E−04	2.62E−04	9.40E−06	0.10
HY	Isooctane	5.9	0.0	1.18E−09	1.50E−04	0.00E+00	0.06
H-LZY-82	Isooctane	7.1	0.0	1.01E−02	1.98E−02	4.87E−06	0.09
H-Beta 12.5	TBME	7.8	0.0	2.80E−06	2.84E−05	3.83E−03	0.13
H-Beta 75	TBME	5.2	0.0	5.27E−06	0.00E+00	1.22E−03	0.08
HY	TBME	7.1	0.0	3.20E−08	1.46E−08	1.23E−03	0.12
H-LZY-82	TBME	7.0	0.2	9.77E−06	6.25E−05	3.07E−03	0.14
H-Beta 12.5	VA	6.3	0.3	4.51E−04	1.12E−04	0.00E+00	0.11
H-Beta 75	VA	8.4	0.0	0.00E+00	1.31E−02	1.10E−03	0.04
HY	VA	8.3	0.0	2.94E−04	1.59E−03	0.00E+00	0.18
NaHY 1.6	VA	5.3	0.0	5.07E−04	2.04E−04	4.04E−03	0.41
NaHY 76	VA	8.5	0.0	1.99E−08	2.59E−05	1.16E−03	0.09
H-LZY-82	VA	7.9	0.0	4.17E−05	1.01E−03	2.64E−02	0.15
H-Beta 12.5	Water	8.5	0.1	8.39E−05	1.20E−05	0.00E+00	0.12
H-Beta 75	Water	7.7	0.0	8.46E−05	3.05E−05	0.00E+00	0.30
HY	Water	8.5	0.0	0.00E+00	1.35E−03	0.00E+00	0.12
H-LZY-82	Water	9.5	0.0	0.00E+00	5.22E−04	0.00E+00	0.13

[a] EA, ethyl acetate; TBME, *tert*-butyl methyl ether; VA, vinyl acetate.

This model was fitted to the experimental data using a least-squares regression technique using k_1, k_2 and α as model parameters. To minimize the impact of the inaccuracy of the initial concentrations of (*R*)-1-PE and (*S*)-1-PE on the model results, these initial values were also used as fitting parameters, respectively, rPE_0 and sPE_0 (in mg mL^{-1}).

In the model optimization results (Table 2), σ represents the quotient between the square root of the summed squares of the residuals and the number of experimental points, which can be used to analyze the quality of the fitting.

The kinetic constant for the racemization process, k_1, is not as clearly related to the type of catalyst as anticipated, indicating that the solvent might significantly affect the reaction rate. Even so, in general, zeolite H-Beta Si:Al = 75 shows the best performance in the reaction, followed by H-Beta Si:Al = 12.5, zeolite H-LZY-82 and finally zeolite HY. The combination of zeolite H-LZY-82 with isooctane showed an unusually high value for k_1, although also a high value for k_2, when compared to other experiments with isooctane. Fig. 3 shows two examples of model fittings, one of which illustrates the high reaction rates of both racemization and 1-PE consumption in the case of zeolite H-LZY-82 in isooctane.

Table 2 shows that k_1 is not just related to the type of zeolite but also heavily dependent on the solvent in which the reaction is carried out. As a rule, isooctane and vinyl acetate are the solvents that allow a faster racemization, followed by water when used with Beta zeolites, then ethyl acetate, TBME and finally water in combination with Y type zeolites. The different behavior observed with water is likely related to zeolite Y having a higher degree of hydrophilicity than Beta zeolites [17], hindering the access of 1-PE molecules to the acid sites and slowing the racemization down.

Alongside the experimental data for zeolite H-Beta Si:Al = 12.5, the lines in Fig. 2 exemplify a representation of the fitted model and have been obtained by calculating the ee with the concentrations values that resulted from integrating the model equations for the total reaction time.

The results for the racemization kinetic constant in the zeolite H-Beta Si:Al = 12.5 experiments confirm the order displayed in Fig. 2: the reaction rate is lowest in TBME and increases progressively when occurring in ethyl acetate, water, isooctane and finally vinyl acetate. Nevertheless, in the latter solvent k_2 is very high, which substantially reduces the product yield. Isooctane can be considered the most appropriate solvent because it presents a compromise between good racemization rate and relatively low substrate decomposition.

The value of k_1 obtained for zeolite Beta Si:Al = 12.5 in water, 0.000084 h^{-1} $mg_{zeo}{}^{-1}$ was compared with values obtained by Wuyts et al. [12]; although the work presented in Ref. [12] has been done in a different range of temperatures, the Arrhenius plot for the same reaction was extrapolated to 30 °C. The result of 0.000378 h^{-1} $mg_{zeo}{}^{-1}$ is around five times higher than the one obtained in this work. Even though the model used by Wuyts et al. does not include substrate consumption, the relatively low value of k_2 for this case indicates that this is not the most important reason for the discrepancy. Rather, the variation in stirring velocity (900 rpm versus 250 rpm in the present work) may be responsible for the difference in results, since diffusion is likely to play a key role in the migration of the substrate to the zeolite surface, before entering the zeolite pores and coming in contact with the acid sites.

A limitation in comparing results based on the MB parameter is that evaporation can often mask the disappearance

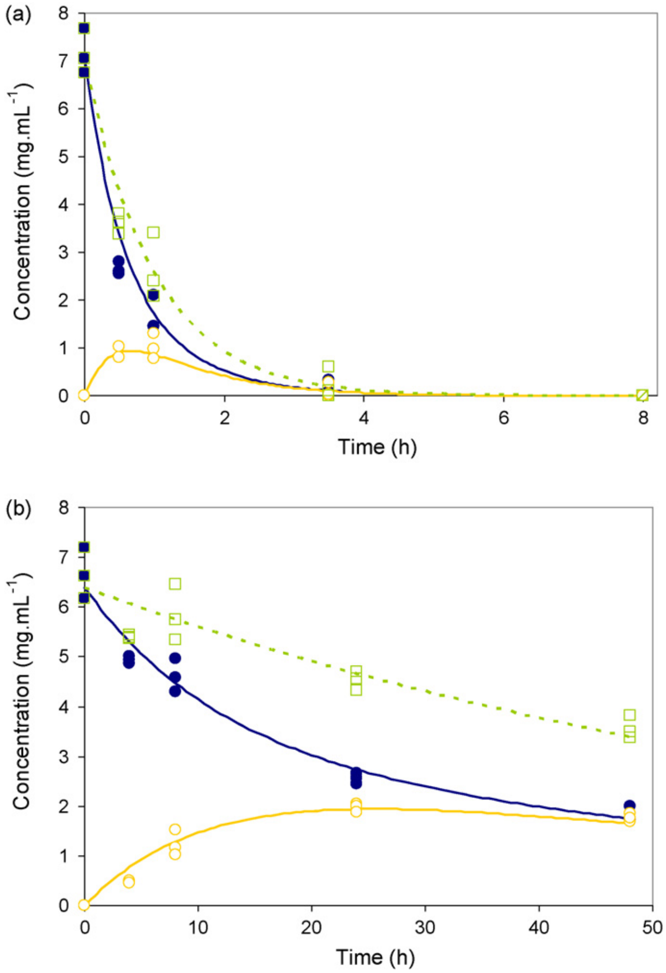

Fig. 3. (*R*)-1-PE (●), (*S*)-1-PE (○) and total 1-PE (□) concentrations in the racemization reactions in isooctane with (a) zeolite H-LZY-82 and (b) zeolite H-Beta Si:Al = 75. The lines are the result of kinetic modeling.

of 1-PE. Modeling, however, allowed the separation of these phenomena to a certain extent. The kinetic constant k_2 results show that, in general, vinyl acetate is the solvent most prone to host the formation of side products, followed by isooctane. The use of water and TBME as solvents reduces those effects and ethyl acetate only caused substrate consumption with zeolite H-Beta Si:Al = 75. When comparing both Beta zeolites, it is clear that the occurrence of by-products is more significant for the catalyst with a higher Si:Al ratio value in all solvents except for TBME. In vinyl acetate, zeolite H-Beta Si:Al = 75 degraded the substrate very rapidly, preventing the detection of (*S*)-1-PE.

Observing the modeling results for the evaporation rate, α, the order of solvent volatility is essentially the same for every zeolite, as expected, with TBME being the most volatile, then vinyl acetate, ethyl acetate, isooctane and finally water. This sequence is in accordance with the vapor pressure values at 25 °C [18], respectively, 33.6 kPa, 15.4 kPa, 12.6 kPa, 6.5 kPa and 3.2 kPa. There were, however, three exceptions. In the experiment with zeolite HY in vinyl acetate, α indicates that there is no significant evaporation of the solvent for the duration of the experiment, even though this is the second most volatile solvent in the series; this was probably due to the short duration of this experiment (4 h).

As for zeolites H-Beta 12.5 and H-LZY-82 in vinyl acetate, the anomalous α values are probably linked to the fact that catalyst deactivation was observed under these conditions. In these two racemization experiments, minutes after adding the substrate to the suspension containing the powdered catalyst, the originally white zeolite particles became noticeably brown and the ee stabilized after 24 h. As such, at 72 h of reaction time, the catalysts were recycled to determine whether a loss of activity had occurred. As a control experiment, the reaction with zeolite Beta 12.5 in ethyl acetate was repeated and afterwards the catalyst was recycled.

Fig. 4 shows that a drastic deactivation of zeolite H-Beta 12.5 occurs during the first cycle of reaction in vinyl acetate, whereas in ethyl acetate zeolite Beta 12.5 shows no loss of activity. This indicates that vinyl acetate is not a suitable solvent for this reaction, as it is very susceptible to phenomena that cause the blockage of the acid sites, probably polymerization and coking involving the solvent and/or the reactant.

To model these results, the equations were modified to include the deactivation of the catalyst. An activity factor, β, ranging between 1 for a completely active zeolite and 0 for an inactive one, which affects both the racemization and the side

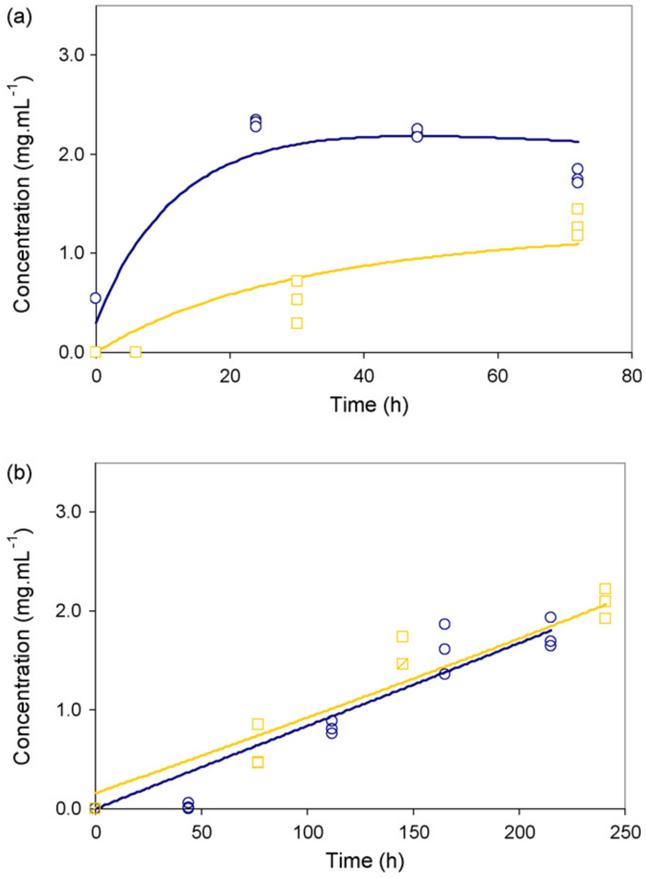

Fig. 4. (*S*)-1-PE concentrations during the first (○) and second (□) cycles of racemization with zeolite H-Beta Si:Al = 12.5 in (a) vinyl acetate and (b) in ethyl acetate. The lines are the result of kinetic modeling with deactivation for each reaction.

Table 3
Optimized kinetic modeling parameters for the racemization experiments involving catalyst deactivation and recycling

Cycle	Zeolite	Solvent[a]	rPE_0 (mg mL^{-1})	sPE_0 (mg mL^{-1})	k_1 (h^{-1} mg_{zeo}^{-1})	k_2 (h^{-1} mg_{zeo}^{-1})	α (mL h^{-1})	k_d (mL mg^{-1} h^{-1})	σ (mg mL^{-1})
1st	H-Beta 12.5	VA	6.4	0.3	5.58E−04	1.66E−04	0.00E+00	2.39E−03	0.10
2nd	H-Beta 12.5	VA	8.7	0.0	9.61E−05	8.42E−05	0.00E+00	2.72E−03	0.12
1st	H-LZY-82	VA	8.0	0.0	2.83E−04	3.21E−03	0.00E+00	2.85E−02	0.06
2nd	H-LZY-82	VA	9.4	0.0	0.00E+00	0.00E+00	3.83E−04	0.00E+00	0.06
1st	H-Beta 12.5	EA	7.4	0.0	2.29E−05	1.02E−07	1.89E−03	0.00E+00	0.09
2nd	H-Beta 12.5	EA	9.6	0.2	1.58E−05	0.00E+00	1.71E−03	0.00E+00	0.31
	NaHY 1.6	VA	8.3	0.0	5.75E−04	7.74E−03	0.00E+00	6.43E−02	0.10

[a] EA, ethyl acetate; VA, vinyl acetate.

reactions (both occur at the same acid sites), was introduced. Several assumptions for the way this parameter varied with time were tested and the one that best fitted the experimental results was considering a rate of deactivation proportional to the concentration of reactant, with a k_d rate constant (in mL mg^{-1} h^{-1}). Assuming that the deactivation was zero order in relation to the reactant (as it would happen if only the solvent was involved in the deactivation process) failed to describe the actual results that were obtained. Eqs. (4)–(6) were used for modeling the recycling experiments and the results are shown in Table 3.

$$\frac{\mathrm{drPE}}{\mathrm{d}t} = -k_1\beta(\mathrm{rPE} - \mathrm{sPE}) - k_2\beta\mathrm{rPE} + \frac{\alpha}{V}\mathrm{rPE} \quad (4)$$

$$\frac{\mathrm{dsPE}}{\mathrm{d}t} = k_1\beta(\mathrm{rPE} - \mathrm{sPE}) - k_2\beta\mathrm{sPE} + \frac{\alpha}{V}\mathrm{sPE} \quad (5)$$

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = -k_\mathrm{d}\beta(\mathrm{rPE} + \mathrm{sPE}) \quad (6)$$

The equations were integrated using the optimum parameters and the results were plotted in Fig. 4 (lines). The graph shows that this deactivation model fits the experimental data adequately. The effect of the deactivation is very noticeable in the experiments with vinyl acetate but the combination of zeolite H-Beta 12.5 and ethyl acetate has good potential for catalyst recycling, as k_d is 0 in this case.

The experiment with zeolite NaHY 1.6 in vinyl acetate was also modeled using catalyst deactivation because the σ value was very high and the plotted experimental data pointed to this possibility (data not shown). In this case, the deactivation model improved the quality of this fitting (σ decreased significantly) and k_d showed a value of the same magnitude as the experiments with vinyl acetate.

Globally, the most effective zeolite/solvent combinations tested for the racemization of 1-PE were considered to be H-Beta 75 in ethyl acetate and H-Beta 12.5 in isooctane, water and vinyl acetate (with deactivation issues that compromise the possibility of catalyst recycling).

4. Conclusions

From the results described we can conclude that, when selecting the zeolite/solvent combination for the racemization of 1-PE, a compromise in the acidity of the zeolite must be considered. In fact, it can be observed that, in general, the faster the racemization goes, as a result of higher acidity of the zeolite, the easier it is for the substrate to be converted into by-products.

Tuning of the zeolite acidity, both in terms of available number and strength of the sites seems, however, possible, and the results indicate that zeolites are promising catalysts for this reaction.

Kinetic modeling of the reaction sets allowed a better understanding and quantification of the influence of the nature of both zeolite and solvent in the racemization activity, by-product formation, solvent evaporation and catalyst deactivation.

Of the 20 combinations tested, zeolite H-Beta Si:Al = 75 in ethyl acetate and zeolite H-Beta Si:Al = 12.5 in isooctane, water and vinyl acetate showed the most promising results.

The results obtained in this work are in agreement with the screening results published by Wuyts et al. [12], indicating that zeolite Beta is the most promising one for racemization when using water as a solvent. However, our results indicate that water is not necessarily the best solvent for the racemization reaction and that organic solvents may also be used for this reaction, opening the way for DKR reaction systems in a single liquid phase.

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