Application of zeolite titanium Beta in the rearrangement of α-pinene oxide to campholenic aldehyde

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Zeolite titanium Beta is found to be an effective catalyst for the industrially relevant rearrangement of α-pinene oxide to campholenic aldehyde, giving selectivities of up to 89% in the liquid phase. In the gas phase, up to 94% selectivity is obtained at conversions above 95%, which exceeds the best values obtained with homogeneous Lewis acid catalysts. The selectivity obtained is profoundly influenced by the solvent or co-adsorbate applied.

Keywords: titanium Beta, Lewis acid, α-pinene oxide, campholenic aldehyde, isomerization

1. Introduction

Campholenic aldehyde is an important intermediate in the synthesis of several sandalwood fragrances which constitutes an important growth area in perfumery chemicals. Earlier work, in our group, on the acid-catalyzed rearrangement of α-pinene oxide showed the potential of solid Lewis acids to promote the selective formation of campholenic aldehyde [1]. In general, Brønsted acids give maximum selectivities of 55%, while Lewis acids, especially the zinc halides, can give selectivities as high as 85%. Recently, Hölderich et al. [2] reported a selectivity to campholenic aldehyde of 78% by using a carefully prepared H-USY zeolite at low reaction temperatures of around 0 °C. These authors claimed that the high selectivity observed was a result of well-dispersed Lewis acid sites in a nearly all-silica matrix.

Recently, the Lewis acid activity of aluminum-free zeolite titanium Beta (Ti-Beta) was demonstrated by van der Waal et al. in the epoxidation of alkenes [3] and in the Meerwein–Ponndorf–Verley reduction of 4-*tert*-butylcyclohexanone to the corresponding *cis*-alcohol with high stereoselectivity [4]. Since the selective production of campholenic aldehyde appears to be favoured by Lewis acids, Ti-Beta has been tested as catalyst in the rearrangement of α-pinene oxide. The high dispersion of titanium sites in this material, with its Si/Ti ratio of 59 and consequent low active-site concentration, suggests that it may be beneficial for reactions involving highly reactive molecules prone to (bimolecular) consecutive reactions.

2. Experimental

2.1. Materials

Ti-Beta was synthesized according to the method of van der Waal et al. [3] with a Si/Ti ratio of 59, a N_2-BET surface of 687 $m^2\,g^{-1}$ and a particle diameter of 1.2 μm (as determined by SEM). α-pinene oxide (97%) was obtained from Aldrich. Campholenic aldehyde was kindly provided by Quest International.

2.2. Methods

Liquid-phase experiments were conducted at 70 °C using 25 ml solvent, 4.22 g α-pinene oxide, 250 mg 1,3,5-*tri*-isopropylbenzene (internal standard) and 50 mg of the catalyst.

Vapour-phase reactions were performed at atmospheric pressure in a fixed-bed continuous down-flow reactor using 0.3 g Ti-Beta (83 μmol Ti), diluted with 1.2 g quartz powder as the catalyst at 90 and 100 °C. The gas flow (50 ml min^{-1}) contained 1 vol% α-pinene oxide (1.22 mmol/h) and 10 vol% of an inert co-adsorbate in nitrogen as the carrier-gas. Products were analyzed by on-line GC, GC-MS and ^{1}H- and ^{13}C-NMR.

3. Results and discussion

The rearrangement of α-pinene oxide is believed to be initiated by the coordination of the epoxide oxygen atom to a Lewis (or a Brønsted) acidic center, thereby inducing ring opening of the epoxide followed by subsequent or concerted alkyl shifts (figure 1) [1]. It is assumed that this mechanism also holds in the case of Ti-Beta as the

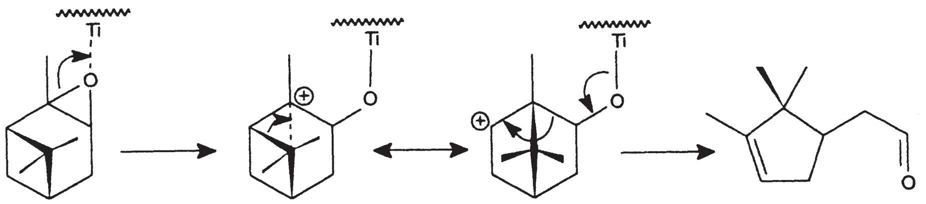

Figure 1. Proposed mechanism for the isomerisation of α-pinene oxide by a Lewis acid (here represented by a Ti atom connected to a zeolite framework) into campholenic aldehyde.

Table 1
Selected solvent properties arranged by an increasing dielectric constant.

Solvent	Dipole moment (Debije)	Dielectric constant	Boiling point (°C)
cyclohexane	0.00	2.02	80.7
1,4-dioxane	0.45	2.21	101.3
benzene	0.00	2.28	80.1
di-isopropyl ether	1.22	3.88	68.5
chlorobenzene	1.54	5.62	132.0
1,2-dichloroethane	0.70	10.36	83.4
butanone	2.76	18.51	80.0
2-propanol	1.66	19.20	82.2
acetonitrile	3.44	37.50	81.6

Table 2
Catalytic activity of Ti-Beta as a function of the solvent applied.

Solvent	Conversion[a] (%) α-pinene oxide[b] (TON)	Initial rate (first 10′) (mmol/min)	Selectivity[a] (%) Camp. aldehyde
cyclohexane	4 (79)	0.036	83
1,4-dioxane	45 (849)	0.083	68
benzene	35 (695)	0.110	55
di-isopropyl ether	16 (318)	0.095	68
chlorobenzene	6 (119)	0.042	72
1,2-dichloroethane	29 (576)	0.108	81
butanone	72 (1430)	0.079	42
2-propanol	100 (1986)	0.076	33
acetonitrile	7 (139)	0.308	89

[a] After 24 h.

[b] Values in parentheses denote turn-over numbers.

Lewis acid catalyst. Furthermore, the unique molecular-sized pore structure of the zeolite may enhance selectivity by shape selectivity, as was shown in the reduction of 4-*tert*-butylcyclohexanone [4].

3.1. Liquid-phase experiments

The effects of various solvents on the activity and selectivity in the Ti-Beta-catalyzed isomerization have been extensively investigated, since the co-adsorption of the solvent into the micropore system of Ti-Beta will greatly influence the intraporous α-pinene oxide concentration. Since α-pinene oxide can give undesired bimolecular or polymerization reactions, low intraporous concentrations are preferred for high yields of campholenic aldehyde. The hydrophobic nature of Ti-Beta [3] will cause it to preferentially adsorb less polar molecules over more polar molecules. Apolar solvents are expected to be adsorbed strongly, thus giving a low intraporous α-pinene oxide concentration and vice versa. In table 1, the dipole moments, dielectric constants and boiling points of the solvents applied have been summarized.

As can be observed from table 2, the solvent employed has a major impact on the selectivity, activity and stability of the catalyst. The low selectivities in the case of the polar solvents 2-propanol and butanone are most likely a result of:

(i) the transformation of the Lewis acidic Ti site into a Brønsted acid site by the coordination of alcohols [3]; and

(ii) products resulting from the reaction of the solvent with α-pinene oxide, as was deduced from GC-MS measurements. We mention here also the unexpected reaction of α-pinene with ketones such as butanone [5].

When an apolar solvent such as cyclohexane is applied, a very low initial reaction rate and conversion are observed. In contrast, acetonitrile, the most polar solvent tested, gives the highest initial rate, but the catalyst deactivates rapidly, resulting in a conversion of only 7% after 24 h. Since the

Table 3
Campholenic aldehyde selectivity as a function of the co-adsorbate and the time on stream in the vapour-phase experiments at 90 °C.

Co-adsorbate	Initial conversion[a] (%)	Campholenic aldehyde initial selectivity[a] (%)
none	95 (36)	63 (25)
1,4-dioxane	95 (95)	90 (70)
1,2-dichloroethane	95[b]	94[b]
benzene	100 (82)	88 (81)
n-heptane	100 (100)	88 (85)
n-octane	100	89
n-nonane	100	88
cyclohexane	100	85
methylcyclohexane	100	93
1,2-dimethylcyclohexane[c]	100	76
1,3-dimethylcyclohexane[c]	100	84
1,4-dimethylcyclohexane[c]	100	92

[a] Values in parentheses denote the conversion or the selectivity after 5 h on stream.

[b] Due to the swelling of “O”-rings in the reactor system, no long-term data could be collected with dichloroethane as the co-adsorbate.

[c] *cis*/*trans* mixtures.

intraporous α-pinene oxide concentration is expected to be the highest for polar solvents, this indicates that the initial rate is dependent on the intraporous α-pinene oxide concentration; when this is high, however, consecutive reactions with another α-pinene oxide molecule will be facilitated, resulting in a faster catalyst deactivation. An optimal intraporous α-pinene oxide concentration thus exists, leading to both high activity and good catalyst stability. Under the experimental conditions chosen, dichloroethane proved to be the most suitable solvent with a selectivity of 81% and a TON of 576.

3.2. Vapour-phase reactions

In heterogeneous catalysis, vapour-phase conditions are usually preferred due to their ease of (continuous) operation. We recently showed that Ti-Beta is an excellent catalyst for the vapour-phase reduction of 4-methylcyclohexanone via the MPV reaction [4]. In the corresponding liquid-phase MPV reduction, both Ti-Beta and Al-Beta could be used as highly shape-selective catalysts, but, in the vapour phase, the strong Brønsted acidity of Al-Beta causes a rapid deactivation, leaving only Ti-Beta as an option for vapour-phase conditions [4].

The absence of a solvent when working under vapour-phase conditions will strongly increase the intraporous α-pinene oxide concentration. This will lead to a decreased campholenic aldehyde selectivity, since from the liquid-phase experiments it was concluded that the intraporous α-pinene oxide concentration should be kept low to suppress consecutive reactions. From the first entry of table 3 for pure α-pinene oxide, it can be seen that the campholenic aldehyde selectivity is indeed only 63%, combined with a fast deactivation of the catalyst within 5 h. A competitive inert co-adsorbate may be added to the reactor feed to control the intraporous α-pinene oxide concentration in an analogous way to that achieved by variation of the solvent in the liquid phase. The ratio co-adsorbate/reactant will usually be lower than the ratio solvent/reactant in the liquid phase. Therefore, more hydrophobic co-adsorbates can be used, which would cause the catalyst to be almost completely filled with solvent under liquid-phase conditions and, consequently, retard the reaction; this is illustrated by the entry for cyclohexane in tables 2 and 3. When an appropriate co-adsorbate is chosen, a very high selectivity to campholenic aldehyde (94%) can be obtained, even at complete conversion (TOF $\geqslant 15\ \mathrm{mol\,mol_{Ti}^{-1}\,h^{-1}}$) of α-pinene oxide, as shown in table 3. Dichloroethane is again found to be a very suitable co-adsorbate, although its undesirable environmental impact provides an incentive to seek alternatives. It is found that the use of alkanes (which have much lower toxicity) as the co-adsorbates also results in very high campholenic aldehyde selectivities of >85%; methylcyclohexane and 1,4-dimethylcyclohexane are found to be particularly effective. The use of the somewhat more bulky 1,3- and 1,2-dimethylcyclohexane, however, leads to reductions in selectivity.

It is possible that the intraporous diffusion coefficients for the bulky dimethylcyclohexanes are lower than for the linear alkanes, leading to a slower diffusion of reactants and products. The resulting increased residence time of α-pinene oxide and products in the internal pore system may result in an increased probability of bimolecular reactions and, consequently, to reduction in the maximum attainable campholenic aldehyde selectivity. This is indicated by GC-MS measurements, which show the formation of several products with molecular mass 304, corresponding to dimers of α-pinene oxide or isomers. The high conversions obtained with the present experimental set-up make it unsuitable for studying the possible differences in sorption behavior and/or kinetic effects caused by the addition of co-adsorbates, which will be investigated in a later stage of this work. It is possible that, at lower conversions, even higher selectivities may be observed than in the present work.

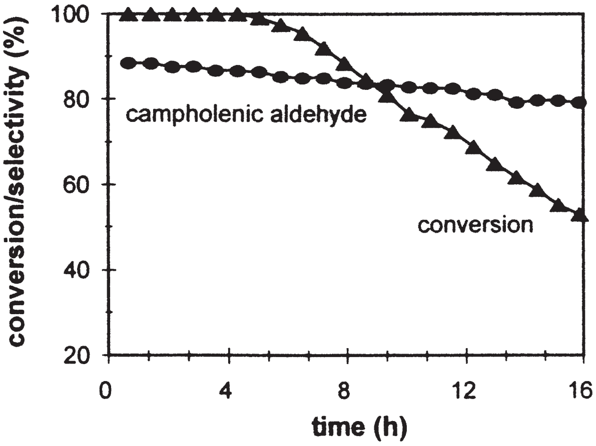

Figure 2. Selectivity to campholenic aldehyde and conversion of α-pinene oxide as a function of the time on stream. Conditions: Ti-Beta (20 wt% in quartz), temperature $= 100\,^{\circ}$C, 10 vol% n-heptane, 1 vol% α-pinene oxide, 50 ml/min total gas stream.

The possible participation of the product in the production of heavy condensate was tested by feeding campholenic aldehyde over a freshly calcined catalyst. However, no formation of products was observed and the catalyst remained colourless. This indicates that dimerization of campholenic aldehyde cannot be a cause of deactivation. When the feed was changed to a mixture of n-heptane and α-pinene oxide, without prior regeneration of the catalyst, the rearrangement occurred with the same selectivity (87%) and conversion (100%), as when no campholenic aldehyde had previously been fed. It appears that intraporous α-pinene oxide is the most likely molecule to be implicated in the heavy-ends formation and in the catalyst deactivation despite its low intraporous concentration.

In an extended vapour-phase experiment, using n-heptane as the co-adsorbate at $90\,^{\circ}$C, it was observed that the catalyst deactivates linearly after 6 h time on stream. The campholenic aldehyde selectivity decreases steadily. Heavier products (GC-MS: MW $= 304$) were also detected with increasing time on stream. After termination of the run, the reactor tube was found to be heavily fouled by condensation products and the spent catalyst bed was black, indicating that at $90\,^{\circ}$C product desorption is severely hindered. Raising the reaction temperature to $100\,^{\circ}$C eliminated the condensation of heavy products, while maintaining the same selectivity to campholenic aldehyde (88–79% in 16 h). In figure 2, the conversion and selectivity (n-heptane as the co-adsorbate, $100\,^{\circ}$C) as a function of the time on stream are displayed, showing the linear decrease in activity and selectivity. Furthermore, after termination of the run the catalyst was only slightly coloured and hardly any condensates were detected inside the reactor. The most likely cause of the deactivation appears to be the accumulation of undesorbed dimeric and heavier oligomers.

It is noteworthy that operation at these industrially practicable temperatures appears possible with Ti-Beta, while for other catalysts low temperatures are required for high selectivity [2]. Complete regeneration of the catalytic activity (up to 100 times) could be achieved by an air burn-off at $480\,^{\circ}$C.

4. Conclusions

Titanium Beta proves to be an excellent catalyst for the rearrangement of α-pinene oxide to campholenic aldehyde in both the liquid and vapour phase. This is mainly attributed to the presence of isolated, well-dispersed titanium sites in a Brønsted-acid-free silica matrix. The very high selectivities observed for Ti-Beta, even at temperatures as high as $100\,^{\circ}$C, in contrast to other Lewis acid catalysts, are proposed to be due to transition-state shape selectivity induced by the pore structure of the zeolite. Since α-pinene oxide may be obtained by oxidation of α-pinene using Ti-Beta as the oxidation catalyst [3], Ti-Beta may be a promising catalyst for the direct synthesis of campholenic aldehyde from α-pinene employing an inexpensive oxidant. However, it is necessary to avoid the use of aqueous reaction mixtures (e.g., aqueous H_2O_2) or alcoholic solvents, if a high selectivity towards campholenic aldehyde is to be achieved. We are currently investigating this reaction in more detail and are including other (mesoporous) Lewis acidic catalysts, which were recently described [6].

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