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Zeolite Titanium Beta

A Selective Catalyst for the Gas-Phase Meerwein–Ponndorf–Verley, and Oppenauer Reactions

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Aluminium-free zeolite titanium beta was tested in the Meerwein–Ponndorf–Verley reduction of 4-methylcyclohexanone with various secondary and primary alcohols as hydrogen donors, using a fixed-bed continuous-flow gas-phase reactor. A high selectivity towards the thermodynamically unfavourable *cis*-4-methylcyclohexanol was observed, which is ascribed to transition-state selectivity in the straight channels of zeolite beta. However, in the gas-phase, the selectivity to the *cis*-alcohol is significantly lower than in the liquid-phase when using 2-propanol as the hydrogen donor. Based on kinetic and adsorption experiments, it is concluded that the concentration of alcohol reductant in the zeolite is an important parameter in determining selectivity. More hydrophobic alcohols give rise to an increased selectivity to the *cis*-alcohol product. From the sorption experiments it was concluded that this is due to a higher internal concentration of the alcohol reductant in the hydrophobic titanium beta zeolite. The observed selectivities and activities are consistent with a mechanism in which this alcohol is not only the hydrogen donor but is also required to remove the *cis*-alcohol product formed from the catalytic site by alcoholysis, before consecutive reactions can take place. © 1998 **Academic Press**

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1. INTRODUCTION

The Meerwein–Ponndorf–Verley reduction of carbonyl compounds and the Oppenauer oxidation of alcohols, together denoted as MPVO reactions, are highly selective reactions (1). For instance, other reducible groups such as C=C double bonds and C-halogen bonds, are not attacked. In MPV reductions a secondary alcohol generally forms the reductant while in Oppenauer oxidations a ketone acts as oxidant. It is generally accepted that MPVO reactions proceed via a complex in which both carbonyl and alcohol are coordinated to a Lewis acid metal ion, after which a hydride transfer from the alcohol to the carbonyl group occurs (Fig. 1). Usually, metal *sec*-alkoxides are used as homogeneous catalysts in reductions and metal *tert*-butoxides in oxidations (1).

Zeolites are crystalline microporous metal oxides which have potential as regenerable heterogeneous catalysts in various organic reactions (2). Because of their unique microporous structures, zeolites are especially promising in the field of shape-selective catalysis. Only a few examples of the use of zeolites in MPVO reactions have been reported (3–9) so far. The reactions were carried out in the gas phase over zeolites A, X, and Y, exchanged or impregnated with alkali or alkaline-earth cations (3–5) or in the liquid or gas phase over beta type zeolites (6–9). Shape-selectivity in gas-phase reactions was observed by Shabtai *et al.* (3) in the conversion of citronellal over zeolite X. It was shown that selectivity could be tuned by the size of the exchanged metal ion. In NaX there was enough space for the substrate to perform an intramolecular ring closure to isopulegol, whereas over CsX reduction to the linear citronellol was observed. Similar steric effects were also observed for various other substrates.

Recently Creyghton *et al.* (6, 7) and van der Waal *et al.* (8, 9) reported on the use of Al-beta and Ti-beta, respectively, in the liquid-phase MPVO reduction of 4-*tert*-butylcyclohexanone to 4-*tert*-butylcyclohexanol. The high selectivity towards the thermodynamically less favoured *cis*-alcohol, which is the industrially relevant isomer, was explained by a restricted transition-state around a Lewis-acidic aluminium or titanium atom in the straight channels of the zeolite beta pore system (7). In a preliminary report on the possibility of continuous-flow gas-phase MPVO reactions over zeolite beta-based catalysts, we noted significant changes in selectivity compared to the batch-wise conducted, liquid-phase experiments (9). In the gas-phase a lower selectivity towards the *cis*-alcohol, as well as dehydration of the alcohols formed was observed. Since in the liquid-phase experiments the *cis*-alcohol selectivity was constant over the reaction time, it seemed unlikely that the conversion level alone was the cause of this remarkable difference.

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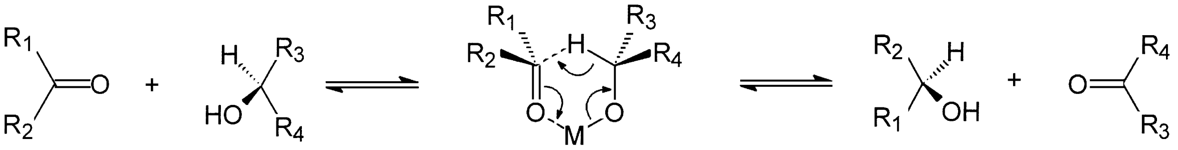

FIG. 1. The Meerwein–Ponndorf–Verley–Oppenauer reaction (1).

The differences in selectivity between the liquid- and gas-phase reactions induced us to study the gas-phase reaction in more detail. Kinetic measurements have been employed to study the effect of the intra-zeolitic alcohol reductant concentration, which could be influenced by changing the alcohol used or by applying different partial pressures of the alcohol, on the activity and the selectivity. Based on the effects observed, a catalytic mechanism is proposed and a dual role of the alcohol reductant is suggested.

2. EXPERIMENTAL

Aluminium-free zeolite titanium beta (Ti-beta) was synthesized according to van der Waal *et al.* (10) using di(cyclohexylmethyl)dimethylammonium hydroxide (DCDMA.OH) as the template. For a typical synthesis, 0.25 g titanium(IV) ethoxide (TEOT, Acros 33–35% TiO_2) was added to 30.0 g of a 19.5% w/w DCDMA.OH solution and the mixture was stirred until all TEOT was dissolved. To facilitate the dissolution of TEOT, 1 ml of H_2O_2 (30% w/w aqueous) was added. To the resulting clear solution 3.0 g Aerosil 200 (Degussa), 0.15 g all-silica beta seeds (11), and 11.8 g water were added and the gel was aged for at least 24 h. After crystallisation (14 days at 140°C), the zeolite (1.4 g) was filtrated, washed, dried, and calcined at 540°C in air. Elemental analysis, performed using a LINK EDX system, showed a Si : Ti molar ratio of 69 and confirmed the absence of oligomeric titanium dioxide phases. Zeolite aluminium beta (Al-beta, Si : Al = 11.2) was prepared according to Wadlinger and Kerr (12). UV-Vis spectra were recorded on a Varian Cary-1 spectrophotometer using barium sulfate as the reference. Scanning electron microscopy (SEM) was performed on a Philips Xl-20 apparatus using 15 keV electron beam.

Competitive adsorption experiments were performed in 1,3,5-triisopropylbenzene (10 g, Aldrich 97%) as the solvent, with 1,3,5-tri-*tert*-butylbenzene (Fluka) as the internal standard. For the competitive experiments with 2-propanol, 50 μl 2-propanol (Baker p.a.), 50 μl of the appropriate alcohol and 100 mg zeolite titanium beta, predried at 200°C, were added to the solvent. For the competitive adsorption experiments with 4-methylcyclohexanone (4-Me-ONE, Acros 98%), 50 μl 4-Me-ONE (0.35 mmol) and 3.5 mmol of the appropriate alcohol were used. All samples were analyzed after attainment of the adsorption equilibria and analyzed by GC on a CP-52-Carbowax column (50 m, ID = 0.53 mm, N_2 carrier gas).

The gas-phase MPVO reactions were performed at 85 to 400°C in a fixed-bed continuous down-flow reactor with an internal diameter of 7 mm, operated at atmospheric pressure under plug flow conditions. All auxiliary tubing was maintained at 200°C to prevent condensation of products. The catalyst, Ti-beta or Al-beta (0.30 g), was diluted with 1.20 g α-quartz powder and pressed into pellets which were subsequently crushed and sieved to particles with a diameter of 0.7–1.0 mm. Reactant mixtures were pumped, via an evaporator, into a stream of preheated carrier gas (usually nitrogen) by means of a motor-driven syringe pump. The gas flow, unless otherwise stated, contained 10 vol% 2-propanol (Baker p.a.) and 1 vol% of 4-methylcyclohexanone (4-Me-ONE, Acros 98%). The total gas flow was typically 50 ml/min, the molar gas flow of 4-Me-ONE and products was 2.04×10^{-5} mol min^{-1}, (WHSV = 2.9 $g_{\text{substrates}}\, g_{\text{cat}}^{-1}\, h^{-1}$, GHSV = $1.56 \times 10^3\, h^{-1}$). Other alcohols tested were 1-propanol (Baker p.a.), 1-butanol (Acros, 99%), 2-butanol (Baker p.a.), 1-pentanol (Acros 98%), 2-pentanol (Acros 99%), 3-pentanol (Fluka), 2-heptanol (Fluka), cyclopentanol (Acros 99%), and cyclohexanol (Baker), under similar conditions as described for 2-propanol. Samples of the reactor effluent were taken regularly by means of an autosampler and analysed by an on-line GC equipped with a CP-Sil-19 column (50 m, ID = 0.53 mm, N_2 carrier gas). The temperature-programmed reactions were performed by continuously raising the reactor temperature at 12°C h^{-1}.

3. RESULTS AND DISCUSSION

3.1. *Catalyst Characterization*

Primary characterization of the catalysts used was performed by X-ray diffraction (XRD), UV-Vis spectroscopy, and scanning electron microscopy (SEM). After hydrothermal synthesis, the XRD diffractogram showed that a fully crystalline material was obtained with less than 2% impurities. The incorporation of tetrahedral titanium in the zeolite framework was confirmed by the presence of a single absorption band at 47.000–50.000 cm^{-1} in the UV-Vis spectrum (10). The absence of absorption bands at lower frequencies in the UV-Vis spectrum also confirmed the absence of oligomeric titanium dioxide particles (10). Analysis of the zeolite crystal size and morphology with SEM (Fig. 2) demonstrated a uniform distribution of disk-shaped single crystals with 1.2 μm diameter.

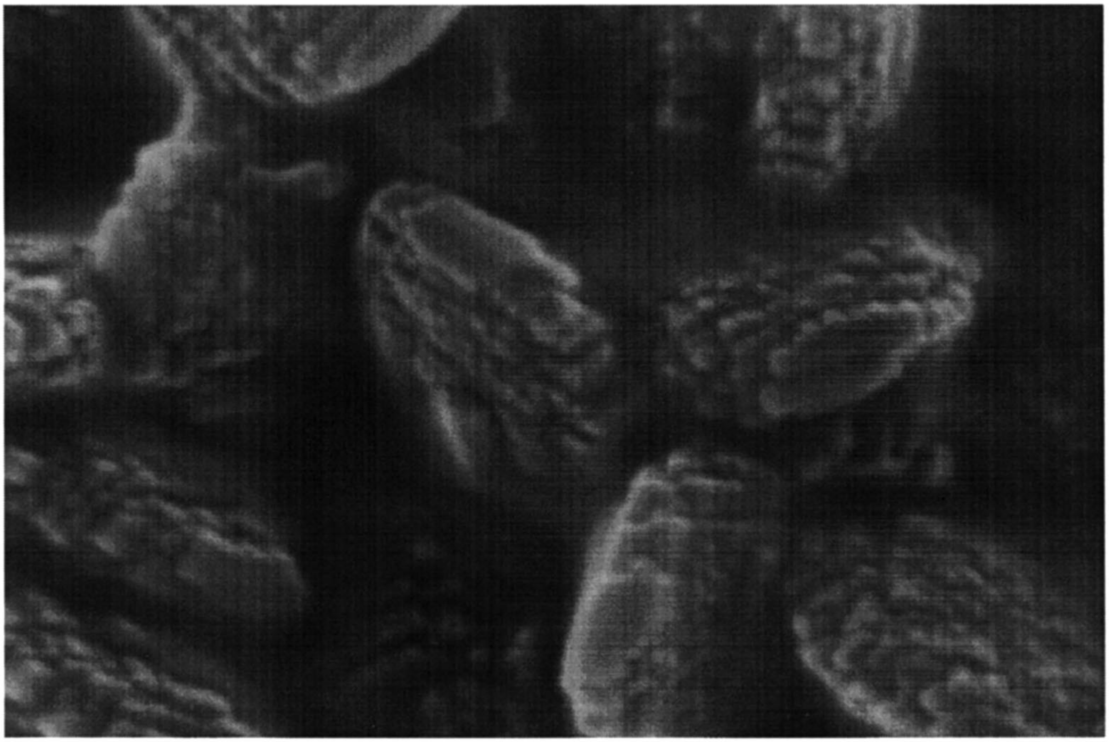

FIG. 2. Scanning electron micrograph (SEM) of the Ti-beta catalyst. The particles are disk-shaped crystallites with a diameter of 1.2 μm.

3.2. *Gas- and Liquid-Phase MPVO Reactions Catalyzed by Zeolite Titanium Beta*

From an industrial point of view, gas-phase reactions are often preferred due to their ease of operation. As we reported recently (9), the gas-phase reduction of 4-methylcyclohexanone and the oxidation of *cis*- and *trans*-4-methylcyclohexanol over Ti-beta and Al-beta showed that the titanium-based catalyst has a considerably lower rate of deactivation, compared with zeolite Al-beta. The higher deactivation rate of zeolite Al-beta is probably caused by the higher acidity of the protic aluminium site compared to the nonprotic titanium site. From the liquid-phase experiments, it was concluded that the major by-products are the acid-catalysed aldol condensation products from two ketone molecules (8). In the gas phase, non- or very slowly desorbing aldol condensates formed from two 4-Me-ONE molecules probably plug the pores of the zeolite thereby deactivating the catalyst.

Two important differences between the gas-phase and liquid-phase reactions were observed over Ti-beta. The most striking is the selectivity towards the *cis*-alcohol. Under liquid-phase conditions a selectivity of 99% at 85°C towards the *cis*-alcohol was observed, while in the gas-phase over Ti-beta only 51 to 62% *cis*-alcohol was obtained at 100°C, using a 2-propanol/4-methylcyclohexanone ratio of 10 : 1 (Fig. 3) (8, 9). Furthermore, the dehydration of the alcohols formed to 4-methylcyclohexene (4-Me-ENE) was a major consecutive reaction in the gas-phase while no dehydrated products could be detected in the liquid phase reductions. The somewhat higher temperature of 100°C, compared with 85°C for the liquid-phase experiments, could not explain this behaviour. Decreasing the gas-phase reaction temperature to 85°C still resulted in an initial *cis*-4-Me-OL selectivity of 62% and a 4-Me-ENE selectivity of approximately 15% over Ti-beta (9). From the Oppenauer oxidation of the *cis*- and *trans*-alcohols, respectively, using acetone as the oxidant, we concluded already that under

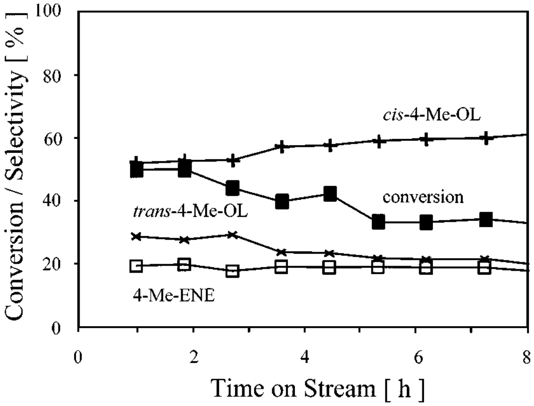

FIG. 3. The gas-phase MPV reduction of 4-Me-ONE with 2-propanol over Ti-beta at 100°C: ■ = conversion; + = *cis*-4-Me-OL; × = *trans*-4-Me-OL; □ = 4-Me-ENE.

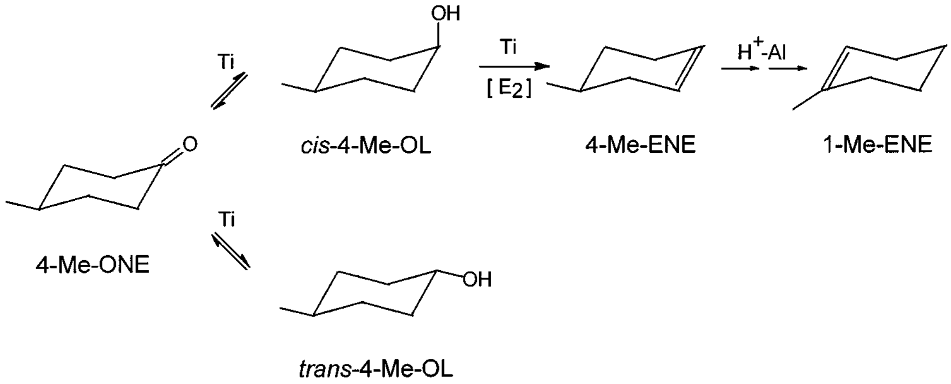

FIG. 4. Reaction scheme for the MPV reduction of 4-Me-ONE.

the experimental conditions used only the *cis*-alcohol dehydrates and that the alcohols can reversibly isomerize over the titanium site, most probably via an MPVO type mechanism (9). The overall reaction scheme for the reduction of 4-methylcyclohexanone in the gas-phase is depicted in Fig. 4.

The dehydration of the *cis*-alcohol yields as the only product 4-methylcyclohexene (4-Me-ENE) while no 1- or 3-methylcyclohexene isomers are observed at low temperatures. This can be understood in terms of an E2-elimination (Fig. 5) of the *cis*-alcohol on the titanium site. Removal of the hydroxy group is facilitated when the molecule adopts the conformation in which the hydroxy group is in its axial position. In this mechanism, both the axial alcohol group and an axial hydrogen atom at the β-position are removed simultaneously without the formation of a carbenium intermediate. Molecular modelling (7) of the most favourable coordination of the *cis*-alcohol on the catalytic site shows that none of the two available axial hydrogen atoms is in close vicinity to zeolite framework oxygen atoms. We therefore assume that the intraporous alcohol molecules act as a base, possibly polarized by interaction with the zeolite framework as shown in Fig. 5. The 4-Me-ENE formed can further isomerize over Brønsted acid sites to the more stable 1-methylcyclohexene (1-Me-ENE) at higher temperatures (9).

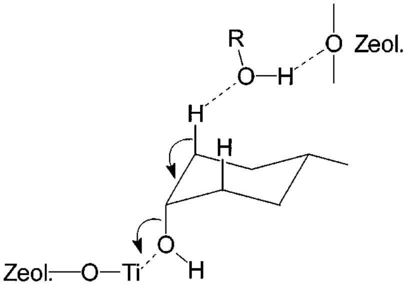

FIG. 5. Proposed mechanism for the formation of 4-Me-ENE via E2-elimination of *cis*-4-Me-OL.

3.3. *Kinetic Experiments*

The kinetics of the 4-Me-ONE/2-propanol system have been investigated in order to acquire insight into the mechanism of consecutive product formation from *cis*-4-Me-OL, i.e. the alkene and the *trans*-alcohol, and thereby reduce their incidence. The influence of the contact time, the substrate partial pressures, the ratio of 4-Me-ONE to 2-propanol, and other parameters have been studied. Due to the limitations in the experimental setup, the conversion usually exceeded the threshold value for differential plug-flow conditions and exact determination of the kinetic constants could not be performed.

3.3.1. Variation of contact time at constant substrate partial pressure. The results of the series of experiments in which the contact time was varied are shown in Fig. 6. A steady increase in the selectivities to the *trans*-4-Me-OL and 4-Me-ENE by-products with contact time is observed, while the selectivity to *cis*-4-Me-OL shows a corresponding

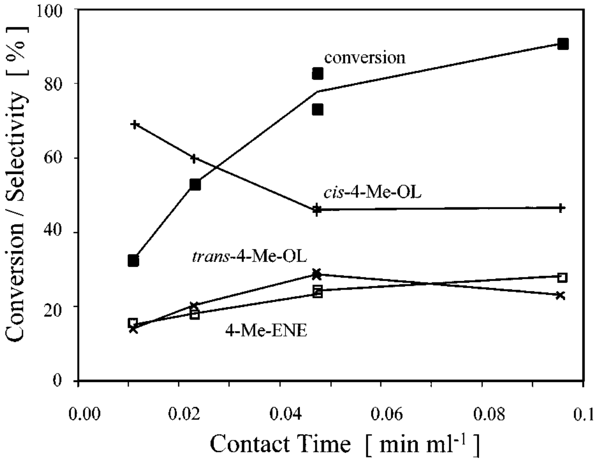

FIG. 6. Influence of contact time under constant partial pressure of reactants on selectivity and activity of the MPV reduction of 4-Me-ONE with 2-propanol at 100°C over Ti-beta. The contact time is defined here as the reciprocal gas flow.

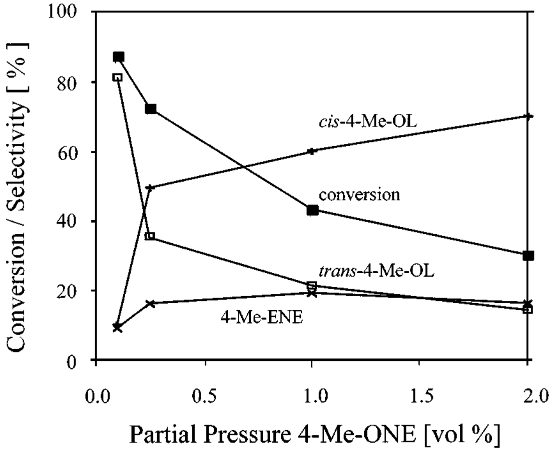

FIG. 7. Influence of the partial pressure of substrates on the selectivity and activity in the MPV reduction of 4-Me-ONE with 2-propanol at 100°C over Ti-beta.

decrease. The increase in conversion with the reciprocal gas flow as a measure of the contact time indicates that the surface reaction and not the desorption of the products from the zeolite into the gas-phase is the rate-limiting step. The increase further shows that the reversible MPVO reaction has not reached its equilibrium and that kinetically determined rates are measured (13). At high contact time the *trans*-alcohol selectivity is seen to decrease somewhat, probably due to the increased alkene formation which is an irreversible process.

3.3.2. Influence of partial pressure. In order to investigate the influence of the sorption equilibrium in the zeolite pores on the activity and selectivity, experiments were conducted in which the substrate partial pressure, at a constant 4-Me-ONE/2-propanol molar ratio of 1 : 10, was varied at constant contact time. For each partial pressure measurement a separate run was performed using a freshly calcined Ti-beta catalyst. As shown in Fig. 7, the effect of increasing partial pressure is a sharp reduction in the conversion (%), indicating a strongly inhibiting effect by one or both of the substrates. At the same time, the selectivity to the *cis*-4-Me-OL increased from 13 to 72%, while that for 4-Me-ENE decreased from 81 to 14%. Since the alkene is believed to be formed by dehydration of the *cis*-alcohol via an E2 mechanism (9), the fact that high partial pressures are required to attain a high selectivity to *cis*-4-Me-OL, suggests that a high internal reactant concentration in the zeolite facilitates the desorption of the *cis*-alcohol from the catalytic site, before irreversible dehydration to the alkene can occur. When seen on an absolute scale (mol/h) the conversion increases with partial pressure of the reactants; i.e., the turn over frequency increases. Therefore, a change in selectivity is related to an intrinsic change in the catalytic performance of the active site.

During the experiments at low partial pressures, it was further observed that the GC analysis of the gas-stream showed initially no 4-methylcyclohexanone or products derived thereof. They could only be detected after a time on stream which was found to correspond roughly with the time required to load the zeolite almost fully with 4-methylcyclohexanone. On the other hand, 2-propanol was always detected. This suggests that under the experimental conditions the zeolite is predominantly filled with 4-methylcyclohexanone and its products, irrespective of the partial pressures applied. This can be explained by the hydrophobic character of the Ti-beta catalyst (11) which preferentially adsorbs the apolar 4-Me-ONE over the more polar 2-propanol. Since the internal 4-Me-ONE concentration does not change significantly with changing partial pressure, the observed effect of the partial pressure on the selectivity should be ascribed to differences in the internal concentration of the 2-propanol.

That it is the alcohol concentration which has a significant effect on the catalytic performance is not surprising. It is well known for the MPVO reactions that the alkoxy intermediate formed may leave the complex via an alcoholysis reaction in which a proton is abstracted from a second adsorbed alcohol molecule (1). The increased selectivity to the *cis*-alcohol is therefore ascribed to an increased alcoholysis reaction rather than to a suppression of the dehydration reaction.

To further investigate the influence of the internal alcohol concentration on the selectivities, the partial pressure of 2-propanol in the feed was varied from 1 to 50 vol% at constant partial pressure of 4-Me-ONE (1 vol%) and constant contact time. The results are shown in Table 1. The selectivity towards the *cis*-alcohol increases substantially at higher partial pressures of 2-propanol. It is seen that, at the highest 2-propanol partial pressure, the *cis*-4-Me-OL selectivity tends towards the high values observed in the liquid-phase. It was noted that the activity also increases with higher partial pressures of 2-propanol, thus confirming

TABLE 1

Influence of the Partial Pressure of 2-Propanol on the Selectivity and Activity at Constant 4-Me-ONE Pressure (1 vol%) at 100°C

2-propanol pressure [vol%]	Conversion[a] [%]	Selectivity to *cis*-4-Me-OL [%][a]	Selectivity to 4-Me-ENE [%][a]
1	15[b]	16	66
3	21[b]	22	39
10	36	60	24
50	68	81	7
Liquid-phase (200)	33.7[c]	97	0

[a] After 6 h on stream.
[b] Strong deactivation of the catalyst was observed.
[c] See van der Waal *et al.* (8) for details.

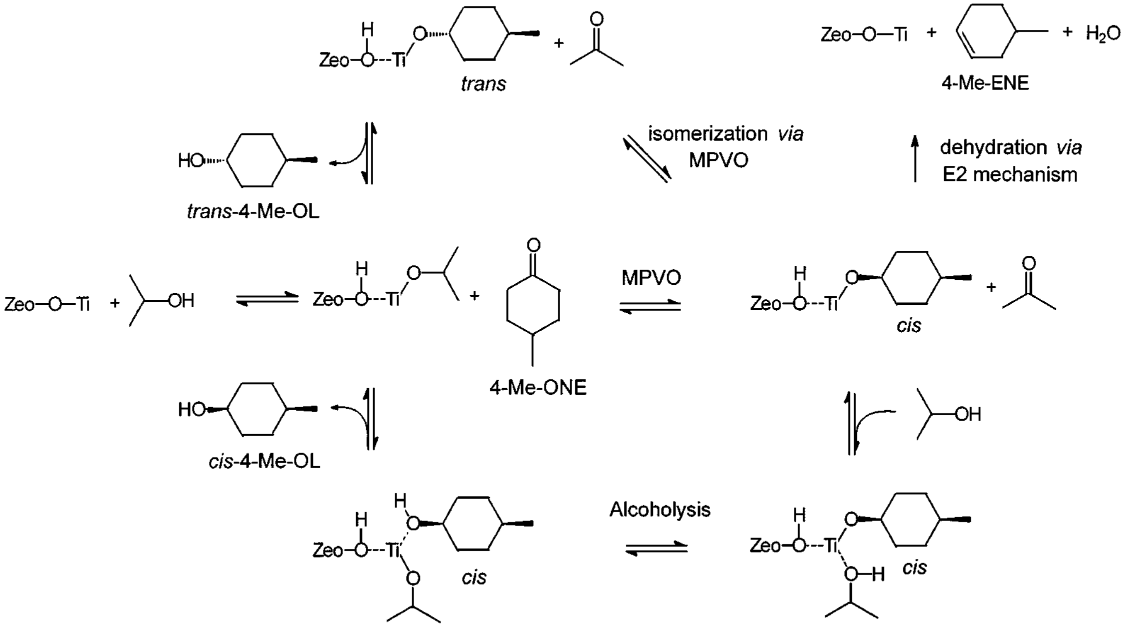

FIG. 8. Mechanism of product formation from 4-Me-ONE and 2-propanol over Ti-beta.

that the intra-porous 2-propanol concentration is an important parameter in the kinetic expression. It should be noted that at low 2-propanol pressures, the deactivation of the catalyst is much more severe than at higher partial pressures, which suggests that also for a high catalyst stability the presence of 2-propanol near the catalytic active centre is necessary to inhibit the aldol condensation of 4-Me-ONE. Also the observed dehydration of 2-propanol to propene may be a contributing factor to the deactivation.

Our kinetic experiments with 2-propanol suggest that a high selectivity could be achieved if the *cis*-alcohol formed could be removed from the catalytic site before isomerization to the *trans*-alcohol or dehydration to the alkene could occur. The desorption of the *cis*-alcohol, via alcoholysis of the *cis*-alkoxide intermediate formed, can be enhanced greatly by a high internal alcohol concentration in the zeolite pores. The function of the alcohol is thus not only to serve as a hydrogen donor, but also to release the *cis*-alcohol from the catalytic site (see Fig. 8).

3.3.3. The influence of alcohols on the catalytic performance. From the kinetic experiments with 2-propanol as the reductant, it was concluded that a high internal alcohol concentration in the zeolite is important to obtain a high selectivity towards the preferred *cis*-alcohol. Even at high molar ratios of 2-propanol to 4-Me-ONE of 50 : 1, only 81% *cis*-alcohol was observed (Table 1). The relatively low selectivity in the case of the gas-phase reductions using 2-propanol is most probably caused by the hydrophobic nature of the Ti-beta catalyst. Ti-beta prefers adsorbing 4-Me-ONE, instead of 2-propanol, under the reaction conditions used, as was observed in the experiments at low partial pressures of substrates. In order to test further whether the internal alcohol concentration directs selectivity, other secondary alcohols with a higher hydrophobic character were tested (Table 2). As can be seen, the selectivity towards *cis*-4-Me-OL increased with increasing aliphatic chain-length of the alcohol in accordance with the above idea.

The activity of various alcohols is also determined by the reduction potential of the alcohol used (1). The reduction potential, ΔH_f°, is here defined as the difference in heat of formation between the alcohol and the corresponding carbonyl compound; i.e., it represents the ease of hydrogen abstraction. Since all secondary alcohols tested (Table 2) have similar reduction potentials, the observed differences in activity must originate from the adsorbed amount of

TABLE 2

Conversion and Selectivity in Gas-Phase MPV Reduction of 4-Me-ONE (1 vol%) with Secondary and Cyclic Alcohols (10 vol%) at 100°C

Reducing alcohol	ΔH_f° [kJ/mol]	Conversion [%][b]	Selectivity to *cis*-4-Me-OL [%][b]	Selectivity to 4-Me-ENE [%][b]
2-propanol	70.0[a]	36	60	24
2-butanol	69.3[a]	67	72	11
2-pentanol	67.9[a]	88	84	6
2-heptanol	n.a.	34	95	—
Cyclopentanol	64.4[a]	71	92	1
Cyclohexanol	77.0[a]	53	95	—

[a] From Pedley *et al.* (14).

[b] After 6 h on stream.

alcohol. High internal alcohol concentrations probably facilitate the reaction by a faster regeneration of the catalytic site. However, when the reducing alcohol approaches the hydrophobicity/polarity of the other reactant, viz. 4-Me-ONE, as is the case for 2-heptanol, cyclopentanol, and cyclohexanol, the amount of alcohol adsorbed is interfering with the amount of 4-Me-ONE adsorbed, thereby limiting the reaction rate.

To test the assumption of alcoholysis being both the rate and selectivity determining step, isomeric alcohols with similar polarity but different reduction potential were applied. These alcohols are expected to adsorb quite similarly under the experimental conditions used. If the rate-determining step is the alcoholysis of the initial *cis*-alcohol formed from the catalytic site via the absorption of a second reductant alcohol, selectivity should hardly change for isomeric alcohols. Equal internal alcohol concentrations will result in approximately equal probabilities of *cis*-alkoxide removal (Fig. 8) and, thus, roughly the same selectivity. Thus, 1-propanol, 1-butanol, and 1-pentanol were compared with the 2-isomers as the reductants. From Table 3 it can be seen that nearly identical selectivities were indeed obtained from both isomers of a pair, thereby confirming that it is the internal concentration of alcohols which largely determines the selectivity towards the *cis*-alcohol.

The activity is also determined by the reduction potential of the alcohol used, since the MPVO reaction is an equilibrium reaction and the choice of reductant strongly influences the amount of *cis*-alkoxide on the titanium site under equilibrium conditions (1). This would suggest that the achievement of the MPVO equilibrium is relatively fast, compared with the desorption of the *cis*-alcohol from the catalytic active site. Thus, the fraction of *cis*-4-Me-OL alkoxide groups on the catalytic site is determined by thermodynamics and the observed rate and selectivity is a reflection of the alcoholysis rate of the product-alkoxide with another alcohol molecule, e.g. 2-propanol. The general influence of the reduction potential on the catalytic activity can be demonstrated by plotting the activity of all alcohols tested against their reduction potential (Fig. 9). A clear decrease in activity is observed with increasing reduction potential. The large spread in activities observed is caused by differences in sorption characteristics, as discussed above for the secondary alcohols (Table 2).

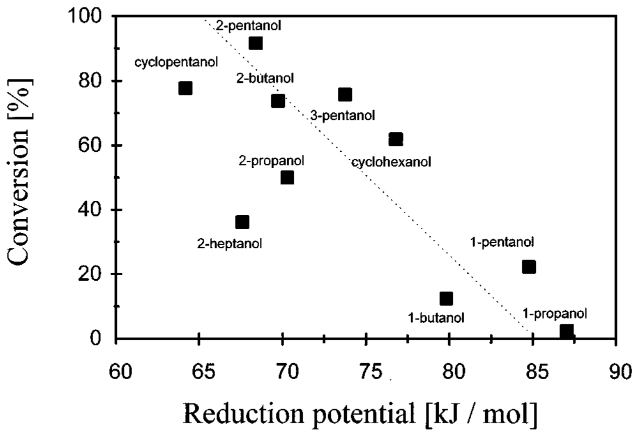

FIG. 9. The activity of Ti-beta in the MPV reduction of 4-Me-ONE at 100°C as a function of the reduction potential, ΔH_f°, of the alcohol used. A dotted line has been added as a guide for the eye.

TABLE 3

Initial Selectivity and Activity in the Gas-Phase MPV as a Function of the Reduction Potential and Polarity of the Alcohol Reductant

Reducing alcohol	ΔH_f° [kJ/mol]	Conversion [%][c]	Selectivity to *cis*-4-Me-OL [%][c]	Selectivity to 4-Me-ENE [%][c]
1-propanol	87.3[a]	≈1	60	22
2-propanol	70.0[a]	36	60	24
1-butanol	79.7[b]	9	74	13
2-butanol	69.3[a]	67	72	11
1-pentanol	84.3[a]	14	85	6
2-pentanol	67.9[a]	88	84	6
3-pentanol	73.8[b]	75	80	8

[a] From Pedley *et al.* (14).

[b] From Cox (15).

[c] After 6 h on stream.

In our view, it is unlikely that the *cis*-alcohol selectivities observed as function of the isomeric alcohol reductants (primary and secondary) are related to the concomittantly changing conversions. One may argue that, since the alkene is a consecutive product from the *cis*-alcohol and the conversions are significantly lower for the primary reductant alcohols than for the secondary reductant alcohols, the primary alcohols actually give an increased alkene selectivity. However, as can be seen from Table 2, the entries of 2-heptanol, cyclopentanol, and cyclohexanol, the conversion of 4-Me-ONE differs widely (34–71%) but the selectivities remain constant.

3.4. *Competitive Sorption Experiments*

To investigate the differences in adsorption between the secondary alcohols used, competitive sorption experiments were performed. From the results, presented in Table 4, it can be seen clearly that the increased chain length for the higher alcohols causes an increased preference in adsorption over 2-propanol, which is in accordance with the hydrophobic character of zeolite titanium beta already mentioned.

In order to show that in the case of the higher alcohols, competitive sorption with 4-methylcyclohexanone also starts to play a role, the sorption characteristics of the secondary alcohols were measured relative to 4-methylcyclohexanone. In a series of competitive sorption experiments, the molar ratio between alcohol and 4-Me-ONE was kept constant, i.e. 10 : 1, similar to the experimental

TABLE 4

Competitive Adsorption Characteristics of Binary Alcohol Mixtures on Ti-Beta

Alcohol	Volume fraction alcohol [%]^{a}	Total adsorbed volume [ml/g$_{zeo}$]	Adsorbed volume 2-propanol [ml/g$_{zeo}$]
2-butanol	56	0.196	0.086
2-pentanol	61	0.209	0.082
2-heptanol	84	0.247	0.039
Cyclopentanol	69	0.239	0.077
Cyclohexanol	78	0.244	0.053

Note. 50 μl 2-propanol, 50 μl of alcohol and 100 mg Ti-beta ($\approx$25 μl pore volume (11)) in 10 ml 1,3,5-triisopropylbenzene at room temperature.

[a] Balance is 2-propanol.

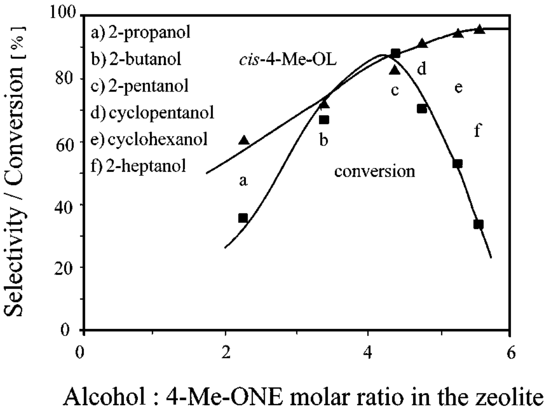

FIG. 10. The conversion of 4-Me-ONE and the selectivity to *cis*-4-Me-OL in the gas-phase MPV reduction as a function of the internal alcohol to 4-Me-ONE ratio, determined by liquid-phase adsorption experiments (see Table 5).

conditions used in the gas-phase experiments. From Table 5 it can be seen clearly that the higher alcohols are more strongly adsorbed. It should be noted that these are liquid-phase adsorption experiments at room temperature and can therefore only be used as an indication of the sorption patterns under catalytic gas-phase conditions. Nevertheless, if the conversion and the selectivity of the related gas-phase experiments are plotted against the alcohol to 4-Me-ONE ratio determined in the liquid phase, it is observed that selectivity, increases with an increasing internal alcohol concentration and that the conversion shows a maximum (Fig. 10). In our view this further confirms that the high selectivity observed for the higher alcohols originates from the higher internal alcohol concentrations. The decrease in the observed conversion, at high internal alcohol to 4-Me-ONE ratios, is probably due to a decreased 4-Me-ONE concentration in the zeolite (see above).

3.5. *Influence of Temperature, Water and Ammonia*

In a further study of the factors influencing the selectivity, the effects of temperature and of the presence of water or ammonia on the selectivity to the *cis*-alcohol were investigated. From Fig. 11 it can be noted that at higher temperatures the selectivity to the *cis*-alcohol decreases. Initially the selectivity to the *trans*-alcohol increases at the expense of the *cis*-alcohol, but at higher temperatures dehydration to 4-methylcyclohexene becomes the major reaction. At higher temperatures (>200°C) the 4-methylcyclohexene is subsequently isomerized to the more stable 1-methylcyclohexene. This is in accordance with the proposed reaction mechanism (Fig. 8) in which the thermodynamically more favoured *trans*-alcohol is formed reversibly and the alkene is formed irreversibly from the *cis*-alcohol in consecutive reactions.

The commonly used MPVO homogeneous catalysts consist of metal alkoxides, which are easily hydrolysed to inactive oxides in the presence of water (1). In the mechanisms proposed for the heterogeneously catalysed reactions, initially formed surface alkoxide groups are reported to be the active sites (16). Since the surface-alkoxide groups can also be hydrolysed easily, the presence of water in the feed stream is usually avoided. As we reported already for

TABLE 5

Competitive Adsorption Characteristics of Alcohols with 4-Me-ONE on Ti-Beta

Alcohol	Volume fraction alcohol [%]^{a}	Internal molar ratio alcohol : 4-Me-ONE	Total adsorbed volume [ml/g$_{zeo}$]
2-propanol	55	2.24	0.215
2-butanol	69	3.36	0.238
2-pentanol	74	4.34	0.248
2-heptanol	85	5.52	0.251
Cyclopentanol	78	4.74	0.249
Cyclohexanol	82	5.25	0.243

Note. 3.5 mmol alcohol, 0.35 nmol 4-methylcyclohexanone (50 μl) and 100 mg Ti-beta ($\approx$25 μl pore volume (11)) in 10 ml 1,3,5-triisopropylbenzene.

[a] Balance is 4-methylcyclohexanone.

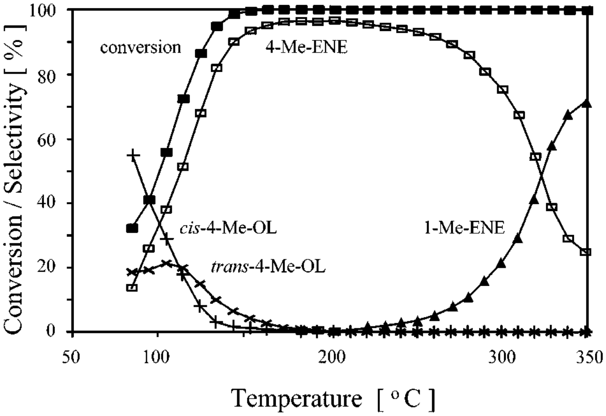

FIG. 11. Temperature programmed MPVO reduction of 4-Me-ONE with 2-propanol over Ti-beta. Temperature increment was 12°C h^{-1}.

the liquid-phase reaction (8), the Ti-beta catalyst has a high tolerance for water due to its hydrophobic interior. As can be seen from Fig. 12, the presence of water is not detrimental to the activity of Ti-beta in the MPV reduction of 4-methylcyclohexanone. The temperature at which a ketone conversion of 50% is measured in the presence of water (2.7 vol%), viz. 112°C, is nearly identical to the temperature required for 50% conversion in the absence of water (108°C, Fig. 11); i.e., water has no effect whatsoever on the overall MPVO activity of the titanium site.

Although water has no influence on the catalytic MPVO activity, the selectivity towards alcohols increased from 62 to 87% at 85°C upon the addition of water to the feed stream. This enhanced selectivity in the presence of water can be ascribed to either:

(i) A kinetic suppression of an irreversible dehydration in a manner similar to the alcoholysis by alcohols.

(ii) A change in the alcohol/alkene equilibrium due to the higher amount of water present.

In the case of a shift in equilibrium (ii), it should be possible to oxidize alkenes with ketones in the presence of water via alcohols formed *in situ*. In an attempt to oxidize cyclohexene with acetone in the presence of water over Ti-beta, no conversion to cyclohexanone was observed between 85 and 400°C. It is therefore concluded that under the experimental conditions used, 4-methylcyclohexene is formed irreversibly from the *cis*-alcohol. The increased selectivity towards alcohols should therefore be ascribed to a suppression of the dehydration, most likely via hydrolysis of the surface Ti-*cis*-alkoxide complex in a similar manner as described for alcoholysis by 2-propanol (Fig. 8).

For liquid-phase reactions at 85°C, we reported that small amounts of a strong base, e.g. pyridine, completely poisoned the catalyst (8). It can be seen from Fig. 13 that, in the presence of ammonia, higher temperatures are required to reduce 4-methylcyclohexene. The higher temperatures are required for the desorption of ammonia from the catalytically active site. The relatively low temperature of 305°C at which 50% conversion is observed, suggests that the ammonia is not bonded to a strongly acidic site. Since Brønsted-acidic aluminium sites desorb ammonia usually above 400°C (17), this confirms that the MPVO reactions proceed via the titanium sites and not via any residual aluminium sites (Si : Al > 5000). This is consistent with the inactivity of the all-silica analogue of zeolite beta (8) even though it has a Si : Al ratio similar to Ti-beta (11). It was also observed that, in the presence of ammonia, no isomerisation of 4-Me-ENE to 1-Me-ENE occurred, even at a temperature of 400°C, suggesting that this isomerisation requires strong Brønsted acid sites, most probably the residual aluminium sites. The aluminium originates from slight contaminations of the Si- and Ti-sources used in the preparation of Ti-beta (Si : Al > 2500).

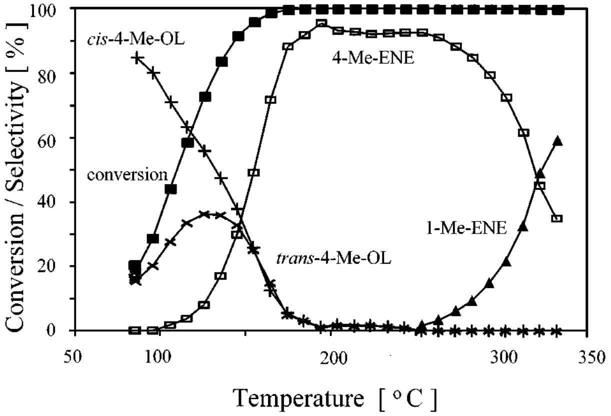

FIG. 12. Temperature programmed MPVO reduction of 4-Me-ONE with 2-propanol over Ti-beta in the presence of 2.66 vol% water. Temperature increment was 12°C h^{-1}.

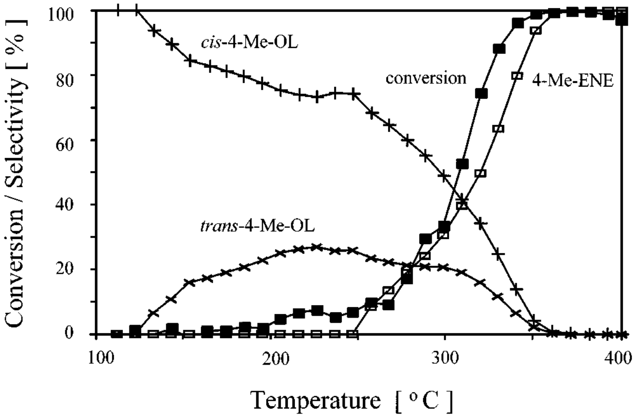

FIG. 13. Temperature programmed MPVO reduction of 4-Me-ONE with 2-propanol over Ti-beta in the presence of 5 vol% ammonia.

4. CONCLUSIONS

Ti-beta is found to be an excellent catalyst for MPVO reactions under gas-phase conditions. Remarkable differences exist between the liquid- and gas-phase reactions at otherwise similar temperatures. Under liquid-phase conditions, a very high selectivity in the reduction of 4-substituted cyclohexanones towards the commercially desired *cis*-alcohols was observed. In the gas-phase, the selectivity to the *cis*-alcohol is significantly lower, but still above the thermodynamically expected value and, in addition, dehydration of the alcohol product to the corresponding alkene becomes an important side-reaction.

In a kinetic study, the parameters affecting activity and selectivity were investigated and a mechanistic model was derived. The selectivity to the desired *cis*-alcohol was found to be determined by the internal alcohol concentration in the zeolite. High partial pressures of 2-propanol in the feed stream or the use of more strongly adsorbed alcohols, e.g. cyclohexanol or 2-heptanol, were found to increase the selectivity towards the *cis*-alcohol significantly. This was explained by an increase in the rate of *cis*-alcohol removal from the catalytic site by accelerated alcoholysis, before consecutive reactions can take place. Consecutive reactions were also found to be suppressed by co-feeding water in the reactant stream. The water probably enhances the selectivity by an increased hydrolysis rate of the *cis*-alkoxide intermediate in a manner similar to that described for alcoholysis.

The activity of the Ti-beta catalyst depends both on the adsorption characteristics and the reduction potential of the alcohol used. Although a high internal alcohol concentration is favourable for a high activity due to regeneration of the catalytic site via accelerated alcoholysis, too high an internal alcohol concentration tends to decrease the activity by reducing the amount of 4-methylcyclohexanone adsorbed. The activity was also found to correlate with the reduction potential of the alcohol reductant used. Alcohols with low reduction potentials, e.g. secondary alcohols, were found to be much more active than with alcohols having higher reduction potentials, e.g. primary alcohols.

Based on the observed relations, a catalytic pathway is proposed in which the ketone is first reduced to the corresponding *cis*-alcohol by a MPVO type mechanism, following which the *cis*-alkoxide intermediate can undergo either:

(i) desorption from the titanium site via alcoholysis,
(ii) reversible isomerization to the *trans*-alcohol via an MPVO mechanism, or
(iii) irreversible dehydration via and E2-elimination mechanism.

The potential of zeolite titanium beta in the gas-phase Meerwein–Ponndorf–Verley and Oppenauer reactions was shown by the high resistance to water and ammonia and the excellent stability.

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