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Zeolite Beta: The Relationship between Calcination Procedure, Aluminum Configuration, and Lewis Acidity

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Zeolite Beta was calcined under a variety of carefully controlled conditions to study the influence of (hydro)thermal treatments on the catalytic activity of zeolite Beta in the Lewis acid-catalyzed Meerwein–Ponndorf–Verley reduction of ketones. The activity of (H)Beta can be increased by several orders of magnitude by mild steaming. The catalytic activity of the materials following reactivation can be diminished again by adsorption of ammonia followed by an induction period. For these changes, an explanation is offered in terms of Lewis acidic framework aluminum atoms which undergo a change of configuration depending on the ligands present, rather than becoming extraframework aluminum. FTIR, ^{29}Si, and ^{27}Al MAS NMR spectroscopy were applied to investigate the changes induced by the (hydro)thermal procedures. © 1998 Academic Press

Key Words: **zeolite Beta; Lewis acidity; Meerwein–Ponndorf–Verley reduction; calcination procedure; Lewis acidic framework aluminum.**

INTRODUCTION

Zeolite Beta, a 12-ring aperture (7.6 × 6.4 Å) three-dimensional high-silica zeolite, currently receives much attention as a potential catalyst in numerous reactions (1). In addition to its Brønsted acidic properties it displays Lewis acidity as well. Interestingly, this Lewis acidity is believed not to be solely generated by extraframework aluminum (EF-Al) species, as is known for USY samples (2), but can also be displayed by framework aluminum atoms in a non-tetrahedral environment.

Several studies point to the flexibility of the coordination sphere of the aluminum atoms in zeolite Beta (3–8). In addition to tetrahedrally coordinated framework aluminum, octahedrally coordinated framework aluminum has been proposed, consisting of an aluminum connected with four bonds to the framework, one water molecule, and a hydronium ion (3–6). The amount of these types of aluminum was shown to depend on the pretreatment of zeolite Beta and on the water content (3, 6). FTIR and ^{29}Si and ^{27}Al MAS NMR were applied to study the changes induced by various calcination conditions (shallow vs deep-bed (4)), temperature treatments and interactions with molecules like ammonia, pyridine, benzene, *n*-hexane, and water (7, 9). Also the influence of cations such as Na^+, K^+, NH_4^+ and protons on the state of the aluminum atoms was investigated (3). Based on the reported results it can be concluded that framework aluminum adopts a tetrahedral symmetry when protons are *not* the charge-compensating cations. Aluminum atoms, which have adopted another coordination symmetry but are still connected to the framework, can revert to their tetrahedral coordination sphere by ion exchange with cations like Na^+ and K^+ and by adsorption of ammonia (3). EF-Al has been reported to be formed during high-temperature treatments of protonic zeolite Beta and was reported to be readily removed by applying aqueous nitric acid solutions (3). The nature of EF-Al has not been explained in detail.

As was shown recently, zeolite Beta is a highly stereoselective catalyst for the Lewis acid-catalyzed Meerwein–Ponndorf–Verley (MPV) reduction of ketones using a (cheap) secondary alcohol as the reductant (10). In the reduction of 4-*tert*-butylcyclohexanone, for example, a mixture of isomeric *cis*- and *trans*-4-*tert*-butylcyclohexanols is formed. While homogeneous and most heterogeneous Lewis catalysts give the thermodynamically most stable *trans*-4-*tert*-butylcyclohexanol with a selectivity of 70–90%, zeolite Beta produces the commercially relevant *cis*-4-*tert*-butylcyclohexanol with >95% selectivity. Clearly, Lewis sites are present in zeolite Beta. The absence of Lewis acidic metal ions as the charge compensating cations indicates that only coordinatively unsaturated aluminum atoms are the possible candidates (11). Both Jia *et al.* (4) and Beck and Haw (5) mention that framework aluminum atoms in a non-tetrahedral coordination may exhibit Lewis acidic properties.

The catalytic activity of zeolite Beta for the MPV reaction was shown to depend strongly on the calcination method (shallow or deep-bed (4)), on the calcination temperature,

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and on the number of calcination steps. A deep-bed, high-temperature calcination resulted in a more active catalyst. Repeated calcination further enhanced the activity without loss of selectivity, and a correlation between the calcination method and the IR data was observed (10). The nature and the formation of the active site have not been resolved as yet. For the MPV reduction, Creyghton *et al.* proposed a five-coordinated framework Al in which both the alcohol and ketone are simultaneously coordinated to the Al atom. No explanation for the correlation between the calcination procedure and the formation of the active sites was given at that time. A deeper insight into the formation of Lewis sites in zeolite Beta is therefore desired. Also, it seems logical to assume that the method of pretreatment will influence the catalytic behavior of zeolite Beta in several other Lewis acid-catalyzed reactions, e.g., Friedel Crafts reactions (12, 13).

Based on ^{27}Al MAS NMR studies on zeolite H-Y and the steamed H-USY (2), various aluminum configurations have been proposed. Interpretation of ^{27}Al NMR data, however, is complicated by the quadrupole moment of the aluminum nucleus ($I = 5/2$) causing quadrupole broadening. Also, not all the aluminum present in a sample might be detected by NMR techniques (3, 14). In addition to NMR techniques, XAFS has also been performed on these materials (15). As well as tetrahedral framework aluminum and octahedral EF-Al, several other species (neutral or cationic) have been proposed, including pentacoordinated EF-Al (16) and distorted tetrahedral EF-Al (2). Earlier, Gilson *et al.* (17) reported on the possible existence of pentacoordinated Al in several aluminosilicates, including zeolites. Also Chen *et al.* (18) have reported on the coordination number of aluminum and the related Lewis acidity in aluminas. Interestingly, for $AlPO_4$-5, a microporous aluminophosphate with a neutral framework, it was reported that part of the framework aluminums could undergo a reversible transition from tetrahedral to octahedral coordination upon hydration (19). The octahedrally coordinated aluminums are still connected to the (phosphate) framework by four bonds and have two additional coordinating water molecules. Pentacoordinated framework aluminum was also detected and was assumed to have only one coordinating water molecule.

In the present work the influence of the calcination procedure on the catalytic activity of zeolite Beta in the MPV reduction of ketones was investigated in more detail. The Lewis acid-catalyzed MPV reaction seems to be an ideal test reaction for studying the changes induced by the (hydro)thermal treatments: the activity is highly dependent on the calcination or activation procedure of zeolite Beta, and the extremely high stereoselectivity offers additional information about the catalytic active site. Furthermore, due to the mild reaction conditions (neutral pH, 82°C), no modifications of the catalyst during a catalytic run are expected, except for the formation of the actual active site. To rule out any influences of the template removal on the catalytic activity, the ammonium form of zeolite Beta was prepared from the as-synthesized material in such a way that partial dealumination of the framework was prevented. This ammonium Beta was used as the starting material for all subsequent (hydro)thermal treatments. Instead of the poorly defined, inhomogeneous deep-bed calcination procedure, all additional treatments were performed using a well-defined shallow calcination bed while varying the atmosphere above the zeolite sample. Hot spots and autosteaming (6), intrinsically related to deep-bed calcination procedures under an oxidative atmosphere, will be prevented in this way, thus permitting a more reproducible calcination method.

Both microcrystalline and macrocrystalline Beta samples were used to study the influence of the crystal size on the pretreatments and to investigate whether the phenomena observed were the same for batches prepared by different synthesis procedures. Based on the combined results of FTIR, ^{29}Si, and ^{27}Al MAS NMR and the catalytic experiments, a mechanism is proposed which accounts for the effects observed as a function of the pretreatment.

EXPERIMENTAL

Zeolite Synthesis

Tetraethylammonium hydroxide (TEA-OH) (20 wt%) solution and tetraethyl orthosilicate (TEOS) were obtained from Janssen Chimica. Sodium aluminate (41 wt% Na_2O, 54 wt% Al_2O_3) was supplied by Riedel–de Haën. NaCl and NaOH were obtained from Baker Chemical. Aerosil 200 from Degussa was used as the silica source.

Macrocrystalline zeolite Beta (Beta1, $\sim$2 μm) was prepared according to Kunkeler *et al.* (20) and microcrystalline zeolite Beta (Beta2) was prepared *via* the Wadlinger synthesis (21). The as-synthesized materials were carefully washed with water until the filtrate attained pH 7 (pH paper). Subsequently, the materials were washed once with a 0.025 M Na_2H_2EDTA solution at room temperature to remove possible debris formed during cooling of the synthesis mixture. Dealumination of the external surface by this treatment is unlikely, as we reported recently (22). X-ray powder diffraction confirmed that with both syntheses zeolite Beta was obtained. The macrocrystalline material contained some mordenite as contamination, as reported earlier (20).

Calcination Procedure (Template Removal)

The calcination steps were performed using a horizontally mounted glass tube, which essentially represents a larger version of the tube shown in Fig. 1. The as-synthesized materials (10 g) were first calcined under a pure ammonia atmosphere from ambient temperature of 400°C (ramp

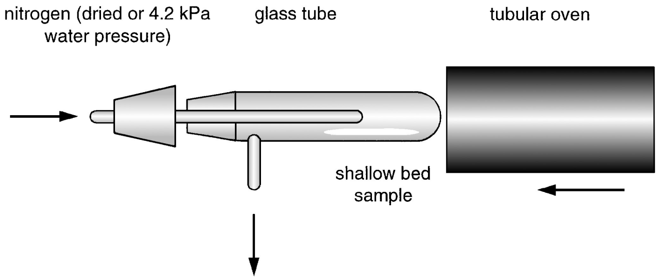

FIG. 1. Experimental setup for small-volume sample activation. Length tube approx. 10 cm, ∅ 20 mm. The sample was positioned in the middle of the oven. The open end of the oven was closed by a quartz-wool plug.

1°C/min, 6 h at final temperature), after which the material appeared white to the eye. Subsequently, the samples were sodium-exchanged overnight using a 1 M NaCl solution (100 ml/g zeolite) under reflux conditions. The thus-obtained sodium Betas were further calcined at 120°C in an oxygen atmosphere containing approx. 1% ozone, followed by a third calcination step at 400°C (ramp 1°C/min, 6 h at final temperature) in an oxygen atmosphere. The calcined sodium Betas were transformed into their ammonium forms by threefold ion exchange with an 0.1 M NH_4NO_3 solution at room temperature.

Activation Method and Sample Coding

Activation of small amounts (100–200 mg) of the ammonium forms of zeolite Beta was conducted in a small glass tube mounted horizontally in a tubular oven. A nitrogen gas stream (atmospheric pressure), either dried or saturated with a water partial pressure of 4.2 kPa, was led over the Beta sample. The samples were spread out equally, thus obtaining a shallow calcination bed; see Fig. 1.

The heating rate was set to 1°C/min for all experiments. The water vapor pressure was regulated by a thermostatted condenser at 30.0°C above an evaporator containing boiling water, through which nitrogen (30 ml/min) was fed via a glass frit (water partial pressure at 30.0°C = 4.2 kPa). When the sample had spent the prescribed time at the ceiling temperature it was allowed to cool to 200°C. The water vapor was switched off and replaced by a dry nitrogen stream 1 h prior to a catalytic run, to ensure that a dry (H)Beta sample was used.

Each sample has been given a code which indicates the conditions of the activation procedure: the ceiling temperature in °C; the time at the ceiling temperature in hours (h), days (d), or weeks (w); and whether the atmosphere was dry or contained water vapor (w30), e.g., (H)Beta1 450(6h)w30.

Characterization

Elemental analyses were performed on a Perkin–Elmer 3000 DV ICP-OES. Nitrogen physisorption measurements were performed on a Quantachrome Autosorb 6B Automated Gas Sorption System, in the partial pressure range of $p/p_0 = 0.01$–0.09. S_{BET} areas were calculated according to ASTM D 3663-92. Powder diffraction data were obtained on a Philips PW 1840 apparatus using Ni-filtered Cu$K\alpha$ radiation, in the range $2\theta = 5$–$50°$. SEM micrographs were taken on a Philips XL-20 microscope using 25 KeV. Transmission FTIR spectra of the microcrystalline Beta2 samples were recorded on a FTIR spectrophotometer equipped with a flow cell enabling the spectra to be taken at different temperatures and atmospheres, including vacuum. The samples were pressed to a self-supporting wafer of equal weight and activated at 450°C (heating rate 10°C/min) under vacuum for half an hour prior to data acquisition at 50°C. Diffuse reflectance FTIR (DRIFT) spectra of the micro- and microcrystalline Beta samples were collected on a Nicolet Magma 550 apparatus, equipped with a flow cell enabling the spectra to be taken at different temperatures under a nitrogen atmosphere. ^{13}C and ^{29}Si MAS NMR spectra were recorded using a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe (spinning speed = 5 kHz), and ^{27}Al MAS NMR spectra were recorded on a Bruker DMX-300 spectrometer (7.1T, spinning speed = 12.4 kHz). TMS was used as external standard for the ^{13}C and ^{29}Si nuclei, and an $Al(NO_3)_3$ solution was used as the external reference for the ^{27}Al spectra.

Deconvolution and integration of the ^{29}Si peaks were performed to be able to calculate the relative contributions of the various species and the framework Si/Al ratio according to the formula $\mathrm{Si/Al} = (\Sigma\, 0.25 \cdot n \cdot I_n)^{-1}$, where I_n is the relative intensity of the $\mathrm{SiO(Al)}_n$ peak ($n = 0$–4). The samples were presaturated with water (desiccator at RT) prior to data collection. For the ^{27}Al MAS spectra a 0.7-μs excitation pulse was used at an rf-field strength of 42 kHz. The recycle delay was 0.25 s. It was checked that these conditions are appropriate to ensure quantitative analysis of the spectra; i.e., all aluminum atoms in the sample (distorted and nondistorted) are visible (23). For the ^{29}Si spectra, a $\pi/6$ pulse—3.0 μs and 10-s delay—was used, which was found to be an adequate compromise between acquisition and relaxation times.

Catalytic Testing

MPV reductions of 4-*tert*-butylcyclohexanone (2.5 mmol) with 2-propanol (50 ml, zeolite-3A-dried, reflux) as the hydrogen donor were performed in a 100-ml three-necked round-bottom flask using 200 mg catalyst and 1,3,5-tri-*tert*-butylbenzene (1 mmol) as internal standard. *Cis*- and *trans*-4-*tert*-butylcyclohexanol were formed as the only products in a ratio of 94 : 6 to 98 : 2. Samples were taken regularly and analyzed by a GC equipped with a CP-52-Carbowax column (50 m, i.d. = 0.53, nitrogen carrier gas) and FID. Before each catalytic run, the Beta samples were activated under the conditions as discussed below. Activated samples were carried in the activation tube to the reaction vessel under ambient atmosphere.

RESULTS AND DISCUSSION

The method of template removal from the as-synthesized zeolite and subsequent activation procedures influence the final condition of the material and thus the catalytic performance. Contradictory results obtained by independent researchers may be caused by the inadequate description of the experimental conditions, in particular those during the calcination (template removal) and subsequent temperature treatments (7, 8). Therefore, the heating rate, the time the samples spend at the ceiling temperature, and the atmosphere under which the calcination and activation procedures were performed are mentioned explicitly.

Due to the difficulty of pressing self-supporting wafers of the macrocrystalline Beta1 samples, only microcrystalline Beta2 samples were used for the transmission FTIR measurements. Diffuse reflectance FTIR was used for both Beta1 and Beta2 samples.

For the interpretation of the IR data, we rely predominantly on the publication of Kiricsi *et al.* (7). According to these researchers, five types of hydroxyl groups can be distinguished by IR spectroscopy: bridging, Brønsted acidic Si–$\underline{\mathrm{OH}}$–Al (3605 cm^{-1}), OH groups attached to extraframework Al (3660–3680 cm^{-1}), internal silanol groups (3730 cm^{-1}), terminal silanol groups (3745 cm^{-1}), and OH attached to an Al (3782 cm^{-1}, VHF (4)). The Al–OH (VHF band) is referred to as a transient species by Kiricsi *et al.* (7), as an unusual aluminum site associated with the framework by Beck *et al.* (5), and as an aluminum species still connected to the framework by Jia *et al.* (4) in accordance with the earlier proposal of Bourgeat-Lami *et al.* (3). Clearly, it is still unknown what the exact nature of this species is.

Calcination of the As-Synthesized Beta Zeolites

In order to avoid dealumination of the framework, template removal from the as-synthesized Beta samples was performed under an ammonia flow at a maximum temperature of 400°C (10, 24). The template degrades via a Hoffman-type mechanism, assisted by the ammonia base, toward ethene and triethylamine, which molecules can desorb as such, and the counterion role of TEA is taken over by ammonium. Formation of water is precluded by the absence of oxygen. According to Bourgeat-Lami *et al.* (3) ammonium cations prevent the formation of octahedrally coordinated aluminium. Sodium exchange after the first calcination step was applied to prevent dealumination during the second and third calcination steps (3). Threefold ammonium exchange was performed to prepare the (preacid) ammonium form of zeolite Beta.

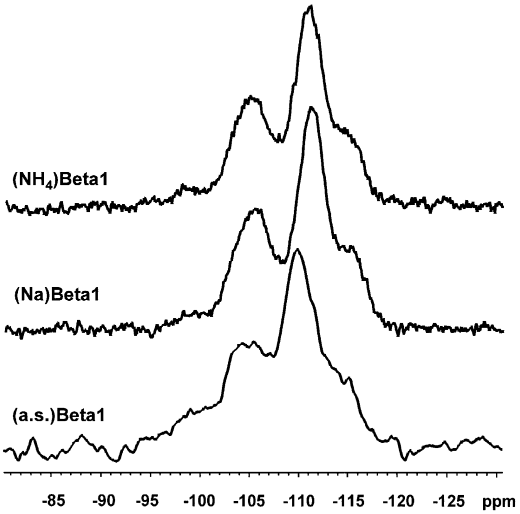

FIG. 2. ^{29}Si MAS NMR spectra of the as-synthesized, sodium-exchanged, and ammonium-exchanged (macrocrystalline) Beta1 samples.

Octahedrally coordinated aluminium was absent in the materials thus obtained, as was concluded from the ^{27}Al MAS NMR spectra (not shown) of the as-synthesized, the sodium-exchanged, and the ammonium forms which showed only a single symmetrical peak centered at 56 ppm. The ^{29}Si MAS NMR spectra (Fig. 2) remained unaltered as well, showing broad overlapping bands at −98 ppm ($Si(OSi)_2(OAl)_2$, relative area (r.a.) = 0.9%), −105 ppm ($Si(OSi)_3(OAl)_1$ or $Si(OSi)_3(OH)_1$, r.a. = 32.4%) −111 ppm, and −115 ppm (both attributed to $Si(OSi)_4$, r.a. = 55.6 and 11.1%) (4, 25). From the data of the (NH_4)Beta1 sample a framework Si/Al ratio of 11.7 was calculated, in good correlation with the wet-analysis data (Table 1).

The IR spectra of the hydroxyl region of the *in situ* activated Beta1 and Beta2 samples (see Fig. 3, lower spectrum) showed absorptions for Brønsted acidic Si–$\underline{\mathrm{OH}}$–Al (3605 cm^{-1}) and silanol groups (3747 cm^{-1}) superimposed on a broad absorption band (3700–3000 cm^{-1}) (3, 4, 7). Compared to the microcrystalline sample, the macrocrystalline Beta1 showed less silanol groups, likely due to the smaller external surface area and consequently less terminal silanol groups.

TABLE 1

Composition and Surface Areas of the Beta Samples

Sample	Si/Al ratio	Na/Al ratio	S_{BET} (m^2/g)
(a.s.)Beta1	10.4	0.14	
(Na)Beta1	11.4	0.94	
(NH_4)Beta1	11.6	0.01	660 ± 12
(a.s.)Beta2	11.6	0.06	
(Na)Beta2	11.6	1.02	
(NH_4)Beta2	11.6	0.01	687 ± 8
(H)Beta1 450(6h)w30	11.6	0.01	635 ± 15
(H)Beta1 550(10h)w30	11.6	0.02	
(H)Beta1 550(3d)w30	11.6	0.01	

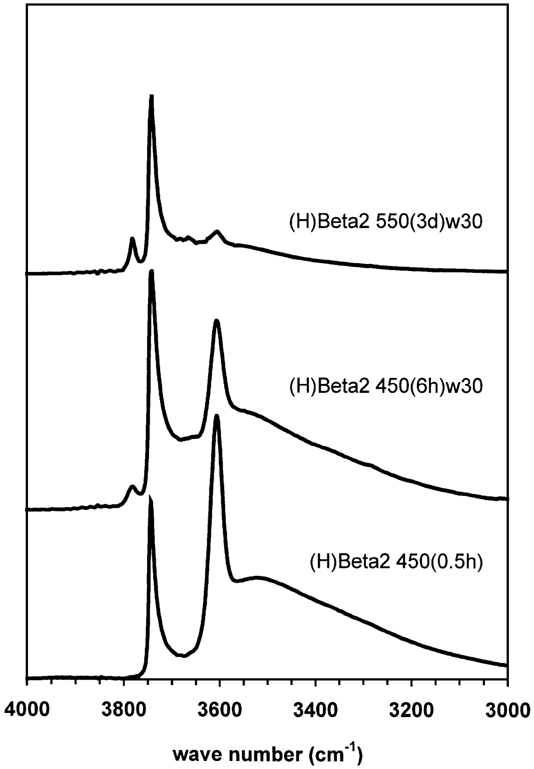

FIG. 3. Transmission FTIR spectra of the hydroxyl region of the (H)Beta2 samples. Prior to data acquisition the samples were activated *in vacuo* at 450°C for 0.5 h.

These parent materials were further modified by the application of additional (hydro)thermal treatments.

Activation of the NH_4 Beta Samples

To simulate deep-bed calcination conditions but without the temperature inhomogeneities (hot spots (4)), the atmosphere above the sample was saturated with a water partial pressure of 4.2 kPa, thus enabling controlled hydrolysis (mild steaming) of Si–O(H)–Al bonds in the framework, forming silanol groups and Al species with a coordination geometry differing from that of the tetrahedral framework Al atoms. These aluminum species, or some of them, are believed to be the active centers in the MPV reaction. We thus assume that the water normally liberated during deep-bed oxidative calcination procedures is the main cause of the formation of aluminum species active in the MPV reaction. Liberation of water by the annealing of silanol nests may also contribute (26). In a deep bed, the water formed will spend more time in the zeolite sample than in a shallow bed and consequently has an increased chance to get involved in hydrolysis (autosteaming). On a smaller scale, this may also be important for the effect of the primary crystallite size, a large crystal retaining water longer during activation than a small crystal, while during steaming a large crystal may limit the intraporous supply of water necessary for hydrolysis. This may result in fewer MPV active sites when compared to the microcrystalline sample treated in a similar way. The effect on the catalytic activity also depends on whether all possible active sites are reached by the reactants to the same extent. It is likely that for larger crystallites the available micropore volume is not used as efficiently as the micropore volume of the smaller crystals. Activation under dry conditions may result in some autosteaming when water is liberated at high temperatures from hydroxyl nests. These are known to be abundant in zeolite Beta because of the stacking faults present in the structure (27).

Creyghton *et al.* (10) showed that any water present during the MPV reaction has a detrimental effect on the catalyst system. Therefore, the steam-treated (H)Beta samples were flushed with dry nitrogen for 1 h at 200°C prior to the catalytic run.

Catalytic Activity as a Function of the Pretreatment

Protons as the charge compensating cations are essential for the catalytic activity since Beta samples with a Na/Al ratio of 1.0 proved to be completely inactive. It was observed that samples with a Na/Al ratio of <1 are active, even when only 6% of the cations were protons. Since the acidic OH groups are not assumed to be the active site for the MPV reaction, their presence seems to be essential in the formation of the active site, which points to the simultaneous formation of silanol groups with the formation of the active site. (Note that Na^+ cations prevent the formation of octahedrally coordinated aluminium upon heating.)

To ascertain that the combination of the activation procedure and the catalytic testing indeed gave reproducible results and that the differences observed between different activation procedures were significant, we subjected several Beta samples of the same batch to the same activation procedure and tested their catalytic activity. The deviation in the initial activities was within ∼2%.

Effect of Activation Temperature

Activation at 450°C under dry conditions for 1 h results in barely active catalysts; see Fig. 4. Raising the ceiling temperature to 550°C increases the activity significantly. As was to be expected on the basis of the crystal sizes, the activities of the macrocrystalline Beta1 samples (activated and tested under the same conditions) are lower.

The temperature effect observed may indicate that the formation of the active sites for the MPV reaction has a high activation energy and/or that silanol groups from hydroxyl nests are consumed and water is liberated (see below). (Note that the heating rate of 1°C/min will cause a sample activated at a ceiling temperature of 550°C actually to be activated 100 min longer ($450°C < \text{Temp.} < 550°C$) than the sample activated at 450°C.)

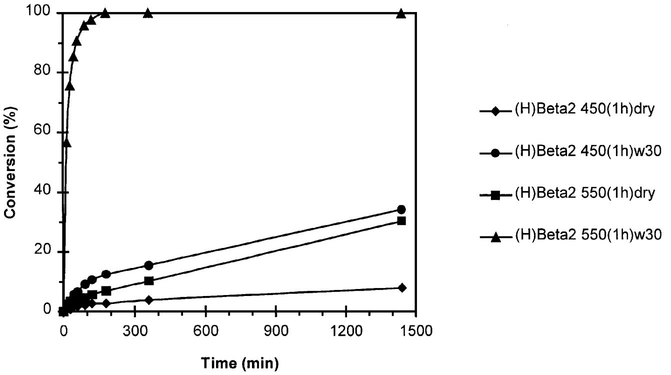

FIG. 4. Conversion of 4-*tert*-butylcyclohexanone vs time. The effect of water vapor during activation at 450 and 550°C on the catalytic activity of microcrystalline Beta2 samples.

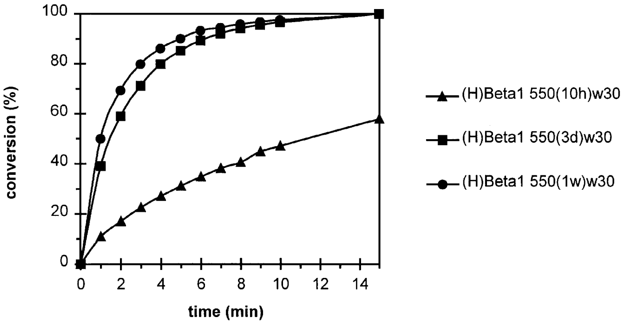

FIG. 5. Conversion of 4-*tert*-butylcyclohexanone vs time. Effect of catalyst activation time. Reaction conditions: 100 mg zeolite (H)Beta1, 5 mmol ketone, and 100 ml 2-propanol under reflux.

Effect of Water during Activation

The effect of the presence of water during activation at 450 and 550°C on the catalytic activity of the zeolite Beta samples becomes apparent from Fig. 4. Clearly, water has a profound influence and leads to a drastic increase of the catalytic activity. Formation of the precursor for the MPV active sites is thus strongly dependent on the availability of water. The combination of a high temperature and the presence of water results in very active Beta samples. The assumption that template removal under oxidative conditions in a deep-bed configuration leads to autosteaming and enhanced activity therefore seems correct.

For both micro- and macrocrystalline samples the activity could be enhanced further by increasing the time of steam activation (6 or 10 h vs 1 h). At 450°C, an increase of the activation time from 6 to 10 h does not result in a pronounced increase in activity, while for the samples activated at 550°C the activities became so high that differences could no longer be observed under the reaction conditions applied.

To examine whether a plateau or a maximum for the activity exists depending on the time of activation, three steam-activated active Beta1 samples were tested with half the amount of catalyst (100 mg) and a doubled amount of reactants (5 mmol ketone and 100 ml 2-propanol). The samples tested were (H)Beta1 550(10h)w30, (H)Beta1 550(3d)w30, and (H)Beta1 550(1w)w30. The latter two samples showed under the standard reaction conditions conversions of 100% within 5 min with a *cis*-alcohol selectivity of 98%. This suggests that the zeolite has become very stable toward further hydrolysis, at least at 550°C. The XRD pattern, however, had almost completely vanished, indicating that long-range ordering was absent. From Fig. 5 it becomes clear that a plateau in the catalytic activity is approached when the Beta sample has been steamed for 3 days at 550°C; steaming for 1 week does not increase the activity much more. This indicates that the maximum amount of aluminium that can be transformed into a MPV active site has been reached. A turnover number (TON) of 19 (mol/mol$_{\mathrm{Al}}$) was reached in 1 min for the most active sample. Note, however, that not all the aluminums present will be transformed into an active site and consequently the actual TON per active aluminum will be higher.

Reversibility of the Catalytic Activity

As described in the Introduction, some framework aluminum atoms in Beta can undergo a reversible transformation from tetrahedral to octahedral coordination. To examine whether the formation of the MPV active site could also be reversed by the adsorption of ammonia, (H)Beta1 450(6h)w30 samples were catalytically tested before and after admission of ammonia at 100°C (3). Prior to the catalytic run the ammonia was again removed at 450°C (under nitrogen flow) to obtain the protonic form. As a reference, one sample was only cooled and exposed to the ambient atmosphere for 1 h, in order to verify whether ambient water at RT already reduces the amount of active sites. It is known that the presence of water influences the aluminum coordination (3, 6).

From Table 2 it becomes clear that the adsorption of ammonia results in a decrease of the number of active sites. This decrease is more pronounced when the induction time is extended from 1 h to 4 days. However, not all the active sites disappear within 4 days: the sample still displayed a higher activity than the (H)Beta1 450(1h) sample (the least

TABLE 2

Influence of Ammonia Adsorption and Induction Time on the Catalytic Activity of (H)Beta1 450(6h)w30 (Standard Reaction Conditions)

Sample treatment	Conversion (%) after 6 h
(H)Beta1 450(6h)w30	49.2
(H)Beta1 450(6h)w30 + ambient + 450(1h)	37.8
(H)Beta1 450(6h)w30 + NH_3 100(1h) + 450(1h)	27.4
(H)Beta1 450(6h)w30 + NH_3 100(4d) + 450(1h)	18.1

active macrocrystalline sample). Exposure of an activated sample to the ambient atmosphere for 1 h, followed by a short activation to remove the water adsorbed, also reduces the activity, although less effectively than when ammonia had previously been absorbed. These results support the idea of a Lewis-acidic framework aluminum whose coordination sphere can undergo a change of coordination depending on the ligands present.

IR Study

The effect of mild steaming can be made clearly visible with IR spectroscopy; see Fig. 3. Upon steaming, the bridging OH peak (3605 cm^{-1}) decreases, while the silanol peak (3745 cm^{-1}) increases. Furthermore, two new absorptions arise: a broad one around 3660–3680 cm^{-1} and a clear peak at 3782 cm^{-1} (VHF). These four absorptions are superimposed on a very broad band spanning 3700–3000 cm^{-1}. It is believed that this broad absorption stems from the presence of hydroxyl nests ($(SiOH)_4$) created by imperfections of the lattice (3, 4, 7). The intensity seems to be decreased for the (H)Beta2 550(3d)w30 sample, which might indicate that some hydroxyl nests are repaired and that siliceous species formed during the steaming process have been inserted. This may result in a more silica-rich framework which is less susceptible to further hydrolysis; this seems to be in agreement with the plateau in the catalytic activity. The latter sample also shows a sharpening of the small peak at 3666 cm^{-1}. Qualitatively similar results were obtained for the macrocrystalline Beta1 samples using the DRIFT technique. Upon steaming, the 3605 cm^{-1} peak decreases, the 3745 cm^{-1} peak increases, and a new peak at 3782 cm^{-1} becomes visible.

The decrease of the amount of bridging hydroxyls can be explained by breaking of the Si–OH–Al bond into a SiOH group, with concomitant increase of the 3745 cm^{-1} band, and formation of an aluminum connected to three framework silicon atoms and coordinating a water ligand. Further hydrolysis may result in an aluminum species connected to the framework by two remaining bonds and bearing a hydroxyl group which is responsible for the VHF band (7). Another explanation for the decrease of the 3605 cm^{-1} band may be the replacement of the charge-compensating proton by a cationic EF-Al species (28) (upon steaming a peak appears at 3666 cm^{-1} which is ascribed to EF-Al species) although its nature is unclear (7).

^{29}Si and ^{27}Al MAS NMR Study

The ^{27}Al MAS NMR spectrum of the Beta1 sample following the short activation procedure (450(1h)dry) (see Fig. 6, bottom) is distinctly different from the (NH_4)Beta1 spectrum (single line at 56 ppm). (Note that before the NMR measurements, all samples were hydrated.) A peak around 0 ppm becomes visible which is ascribed to octahedrally coordinated Al (Oh-Al). As discussed in the Introduction, it is now believed that this Oh-Al is still connected to the framework (3–8) instead of being extraframework Oh-Al as is usually proposed for USY (2). This is also confirmed by our ^{29}Si MAS NMR data: upon dry activation (450(1h)dry) the spectrum (Fig. 7, bottom) did not change, indicating that no changes took place in the environments of the silicon atoms; in other words, dealumination of the framework did not occur. From this, it can be directly concluded that the Oh-Al visible in the ^{27}Al NMR spectra of the 450(1h)dry samples cannot be extraframework aluminum. Since the catalytic activity for the 450(1h)dry samples is very low, this indicates that Oh-Al is not involved in the MPV

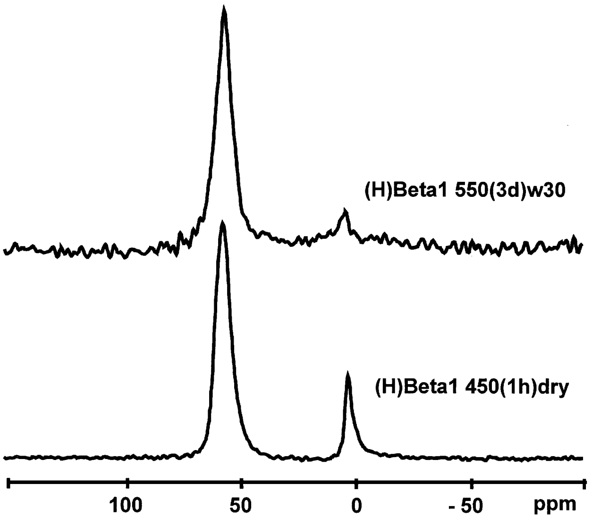

FIG. 6. ^{27}Al MAS NMR spectra of Beta1 samples: lower spectrum dry activated at 450°C, upper spectrum steam activated at 550°C. Prior to data acquisition both samples were hydrated. (The lower signal-to-noise ratio of the upper spectrum is due to the shorter aquisition time we had available.)

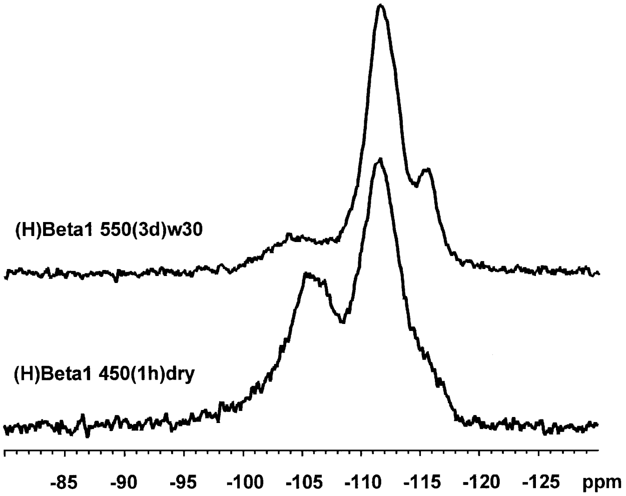

FIG. 7. ^{29}Si MAS NMR spectra of Beta1 samples: lower spectrum dry activated at 450°C, upper spectrum steam activated at 550°C.

active site, in accordance with Creyghton *et al.* The reversal of the Oh-Al back to Td-Al was shown by the treatment of the sample with ammonia. Indeed, after 4 days at 100°C, no Oh-Al signal is present in the ^{27}Al-NMR spectrum, in agreement with the results obtained by Bourgeat-Lami *et al.* (3).

The ^{27}Al NMR spectrum of the (H)Beta1 550(3d)w30 sample (see Fig. 6) shows a decrease of the octahedral peak (0 ppm) and a broadening of the tetrahedral peak (60 ppm). Preliminary results obtained with the newly developed ^{27}Al MQ MAS NMR technique (23, 29), which enables the determination of the quadrupole interactions, show the 60 ppm peak to be built from (at least) two contributions: the normal framework, nondistorted, tetrahedrally coordinated aluminum and a distorted, tetrahedrally coordinated aluminum. This distorted, tetrahedrally coordinated aluminum is absent in the parent (H)Beta1 450(1h)dry sample. Thus, steaming causes some aluminum atoms previously able to attain an octahedral coordination to adopt a distorted tetrahedral geometry.

The ^{29}Si MAS NMR spectrum of the (H)Beta1 550(3d)w30 sample shows a clear decrease of the −105 ppm peak and a sharpening of the −115 ppm peak (assigned to $Si(OSi)_4$); see Fig. 7. The framework Si/Al ratio calculated is 34, indicating that dealumination occurred and EF-Al must be present, whatever its nature. ^{29}Si CP MAS NMR showed that the −105 ppm peak has a contribution from silanol groups and consequently the calculated Si/Al value is a minimum value (30). The ^{29}Si MAS NMR spectrum of the (H)Beta1 550(1w)w30 sample was identical, and possible progress in the dealumination could not be observed. The sharpening of the −115 ppm peak might indicate a decrease of the anisotropy of the Si atom under study. Presumably, the next nearest neighbor (NNN) shell becomes deficient in aluminum and, under the conditions applied (high temperature and steam), siliceous species may fill up the vacancies in the framework, thus creating a more isotropic environment for the $Si(OSi)_4$ (31). These siliceous species are assumed to be created during structural collapse of the framework at positions where severe dealumination has taken place. This structural loss also becomes clear from the XRD patterns (not shown) of the severely steamed samples, which show decreased long-range ordering. This is especially pronounced for the macrocrystalline samples, which show initially a highly resolved diffraction pattern (20). The insertion of silicon species into the framework will have a stabilizing effect toward further hydrolysis, which is in agreement with the catalytic plateau observed.

Proposal for the Precursor for the MPV Active Site

Creyghton *et al.* observed a correlation between the calcination method and the IR spectra of the Beta samples (10). Especially the appearance and the increase of the 3782 cm^{-1} (VHF) peak with the increase of the catalytic activity were obvious. Concomitantly the 3605 cm^{-1} peak (Si–$\underline{OH}$–Al) decreased and the 3745 cm^{-1} peak (silanol groups) increased. Our IR data, based on dry and steam-activated zeolite Beta samples, support these observations. It is obvious that water is essential during the activation of zeolite Beta to create a (partially) hydrolyzed aluminum species that functions as the precursor for the MPV active site.

An important question to be answered is, "Can the catalytic activity be due to the presence of extraframework aluminum species?" We think not. In this respect, it is essential to mention that aluminum-free titanium Beta is also active in the MPV reaction and displays an almost identical *cis*-alcohol selectivity (98%) (32–34). It seems logical to assume that there are analogies between the active sites in titanium Beta and aluminum Beta. The titanium Beta catalyst could be regenerated up to 100 times without any change in the activity and the selectivity. Additionally, the UV–Vis spectrum showed that the titanium remained in tetrahedral coordination in the zeolite framework after regeneration. In our view, this proves that the active titanium sites are framework atoms (33, 34). Extrapolation of this to aluminum Beta suggests that the catalytically active aluminum species is also part of the framework. The reduction of the catalytic activity upon adsorption of ammonia supports the idea of a Lewis-acidic framework aluminum site as well.

Formation of large amounts of alumina species from a high-silica zeolite such as Beta is not expected. Furthermore, if aluminum-rich phases were present and catalytically active, they would be expected to display an activity and stereoselectivity that resembles those of USY or amorphous silica–alumina (ASA) samples (10% *cis*-alcohol) (10). Cationic EF-Al species which act as charge compensators are not confined to the zeolite pores and can also be present at the external surface. The high stereoselectivity and the fact that the external surface proved to be catalytically inactive for the MPV reaction (10) point to a reaction occurring in the internal pore system.

If EF-Al (present in steamed samples) is the active species, then a reduction of the catalytic activity should be observed after removal of the EF-Al. To test whether EF-Al could be removed selectively by applying a 0.01 M HNO_3 aqueous solution as described by Bourgeat-Lami *et al.* (3), a steamed (H)Beta1 450(6h)w30 sample was subjected to an acid wash at RT; as a reference an unsteamed (H)Beta1 450(1h)dry sample was given the same treatment. Both samples proved to be catalytically inactive (conversion after 24 h: 3%) and the elemental analysis gave identical Si/Al ratios of 30. The XRD of both samples was deteriorated, indicating a loss of long-range ordering and the N_2-BET analysis showed a reduction of the surface area to 500 m^2/g (−160 m^2/g) for both samples; mesopores were not detected. Clearly, EF-Al was not removed selectively, and we were unable to make a distinction between framework and nonframework aluminum.

The presence of extraframework species becomes indirectly apparent by the *cis*-4-*tert*-butylcyclohexanol selectivity. As reported by Creyghton *et al.* (10), the *cis*-alcohol selectivity can be increased from 95% up to 99% by partially (∼60%) replacing the protons by large cations (K^+, Rb^+, Cs^+). It was suggested that the large cations limited the available micropore volume to such an extent that the formation of the bulky *trans*-alcohol was even more suppressed. We observed that the more active zeolite Beta samples (steam-activated) displayed *cis*-alcohol selectivities of up to 98%, whereas the less active samples (dry-activated) gave 94% *cis*-alcohol selectivities. We therefore propose that in steamed Beta samples extraframework species act in a manner analogous to that exerted by large alkali cations in Beta.

Taking all the above into consideration, we propose a partially hydrolyzed framework aluminum as the precursor for the catalytic active species, as indicated in Fig. 8. Based on the very high stereoselectivity we think that only one type of aluminum site is responsible for the catalytic activity. Only some of the aluminum atoms present will undergo the transformation, presumably those which are in framework positions under strain, e.g., are part of a four-ring in the structure (in Beta, five four-rings are connected in an S shape).

Upon heating, ammonia is released and the remaining proton is transferred to another oxygen. At this point the framework becomes deformable; if instead of the ammonium ion a metal cation were present, the aluminum would be locked into its tetrahedral coordination. The presence of some water may facilitate the breaking of a Si–OH–Al bond, forming a silanol group and an aluminum connected to three framework silicon atoms and bearing a water molecule. The aluminum atom probably inverts its coordination geometry upon the coordination of water. Instead of being “buried” within the larger oxygen framework atoms it is now exposed into the zeolite pore and thus becomes available to other ligands like water or reactants. If the heating (activation) is stopped at this point and water is adsorbed at room temperature, an octahedrally coordinated framework aluminum may be formed and observed by ^{27}Al MAS NMR. On the other hand, if ammonia is adsorbed, the process may be reversed by an equilibrium shift and finally only tetrahedral aluminum will exist. When the heating is continued and some water is present in the pores (to maintain water adsorbed onto the aluminum), an Al–O–Si bond may be hydrolyzed and a new tetrahedrally coordinated aluminum species forms which bears the hydroxyl group vibrating at 3782 cm^{-1} (VHF). This species was also suggested by Kiricsi *et al.* as a possible explanation for the observed VHF band (7). Formation of this new aluminum species will result in a decrease of the amount of aluminum able to attain an octahedral coordination and thus in a decrease of the Oh-Al peak in the ^{27}Al MAS NMR spectrum (Fig. 6). We mention again that the NMR data were obtained on hydrated samples and therefore differ from those of the actual catalyst. Table 2 shows that absorption of ambient water at room temperature already reduces the catalytic activity, which suggests that some active sites are annihilated, possibly by an equilibrium shift toward octahedral aluminum. Therefore, the ^{27}Al MAS NMR spectrum of the (H)Beta1 550(3d)w30 sample may indicate more octahedral aluminum to be present than in the actual catalyst.

Upon reaction of this new aluminum species with 2-propanol, an Al-isopropoxide species is formed which will act as the initial catalyst in the MPV reaction ($Al(O\textit{i}Pr)_3$ is an MPV catalyst (10)). Coordination of the ketone to the Al-isopropoxide species initiates the MPV reaction cycle. Subsequent hydride transfer, acetone elimination, and finally alcoholysis of the product alcohol and concomitant regeneration of the active site complete the reaction cycle, as was proposed recently by van der Waal *et al.* (34); see Fig. 9. The presence of water (as contaminant) in the reaction mixture may (besides the above mentioned)

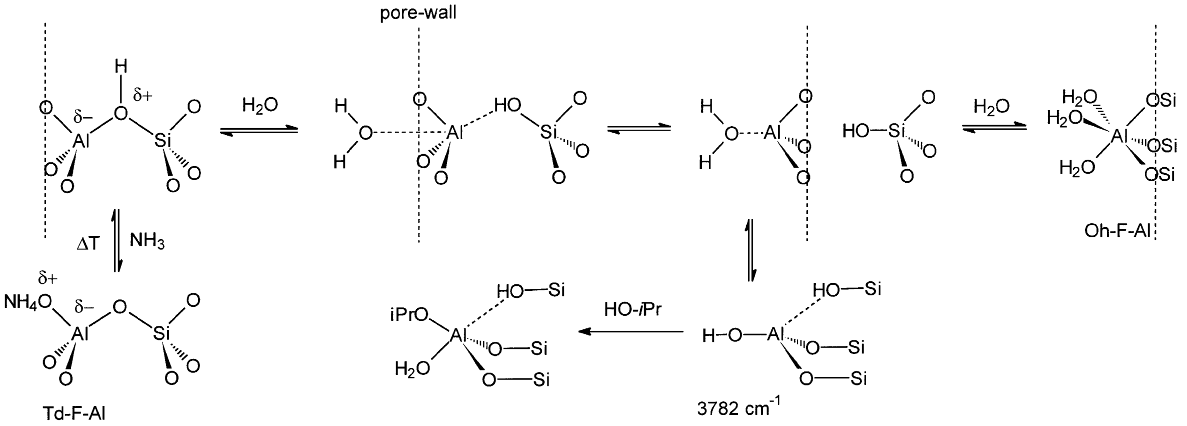

FIG. 8. Proposed mechanism for the formation of the catalytic active site (Al-isopropoxide species) in zeolite Beta for the MPV reduction.

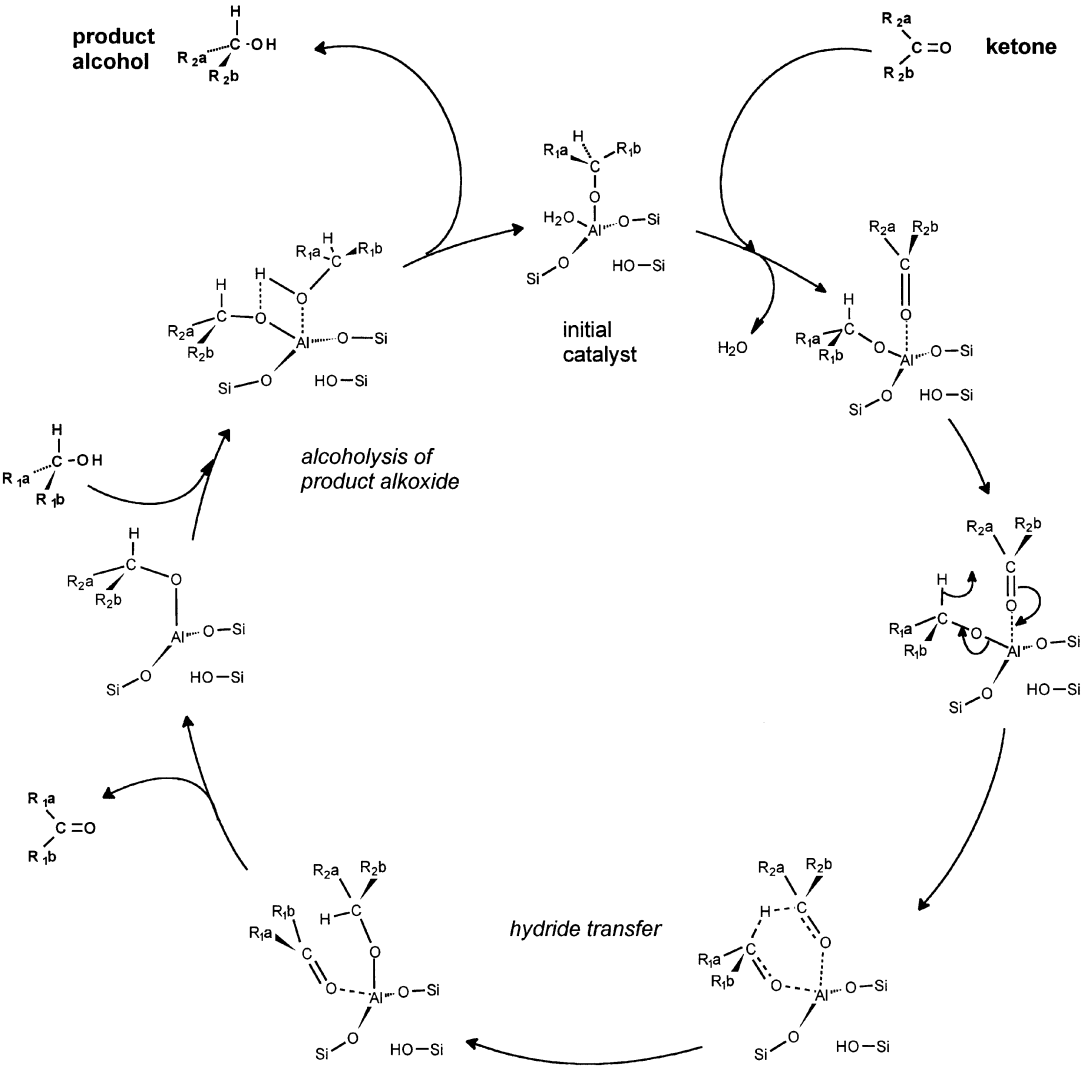

FIG. 9. Proposed MPV reaction scheme starting with an aluminium-alkoxide species in zeolite Beta.

reverse the formation of the isopropoxide species or may prevent the ketone from coordinating, thus inhibiting the reaction (10).

The nature of the EF-Al remains unclear, although it is unlikely to be an octahedrally coordinated species since the steamed samples show a decreased 0 ppm peak intensity in the ^{27}Al-NMR spectra. A possible explanation may be the formation of a distorted, tetrahedrally coordinated EF-Al from tetrahedral framework aluminum atoms. The presence of various tetrahedrally coordinated aluminum species makes identification by NMR techniques difficult. Currently, we are extending the (2D) NMR investigations (35).

CONCLUSIONS

The catalytic activity of zeolite Beta in the stereoselective Meerwein–Ponndorf–Verley reduction of ketones using secondary alcohols as reductant can be tuned by appropriate pretreatment. During activation, water is essential to obtain an active catalyst. On the basis of IR, NMR, and the catalytic data a partially hydrolyzed framework aluminum is proposed as the precursor for the active site. The formation of the initial catalytic site from the precursor is thought to be a lattice-attached aluminum-isopropoxide species; its formation can be easily reversed when water is present in the reaction mixture, thus explaining the sensitivity of the reaction toward water. We assume that EF-Al species are present as catalytically inactive species although, by their size, they reduce the amount of *trans*-alcohol formed in a manner analogous to that previously described for large alkali cations.

Since the specific aluminum site has not been observed unambiguously by either IR or NMR techniques, additional research employing other techniques seems necessary to observe the Al species directly.

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