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Gas-phase Meerwein–Ponndorf–Verley reaction: correlation of the 3665 cm^{-1} IR band with the *cis*-alcohol selectivity

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Abstract

The two Lewis acid sites assumed to catalyze the Meerwein–Ponndorf–Verley (MPV) reaction are identified by IR bands at 3782 and 3660–3680 cm^{-1}. Different combinations of heat-treatment protocols were used and the results indicated that the final temperature, ramp rate, and gas environment make a difference in the relative intensities of the 3782 and 3665 cm^{-1} bands. Combining different heat-treatment procedures, samples were produced where the 3782 and 3665 cm^{-1} band intensities moved in opposite directions (i.e., one increasing and the other decreasing). The MPV reduction of 4-*tert*-butylcyclohexanone with 2-propanol in the gas phase was studied at 100 °C in a nitrogen atmosphere. The increasing trend of the relative intensity of the 3665 cm^{-1} band showed a correlation in favor of the formation of *cis*-4-*tert*-butylcyclohexanol (*cis*-4-TBCHL). This suggests that the species associated with the 3665 cm^{-1} band are likely responsible for *cis*-4-TBCHL selectivity.

Keywords: IR spectroscopy; Lewis acidity; Meerwein–Ponndorf–Verley reaction; Zeolite Beta

1. Introduction

The changes observed upon dealumination of zeolites and zeo-type materials by hydrothermal treatment have received much attention [1,2]. Enhanced catalytic activity is hypothesized to be caused by the formation of catalytic sites due to the partial and/or complete removal of Al from the tetrahedral framework owing to the hydrolysis of the framework Si–O–Al bonds [3]. Zeolite Beta, a wide-pore zeolite, is easily dealuminated by thermal treatment with the simultaneous formation of more than one type of Al species. These species may be completely removed from the framework (extraframework Al (EFAl) species) and/or still be a part of the framework (partially framework Al (PFAl)) species [4–12]. They exhibit a Lewis acid character [10–12], and thus make zeolite Beta an active catalyst in Lewis acid-catalyzed reactions. However, the nature of active sites formed after dealumination and their role in the catalysis of reactions such as the Meerwein–Ponndorf–Verley (MPV) reaction is still a matter of debate [6,7,13,14]. Characterization of zeolite acid sites under conditions as close as possible to those found in actual reactions is important in understanding the actual catalytic mechanism.

Experimental evidence suggests that MPV reaction occurs only in the micropores [7]. It was hypothesized that it proceeds via a cyclic six-membered transition state in which both the reductant and the oxidant are coordinated to the same Lewis acid Al center [15]. Because Lewis acidity is created by the removal of water molecules from the Brønsted acid sites [16], changes in the number of different types of Lewis acid sites are influenced by the calcination temperature and environment [6,13]. Ideally, the catalyst environment (moisture content, temperature, pressure, etc.) in the reactor should match that used for catalyst characterization. IR spectroscopy and ^{27}Al NMR spectroscopy are the most frequently used methods for characterizing the state of Al in zeolites after heat treatment. However, these techniques require different conditions (moisture content, temperature, etc.) for sample characterization and thus can be ambiguous in their interpretation. The applicability of ^{27}Al NMR is limited in that some Al species identified by IR spectroscopy escape its detection (NMR invisible species) [5,8]. Also, it has been shown that completely dehydrated zeolite Beta does not give any ^{27}Al NMR signal [5,17], or results in only a broad hump [18]. Samples need to be rehydrated before analy-

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sis [4–7,10,17]. ^{27}Al NMR can detect the presence of octahedrally coordinated Al species in zeolite Beta; however, there is no agreement in the literature whether these are EFAl or PFAl species. Creyghton et al. [7] observed an increase of the activity of zeolite Beta in the MPV reaction upon increasing calcination temperature; however, no change in the ^{27}Al MAS-NMR spectrum was detected for catalysts exhibiting different activities. Thus, no correlation could be established between the amount of octahedral Al present in zeolite Beta characterized by ^{27}Al MAS-NMR and its catalytic activity in the MPV reaction [7]. IR spectroscopy used to characterize these samples, however, showed increasing intensities of both 3782 and 3665 cm^{-1} IR bands for the more active catalysts [7]. These findings are similar to those reported by Jia et al. [4] who were unable to correlate the changing relative intensities of 3782 and 3665 cm^{-1} bands with the relative intensity of ^{27}Al NMR octahedral aluminum signal (0 ppm).

There are disagreements in the literature in the assignment of a given IR band to a particular Al Lewis site, and thus it is difficult to determine which Lewis site is responsible for the catalytic activity of zeolite Beta catalyst in reactions such as the MPV reaction. The two Lewis acid sites that have been reported to be responsible for zeolite Beta activity in the MPV reaction are identified by the IR bands located at 3782 and 3660–3680 cm^{-1}. The band at 3782 cm^{-1}, suggested to be a true fingerprint of a Lewis site in zeolites [11], was variously assigned either to the OH groups associated with the EFAl species [12,19,20] or to the OH groups attached to the tricoordinated Al atoms partially connected to the framework by two oxygen atoms [8,9,11]. It was reported by several investigators [6,7] that the relative intensity of the 3782 cm^{-1} band increased with increasing temperature and/or duration of the steam treatment and that this coincided with the increasing activity of zeolite Beta in the MPV reaction. However, other investigators suggested that the EFAl species associated with the band at 901 cm^{-1}, but not with the 3782 cm^{-1} band, are responsible for the activity and *cis*-alcohol selectivity of zeolite Beta in the MPV reaction [13]. Additionally, the band at $\sim$ 3660 cm^{-1} was observed to grow during hydrothermal treatment but due to its low intensity it was not usually correlated to MPV activity [13].

The band at 3665 cm^{-1} was also assigned to the OH groups attached either to the EFAl [8,9] or to the PFAl species linked to the framework by one or two remaining bonds [4,5,20]. Both of these specie types were considered to have octahedral symmetry [4,5,8,9]. However, recently, the Lewis acid activity of zeolite Beta was associated with the ability of the framework to create octahedrally coordinated PFAl species [14]. One of the difficulties in correlating the catalytic performance of zeolite Beta in the MPV reaction with Al Lewis site(s) associated with the IR bands at 3782 and/or 3665 cm^{-1} is due to the fact that the relative intensity of both these bands changed in concert; i.e., both intensities simultaneously either increased or decreased, depending on the severity of the hydrothermal treatment [4,6,7]. Since the intensities of both the 3780 and 3665 cm^{-1} bands exhibited the identical trend, the catalytic results of these investigations, attributed to the species associated with the 3782 cm^{-1} band [6,7], could also be interpreted in terms of the species associated with the 3665 cm^{-1} band.

This investigation focused on studying the formation of Al-based Lewis acid sites suspected for zeolite Beta activity/selectivity in the MPV reaction using IR spectroscopy. IR spectroscopy allowed investigation of the catalyst under heat treatment/reaction conditions nearly identical to those employed in the catalytic experiments. The aim of this investigation was to ascertain if a correlation existed between the *cis*-alcohol selectivity and the different types of Lewis acid sites, characterized by the 3782 and 3665 cm^{-1} IR bands.

2. Experimental

2.1. Characterization

Zeolite Beta used in this study was a commercial product H-BEA-25 in the H$^+$ form purchased from Sud-Chemie. X-ray powder diffraction (XRD) analysis of all materials was performed using Cu-K$_\alpha$ radiation on a Bruker D5005 θ:2θ Bragg-Brentano diffractometer equipped with a curved graphite crystal-diffracted beam monochromator and a NaI scintillation detector. The XRD patterns were recorded in the 5–35° 2θ range with a step of 0.02° 2θ and a count time of 40 s/step. The apparent crystallinity of all the catalyst samples was estimated by normalizing the integrated intensity of the (004), (300), (302), and (008) peaks of the sample to those of the parent zeolite Beta considered as 100% crystalline. The energy dispersive X-ray spectroscopy (EDX) analysis of the parent and all the catalyst samples was carried out utilizing a Phoenix EDAX X-ray analyzer equipped with Sapphire super ultrathin window detector attached to the Hitachi S-4700 FE-SEM. The accelerating voltage of the electron gun was set to 5 kV, the beam current was at 10 µA, and the counting time was 100 s. Uncoated samples were dispersed on Cu specimen stubs coated with conductive carbon paint (colloidal graphite in isopropanol, 20% solids, SPI Lab Supplies). Ten measurements for each sample were performed, and the results were found to be reproducible to ±10% for all samples. The particle-size distributions for all the catalysts and the parent zeolite Beta were measured on an API Aerosizer LD equipped with an API Aero-Disperser dry powder dispersion system (TSI, Inc., Particle Instruments/Amherst). For all partical-size distributions crystal density was assumed to be 1.61 g/cm^3 [21].

2.2. Pretreatment and activation

Three different catalyst samples were prepared from the parent zeolite Beta by combination of different heat treatment procedures (“pretreatment” and “activation,” Table 1).

Table 1
Heat-treatment procedures used to prepare the catalyst samples

Sample	Pretreatment (furnace)			Activation (reactor/FTIR cell)		
	Final temperature (°C)	Rate (°C/min)	Duration at final temperature (h)	Final temperature (°C)	Rate (°C/min)	Duration at final temperature (h)
A	500	1	10	500	1	6
B	500	1	10	700	1	6
C	700	10	10	500	1	6

In the first pretreatment, two batches of the parent material (4 g per batch) were placed into crucibles and separately heat-treated in a conventional furnace (Model 47900, Thermolyne) under ambient air. Zeolite Beta sample A was heated from 25 to 500 °C at a rate of 1 °C/min, maintaining 500 °C for 10 h, and then cooled to 25 °C at a rate ∼ 2 °C/min. The other sample C was heated from 25 to 700 °C at a rate of 10 °C/min, maintaining 700 °C for 10 h, and cooled to 25 °C at a rate ∼ 2 °C/min. Samples A and C were then subjected to the identical activation procedures (heated from 25 to 500 °C at a rate 1 °C/min, maintaining 500 °C for 6 h and cooling to 100 °C (reaction temperature) at a rate ∼ 2 °C/min) both in the IR spectrometer (0.02 g) and in the reactor (0.2 g of sample mixed with 3 g of quartz sand). Catalyst sample B was pretreated by initially heating a 4-g sample in a furnace under ambient air from 25 to 500 °C at a rate of 1 °C/min, maintaining 500 °C for 10 h, and cooling to 25 °C at a rate ∼ 2 °C/min. This was followed by activation in both the IR spectrometer and the reactor that consisted of heating from 25 to 700 °C at a rate 1 °C/min, maintaining 700 °C for 6 h, and cooling to 100 °C at a rate ∼ 2 °C/min. Once the activations in the IR spectrometer and in the reactor were completed, the IR spectra were taken (at 100 °C under N_2 flow, 33 ml/min STP) and the reactants were introduced. The heat-treatment methods used in this study were determined to obtain the maximum difference in the relative intensities of the IR bands at 3782 and 3665 cm^{-1} in the three different catalyst samples (i.e., A, B, and C). None of the samples showed a change in sample crystallinity (XRD) or in the particle-size distribution.

2.3. Catalytic experiments

The MPV reactions were carried out in a vertical, downflow, fixed-bed stainless-steel reactor at 100 °C under atmospheric pressure. The reactor consisted of a 12.7-mm-i.d. stainless-steel tube placed inside a three-zone furnace (vertical split-tube furnace, Thermcraft Inc.) where the isothermal zone temperature was maintained at 100 ± 1 °C. The reactants were 2-propanol (IPA, HPLC grade, Acros) and 4-*tert*-butylcyclohexanone (4-TBCH, 99%, Acros). Prior to reaction 4-TBCH was purified by dissolving the 4-TBCH crystals in IPA, recrystallizing them by evaporation of the IPA, and filtering (qualitative filter paper, grade 1 (11 μm), Whatman). This procedure increased the purity of 4-TBCH from ∼ 99.0 to 99.9%. The IPA/4-TBCH mixture (100 g of IPA per 1 g of 4-TBCH) was introduced with a controlled rate of 10 ml/h using a syringe pump (kdScientific, Model 100, ±1% accuracy). The catalyst sample (0.2 g) was mixed with quartz sand (3 g, 3Q-Rock, US Silica) and then loaded into the reactor. 4-TBCH was delivered to the reactor using nitrogen (99.9%, < 10 ppm moisture, Med-Tech Gases) as a carrier gas (110 ml/min, STP), at a weight hourly space velocity (WHSV) of 0.4 $\text{g}_{\text{4-TBCH}}\,\text{g}_{\text{cat}}^{-1}\,\text{h}^{-1}$. Reaction products were analyzed using an on-line Agilent 6890 gas chromatograph equipped with an FID detector, and a 30-m, 5% phenylmethylsiloxane capillary column. Before the catalytic studies a "blank" experiment was performed using the identical temperature, feed composition, and nitrogen flow conditions but over only quartz sand. This resulted in no *cis*-alcohol in the product and no more than 3% *tr*-alcohol selectivity (activity was < 1%). All catalytic results described were acquired after steady state was reached (i.e., between 6 and 10 h). External mass-transfer limitations were experimentally checked (varying flow rate and catalysts' bed volume) and none were found. The catalyst samples (i.e., A, B, and C) did not show any change in the particle-size distribution, and it was calculated that no internal mass transfer limitations exist.

2.4. Infrared spectroscopy

For the analysis of the OH-stretching region (4000–3200 cm^{-1}), diffuse reflectance infrared Fourier-transform (DRIFT) spectra were acquired at 100 °C on a Nicolet Magna-IR 560 spectrometer equipped with a DTGS KBr detector and a Spectra-Tech diffuse reflectance high-temperature/vacuum chamber with KBr windows. Fine powder of each sample (identical mass of 0.02 g) was loosely packed into a ceramic sample cup located inside the chamber and flattened using a glass microscope slide. The samples were under dry nitrogen (99.9% purity with < 10 ppm moisture content, Med-Tech Gases) flowing at 33 ml/min (STP) during the heat treatment in the chamber and during spectra acquisition. Thermocouples were located in the sample cup and temperature was controlled to ±1 °C (Eurotherm). Potassium bromide (99+% KBr, infrared grade, Acros) was used as the background and the catalyst samples were analyzed neat. Before collection of the IR spectrum, nitrogen was purged through the beam path at 14 L/min (NTP). The spectra were collected with resolution of 2 cm^{-1} using 128 scans. Spectra were collected after the sample was cooled to 100 °C, at 40 min and at 12 h. There were no changes in the spectra collected at these times. For the analysis of the framework vibration region (1250–450 cm^{-1}), the zeolite samples were mixed with KBr (1/200 weight ratio) and the spectra were collected at room temperature under nitrogen flow (33 ml/min, STP).

3. Results and discussion

3.1. Framework versus nonframework aluminum

The surface Si/Al ratio of the parent zeolite Beta was found to be 10 ± 1 as measured by EDX. All three catalyst samples (i.e., A, B, and C) prepared from the parent material showed the same value (10 ± 1). This value is close to the value of the bulk Si/Al ratio of 12.5 for the parent zeolite Beta, supplied by the manufacturer. Thus, it appears unlikely that different combinations of heat-treatment procedures resulted in any significant changes in its Si/Al ratio. The parent material and the catalyst samples after heat treatments (A, B, and C) were also characterized by their structural vibrations (1250–450 cm^{-1} range). All samples exhibited the characteristic IR bands for zeolite Beta at 1094, 575, and 525 cm^{-1} [9,22]. The positions of the bands at ~ 1090 and ~ 575 cm^{-1} are sensitive to the zeolite Beta framework Si/Al ratio, and their wavenumber increases upon progressive framework dealumination [8,12,22]. Framework Si/Al ratios were calculated using linear correlations between the wavenumbers of the ring breathing vibration band at ~ 575 cm^{-1} [22], as well as the T–O-stretching vibration band at ~ 1090 cm^{-1} [8] and the number of framework Al atoms per unit cell. Both correlations gave the same framework Si/Al ratio of 33 ± 2. The framework Si/Al was higher than the total Si/Al inferred from EDX. This indicates that in all samples only about 35% of total Al is in the zeolite framework. Thus, combinations of heat treatments were insufficient to further dealuminate the parent zeolite Beta sample to the extent that could be detected within the error limits of the spectroscopic method utilized. These results are further corroborated by the analysis of the intensity of band at ~ 950 cm^{-1}, which is responsible for Si–O bonds in the structural vacancy [8]. None of the catalyst samples prepared by different heat treatment combinations showed an increased intensity of the ~ 950 cm^{-1} band compared with the parent material, suggesting again that there was no further dealumination of the parent zeolite Beta framework. Taken in total, these results indicate that both the parent zeolite Beta and all the catalyst samples used in this study contained significant amounts of the EFAl species and that no further EFAl species were formed upon the pretreatment/activation of the parent material.

3.2. Infrared spectroscopy

The IR spectra in the OH-stretching region of the three catalyst samples acquired at 100 °C are shown in Fig. 1. Each sample exhibited four IR bands at 3782, 3745, 3665, and 3610 cm^{-1}. The band at 3745 cm^{-1} is commonly assigned to the terminal silanol groups on the outer surface of crystals [9]. The classical band at 3610 cm^{-1} is due to the bridging hydroxyl groups connected to the framework with Al in tetrahedral coordination and is responsible for Brønsted acidity. As noted earlier, the true nature of the 3782 and 3665 cm^{-1} bands is still a matter of debate; however, Al species associated with these bands are suspected to be the active sites in the MPV reaction. In the present study, different combinations of heat-treatment procedures were tried to unequivocally separate relative intensities of these bands, such that the relative intensity of the 3665 cm^{-1} band increases while the 3782 cm^{-1} band decreases. In order to compare these intensities after the applied heat-treatment procedures, the relative integral intensity of the 3782 and 3665 cm^{-1} bands was calculated by normalizing the integrated intensity of a given band in each sample to the largest integrated intensity of this band among the catalyst samples. The comparison of the relative integral intensities of the 3782 and 3665 cm^{-1} bands for the three catalyst samples is shown in Table 2. Fig. 1 (as well as Table 2) shows when the activation procedure was changed from less severe in the furnace (pretreatment) and more severe in the reactor (activation), producing sample B, to the relatively more severe in the furnace and less severe in the reactor, producing sample C (Table 1), the relative intensities of the 3665 cm^{-1} band decreased with a simultaneous increase in the relative intensity of the 3782 cm^{-1} band. A less severe heat treatment performed in the furnace to produce sample A and

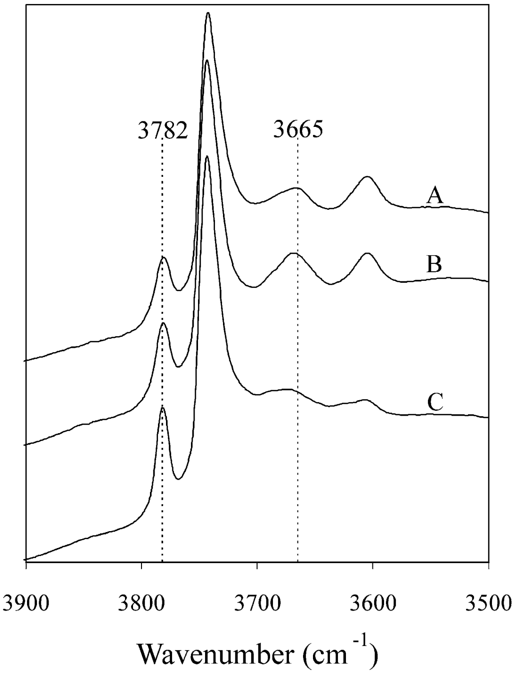

Fig. 1. DRIFT Spectra in the OH-stretching region of catalyst A (treated in the furnace at 500 °C, in the reactor at 500 °C), B (treated in the furnace at 500 °C, in the reactor at 700 °C), and C (treated in the furnace at 700 °C, in the reactor at 500 °C) recorded at 100 °C.

Table 2
Relative integral IR intensity of the 3782 and 3665 cm^{-1} bands

Catalyst type	3782 cm^{-1}	3665 cm^{-1}
A	0.58	0.56
B	0.69	1.00
C	1.00	0.35

B compared to that producing sample C, and a less severe activation of sample A performed in the reactor to produce sample A compared to that producing sample B, resulted in the 3665 cm^{-1} band relative intensity of sample A to fall in between the two other samples B and C (Fig. 1). These results are also illustrated in Table 2. When the heat-treatment temperature and rate in the furnace were increased from 500 to 700 °C and 1 to 10 °C/min, respectively, with the same activation temperature (500 °C) and rate (1 °C/min) in the reactor (sample A versus C), the relative intensity of the 3782 cm^{-1} band increased, whereas the relative intensities of the band at 3665 cm^{-1} decreased substantially, as shown in Fig. 1 and in Table 2.

The Al species associated with the 3665 cm^{-1} band have been suggested to possess octahedral symmetry; however, their partial attachment to the framework is still a matter of debate [4,5,8,9,20]. One of the methods used to determine the extent of dealumination of zeolite Beta samples compares their T–O-stretching and/or ring-breathing vibration frequency [8,12]. As previously discussed, all heat-treated samples were dealuminated to the same extent as indicated by the constant value of ring-breathing vibration and T–O-stretching vibration frequencies. This strongly suggests that the same number of EFAl species exists in all these samples. Thus, any changes in the relative intensity of the 3782 and 3665 cm^{-1} bands are very likely related to Al species still associated with the framework.

These results indicate that the temperature, rate, and gas environment of heat treatment made a difference in the relative (integral) intensities of the 3782 and 3665 cm^{-1} bands. However, it appears that the pretreatment of the parent zeolite Beta performed in the furnace influenced more the relative intensities of these bands compared to the activation performed in the reactor. In fact, when only activation of the catalysts was performed with no prior pretreatment, the intensities of bands at 3782 and 3665 cm^{-1} changed in the same direction (i.e., both increased or both decreased). The heat-treatment procedure where 4 g of the parent zeolite Beta was placed in a crucible and calcined under ambient air in the furnace and the activation procedures utilized in the reactor where only 0.2 g of sample was mixed with quartz sand and calcined under dry nitrogen simulate the deep-bed and shallow-bed calcination methods, respectively [7]. It had been previously reported that deep-bed calcination methods resulted in samples with more intense 3782 and $\sim$ 3665 cm^{-1} bands [4,7]. However, the case where the intensity of one of these bands increased whereas the intensity of the other band decreased after heat treatment has not been reported. Thus, the choice of our heat-treatment conditions allowed for the first time the dissociation of the 3782 and 3665 cm^{-1} IR bands.

The pretreatment applied in the present study can play a role of an “in situ steaming” [6,23] where the water leaving the zeolite structure could have more impact on the formation of different Al species. In this sense, the harsher pretreatment applied to catalyst C and resulting in an increase of the relative intensity of the 3782 cm^{-1} band is consistent with what was observed in the previous studies [4,6]. However, in the present study the harsher pretreatment also resulted in the decrease of the relative intensity of the 3665 cm^{-1} band, results unlike these reported previously [6]. It is hypothesized that the trend of decreasing intensity of the 3665 cm^{-1} band was achieved upon harsher pretreatment (catalyst C), because no additional moisture (steam) was supplied for the formation of this catalyst sample, unlike in other studies where the harsher heat treatment was applied through action of steam at higher temperatures [6,9,12]. These results suggest that the formation of the Al species that are able to attain the suggested octahedral symmetry, represented by the 3665 cm^{-1} vibration, is possible in a highly controlled environment. In the present study the activation of the catalyst samples in the reactor/IR spectrometer under dry nitrogen prevented further exposure of the “pretreated” catalyst to moisture, which led to some control of the reaction/characterization environment. The MPV reaction was tested and the *cis*-4-TBCHL selectivities were compared using these catalyst samples.

3.3. Catalytic selectivity

Fig. 2 demonstrates the change in the amount of *cis*- and *tr*-4-TBCHL produced in the MPV reduction of 4-TBCH with IPA as a function of reaction time over B and C catalysts. It was previously shown that the increased amount of secondary reactant resulted in an increased *cis*/*tr* ratio in the product stream [24]. Therefore, the higher *cis*- than *tr*-alcohol selectivity in the product stream (Fig. 2) is due to a relatively high weight ratio of IPA to 4-TBCH (100) in the reaction mixture. These two catalyst samples (B and C) exhibited the most dramatic difference in the relative intensities of the 3782 and 3665 cm^{-1} bands, as shown in Fig. 1 and Table 2. As illustrated in Fig. 2, the *cis*-4-TBCHL formation was higher over catalyst B, which had a higher relative intensity of 3665 cm^{-1} and a lower relative intensity of 3782 cm^{-1} bands, whereas the *tr*-4-TBCHL formation was identical over both catalysts.

The selectivity results at greater than 95% conversion are shown in Fig. 3. These selectivities were calculated from the data collected at steady state between 6 and 10 h of a typical experiment (Fig. 2). The side-product distribution obtained using all three catalyst samples was essentially the same at steady state. As shown in Fig. 3, the *cis*-4-TBCHL selectivity was higher than the *tr*-4-TBCHL selectivity in the MPV reaction. This is consistent with the literature data for the MPV reactions in the liquid phase [7,25] as well as the

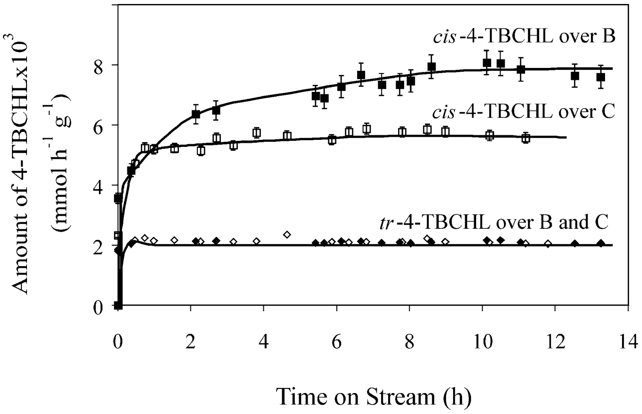

Fig. 2. Amount of *cis*- and *tr*-4-TBCHL produced as a function of time over catalyst B (treated in the furnace at 500 °C, in the reactor at 700 °C) and C (treated in the furnace at 700 °C, in the reactor at 500 °C) at 100 °C.

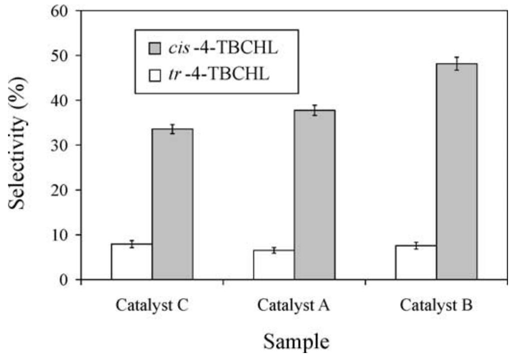

Fig. 3. The *cis*- and *tr*-4-TBCHL selectivities over catalyst A (treated in the furnace at 500 °C, in the reactor at 500 °C), catalyst B (treated in the furnace at 500 °C, in the reactor at 700 °C), and catalyst C (treated in the furnace at 700 °C, in the reactor at 500 °C) at 100 °C.

gas-phase results that were obtained using a higher partial pressure of IPA [24]. Higher *cis*- than *tr*-4-TBCHL selectivity in the zeolite Beta-catalyzed MPV reactions is hypothesized to be due to the fact that the *cis*-transition state can be easily accommodated within the straight channels of zeolite Beta, whereas the bulkier *tr*-transition state cannot [26]. As illustrated in Fig. 3, the *cis*-4-TBCHL selectivity obtained utilizing sample B was ∼ 15% higher than that measured using sample C, with sample A resulting in the intermediate selectivity. This trend of *cis*-4-TBCHL selectivity is due to the formation of larger amounts of *cis*-4-TBCHL with the constant amount of the *tr*-4-TBCHL (Fig. 2) and the constant distribution of side products being formed. The same trend was observed when considering the relative intensity of the 3665 cm^{-1} band in these samples with sample B exhibiting the highest and sample C the lowest relative intensity (Table 2). Thus, it appears that the *cis*-4-TBCHL selectivity results correlate well with the relative intensities of the 3665 cm^{-1} band, and the trend between these quantities is shown in Fig. 4. No trend between the *cis*-selectivity and the relative (integral) intensity of the 3782 cm^{-1} band could be identified because sample B, exhibiting the intermediate relative intensity of this band (Table 2), resulted in the highest *cis*-4-TBCHL selectivity as shown in Figs. 3 and 4. Thus, the results shown in Figs. 2–4 indicate that the Al species that result in band at the 3665 cm^{-1} are most likely in control of the *cis*-4-TBCHL formation in the MPV reaction.

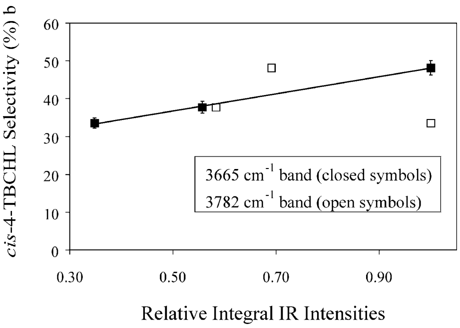

Fig. 4. Dependence of *cis*-4-TBCHL selectivity to the partially framework octahedrally coordinated species.

Previously, the 3665 cm^{-1} band was not discussed in the MPV reaction activity because of its low intensity and due to difficulties in observing any opposite trends in its relative intensity compared to the 3782 cm^{-1} band. As indicated by the constant frequency value of the IR bands at 1094 and 575 cm^{-1}, all the catalyst samples contained significant amounts of EFAl species. However, the different heat treatment procedures used did not result in change of the framework Al atoms. The constant amount of EFAl species in all three catalyst samples allows discussion of the reasons for the relative change of the intensities of 3782 and 3665 cm^{-1} bands without specific assignment of the location of the IR band responsible for the EFAl species. This is because with a constant amount of EFAl species in all the catalyst samples, any change in the relative intensities of these bands must be related to the changing amount of other (i.e., partially framework) Al species. As illustrated in Fig. 1, the IR study (after pretreatment and activation) showed that the harsh treatment in the furnace (pretreatment) lowered the relative intensity of the 3665 cm^{-1} band with a simultaneous increase in the relative intensity of the 3782 cm^{-1} band (catalyst C versus A and B). It was suggested previously that the continuing heat treatment of zeolite Beta would lead to the formation of the Al species represented by the 3782 cm^{-1}. On the other hand, if the heating were stopped at the point where the partially hydrolyzed Al species connected to the framework by three oxygen bonds are exposed in the zeolite pore, it would make them more available to other ligands like water or other reactants [7]. Thus, the formation of the Al species characterized by the 3782 cm^{-1} band was suggested to result in a decrease of Al atoms able to attain an octahedral coordination upon contact with water and still be a part of the framework (PFAl species) [6]. These suggestions are consistent with our observations, since the relative intensity of the 3665 cm^{-1} band decreased with an increase of the relative intensity of the 3782 cm^{-1} band. This further suggests that the Al species characterized by the 3665 cm^{-1} band are the species that are partially attached to the framework.

4. Conclusions

The controversies related to assignment of the type of species associated with the IR bands at 3782 and 3665 cm^{-1}, and to their nature and role in catalysis of the MPV reactions, stem from the inability to increase the intensity of one band while decreasing the intensity of the other. In this investigation, different combinations of heat-treatment procedures of zeolite Beta were utilized to increase the relative intensities of the 3782 or 3665 cm^{-1} bands, while decreasing the other intensity. The environment, heat-treatment technique, analysis/reaction temperature were carefully controlled in both the IR spectrometer and the catalytic reactor, and the catalysts were never exposed to ambient moisture or air. The *cis*-alcohol selectivity correlated with increasing relative intensity of the 3665 cm^{-1} band over the range investigated. This suggests that the species associated with the 3665 cm^{-1} band are responsible for the *cis*-alcohol selectivity. No correlation was observed for *cis*- or *tr*-alcohol selectivity and the intensity of the band at 3782 cm^{-1}. All heat-treated samples were dealuminated to the same extent as indicated by the constant value of T–O-stretching vibration frequency. This strongly suggests that the same number of EFAl species are present in all samples. Thus, the changes of the relative intensities of the two IR bands at 3782 and 3665 cm^{-1} are most likely related to Lewis acid sites still associated with the framework.

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