

Chemo- and regioselective Meerwein–Ponndorf–Verley and Oppenauer reactions catalyzed by Al-free Zr-zeolite beta

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Abstract

Al-free Zr-beta zeolite with Si/Zr up to 75 was synthesized in a fluoride medium. The incorporation of zirconium into zeolite beta induced the formation of increased amounts of polymorph B. Lewis acid sites were predominant in the Al-free Zr-beta. Zr-zeolite beta was found to be an excellent catalyst in the Meerwein–Ponndorf–Verley (MPV) reduction of several alkyl- and aryl-substituted cyclohexanones, with high selectivity to the corresponding alcohols. The catalyst was reusable and no leaching was detected under the reaction conditions. A prominent feature of the Zr-zeolite beta catalyst is its ability to maintain activity even in the presence of rather significant amounts of water, up to 9 wt%. The activity was unaffected by the presence of pyridine but was decreased by added acids. However, the poisoning effect could be easily reversed by washing. The excellent performance of Zr-zeolite beta in the MPVO reaction is due to an appropriate Lewis acidity and the ease of ligand exchange at the Zr active sites within the zeolite beta pore channels.

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1. Introduction

The Meerwein–Ponndorf–Verley (MPV) reduction provides a highly selective reduction of the C=O functional group in unsaturated carbonyl compounds using secondary alcohols as hydrogen donors [1]. The reverse Oppenauer oxidation of alcohols is carried out with oxidants such as furfural, benzophenone, and cyclohexanone. Both reactions (collectively denoted as MPVO) can be catalyzed using homogeneous catalysts such as metal alkoxides. The homogeneously catalyzed MPVO reaction has many advantages, such as chemoselectivity, mild reaction conditions, and ready adaptation both in the laboratory and on a large scale. However, the need for almost stoichiometric amounts of catalyst, the moisture sensitivity, and problems with separation limit the practical applications. Hence, heterogeneous catalysts have been developed for the reaction. These include metal

oxides, such as Al₂O₃ [2], hydrous ZrO₂ [3,4], magnesium oxide or phosphates [5,6], and grafted alkoxides or alkyl complexes [7–9].

Al-zeolite beta has been reported to be a highly active and regioselective catalyst for the reduction of 4-*tert*-butylcyclohexanone to the thermodynamically less stable *cis*-4-*tert*-butylcyclohexanol [10]. The high selectivity toward the *cis*-alcohol was explained by a restricted transition state around a Lewis-acidic aluminum atom in the straight channels of the zeolite beta pore system. Whilst the presence of water was important for the activation of the catalyst prior to reaction, moisture during the reaction severely decreased the activity of the catalyst [11]. Corma et al. [12] recently reported that Sn-zeolite beta showed excellent activity and selectivity in the MPV reduction of several ketones. In addition, the Sn-zeolite beta was found to be more resistant to the presence of water in the reaction media than Ti- or Al-zeolite beta.

Zirconium is increasingly applied as a catalyst in many reactions due to its moderate acidity and oxidizing capabilities [13]. We have found that zirconium in the form

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of hydrous zirconia and zirconium 1-propoxide grafted on supports is a good catalyst for the MPV reaction [14,15]. Besides good activity, both types of catalysts could be easily handled in the ambient environment without a need for moisture-free conditions. In the homogeneous form, zirconium 1-propoxide easily undergoes hydrolysis but after grafting on a support, the catalyst was not deactivated by the presence of water and showed good stability even after exposure to the ambient for 48 h [15]. In contrast, grafted aluminum 2-propoxide required stringent moisture-free conditions for activity and was deactivated when exposed to air. In the present paper, we report on the incorporation of zirconium into zeolite beta, combining the properties of zirconium with the shape selectivity and possibly higher acidity offered by the zeolite. In an earlier communication [16], we have reported on the successful synthesis of Al-free Zr-zeolite beta and showed that Zr-zeolite beta was an excellent catalyst for the MPV reduction of 4-*tert*-butylcyclohexanone. Here, we present the results of a thorough characterization of Al-free Zr-beta and its application to MPV reduction of a number of ketones and Oppenauer oxidation. The robustness of the catalyst is tested by poisoning experiments, ease of regeneration, and activity after successive cycles.

2. Experimental

2.1. Preparation of zeolite beta seeds

Nanocrystalline zeolite beta seeds were synthesized following the procedure described in Ref. [17]. A quantity of 0.216 g of metallic Al (Goodfellow) was dissolved in 41.23 g of tetraethylammonium hydroxide (TEAOH) (40 wt% aqueous solution), and 29.26 g of deionized water and 12 g of fumed silica were added and stirred for 2 h. The molar composition of the final gel mixture was 1.0 SiO₂:0.56 TEAOH:0.02 Al₂O₃:15 H₂O. The mixture was placed in a Teflon-lined stainless steel autoclave and kept at 140 °C for 72 h under autogeneous pressure. The product was separated by centrifugation, washed with deionized water, and dried in air at 100 °C. One gram of the as-made sample was treated with 50 ml of 6 M HNO₃ at 80 °C for 24 h to remove the aluminum. The solid was recovered by centrifugation, washed with deionized water, and dried at 100 °C. ICP analysis showed the Si/Al ratio of the resulting dealuminated zeolite beta to be higher than 500.

2.2. Synthesis of Zr-zeolite beta

Al-free Zr-zeolite beta with Si/Zr 75, 100, and 200 was synthesized in a fluoride medium. Tetraethylorthosilicate (TEOS) was hydrolyzed in an aqueous solution of 40% tetraethylammonium hydroxide (TEAOH) under stirring. A solution of ZrOCl₂ · 8H₂O in water was added and

the mixture was stirred until the ethanol formed upon hydrolysis of TEOS was evaporated. HF was added to the clear solution and a thick paste was formed. Finally, an aqueous suspension of the dealuminated zeolite beta seeds was added. The final gel composition was 1.0 SiO₂:0.02–0.005 ZrO₂:0.56 TEAOH:6–10 H₂O:0.56 HF. Crystallization was carried out in a Teflon-lined stainless steel autoclave at 140 °C for 10, 20, and 25 days for samples with Si/Zr 200, 100, and 75, respectively. The solid product obtained was filtered, washed with deionized water, dried at 100 °C and calcined at 580 °C for 4 h. The Zr-zeolites are designated Zr_n, where *n* = Si/Zr of 75, 100, and 200.

Pure silica zeolite beta (henceforth referred to as Si-beta) was prepared as above but without the addition of ZrOCl₂. The gel, of composition 1.0 SiO₂:0.56 TEAOH:7.50 H₂O:0.56 HF, was crystallized at 140 °C for 10 days. After calcination at 580 °C for 4 h, the Si-beta was added to a solution of ZrOCl₂ to give a Si/Zr ratio of 95, stirred for 4 h at room temperature, followed by the evaporation of water. The sample, Zr-beta (im), was dried at 100 °C and recalcined at 580 °C for 4 h.

2.3. Synthesis of Al-, Ti-, and Sn-zeolite beta

For the purpose of comparison, Al-zeolite beta (Si/Al 100), Ti-zeolite beta (Si/Ti 100), and Sn-zeolite beta (Si/Sn 125) were prepared in a fluoride medium following procedures reported in Refs. [12,18,19], respectively. These samples are referred to as Al100, Ti100, and Sn125 in subsequent text. A high Al-zeolite beta (Si/Al = 12.5) with extraframework aluminum was synthesized according to Wadlinger et al. [20]. The sample was ion-exchanged with 1 M aqueous ammonium nitrate at 80 °C for 24 h. The H-form of the zeolite was obtained by calcining at 500 °C for 6 h (referred to as Al-beta-500). A portion was further calcined at 700 °C for 2 h (Al-beta-700).

2.4. Characterization of the catalysts

The surface area and pore volume were determined by nitrogen adsorption (Quantachrome NOVA 2000). The crystalline phase of all samples was determined by powder X-ray diffraction. The powder patterns were recorded on a Siemens D5005 diffractometer (Cu anode operated at 40 kV and 40 mA) equipped with variable slits. The diffractograms were measured from 5 to 50° (2θ) using a step size of 0.02° and a dwell time of 1 s/step.

Infrared spectra were recorded on a Biorad Excalibur spectrometer with a resolution of 2 cm⁻¹. Typically, samples were pressed into self-supported wafers of 8–10 mg. The wafer was mounted in a Pyrex IR cell with NaCl windows and dried by evacuating under vacuum (10⁻³ mbar) for 2 h at 300 °C. After cooling to room temperature, a background spectrum was recorded. Pyridine was introduced for 15 min before the system was evacuated for an hour and the spectrum was measured at room temperature. Further

IR measurements were made after evacuation at 100 and 200 °C.

^{29}Si MAS NMR spectra of the samples were measured on a Bruker DRX-400 widebore solid state spectrometer operating at a resonance frequency of 79.46 MHz with a spinning rate of 12 kHz, a pulse length of 3 μs , and a recycling time of 20 s. Rotors with diameter 4 mm were used and the ^{29}Si chemical shifts are reported relative to TMS. The ^{13}C CP MAS NMR spectra were acquired at 100.6 MHz, with a pulse width of 5 μs , repetition time 4 s, contact time 5 ms, and a spinning rate of 8 kHz. The carbon content of the samples was evaluated using thermogravimetric analysis (Dupont 2960). About 10 mg of the sample was heated at 10 °C min^{-1} in 100 $\text{cm}^3 \text{min}^{-1}$ air flow. The elemental composition of the samples was determined by ICP-AES analysis after dissolution of the sample in HF. A JEOL JSM-5200 scanning electron microscope was used to determine size and morphology of the crystals.

XPS spectra were collected on an AXIS-His 165 Ultra (Kratos Analysis) spectrometer using an $\text{AlK}\alpha$ X-ray source (1486.71 eV, 400 W) at constant analyzer pass energy of 20.0 eV. Curve-fitting was carried out using nonlinear (Shirley-type) least-squares fitting software (XPS-PEAK 41) to separate the overlapping peaks. Due to the charging of the insulating samples, the binding-energy values were referenced to the C1s line at 284.6 eV (arising from the inadvertent carbon contamination).

2.5. Catalytic reactions

The MPV reduction was carried out in a 25 cm^3 round-bottomed flask equipped with a septum port, reflux condenser, and a guard tube. The reaction mixture containing 1.3 mmol of the ketone substrate and 5 g (83 mmol) of 2-propanol were placed in the flask and heated to 82 °C. A quantity of 100 mg of catalyst, dried at 120 °C, was added to the reaction mixture. Aliquots were removed at different reaction times and the products were analyzed by gas chromatography. An internal standard, *o*-xylene, was added for most of the reactions. When no internal standard was used, the carbon mass balance was checked and found to agree to within 2%. The identity of the products was verified by comparing the retention times and GC-MS spectra with that of authentic samples. Where no authentic samples were available, NMR analysis was performed. Besides 2-propanol, other secondary alcohols such as 2-butanol, 2-pentanol, cyclopentanol, cyclohexanol, and 4-methyl-2-pentanol were used.

The Oppenauer oxidation of 4-*tert*-butylcyclohexanol (*cis:trans* \approx 27:73) was carried out using 2-butanone as oxidant. Samples of 1.3 mmol of 4-*tert*-butylcyclohexanol and 83 mmol of 2-butanone were reacted at 82 °C in the presence of 100 mg of the dried Zr-zeolite beta catalyst.

To test the stability and activity of the catalyst upon exposure to water, different amounts of water, from 0.6 to 9.1 wt%, were added to the reaction mixture. Poisoning by

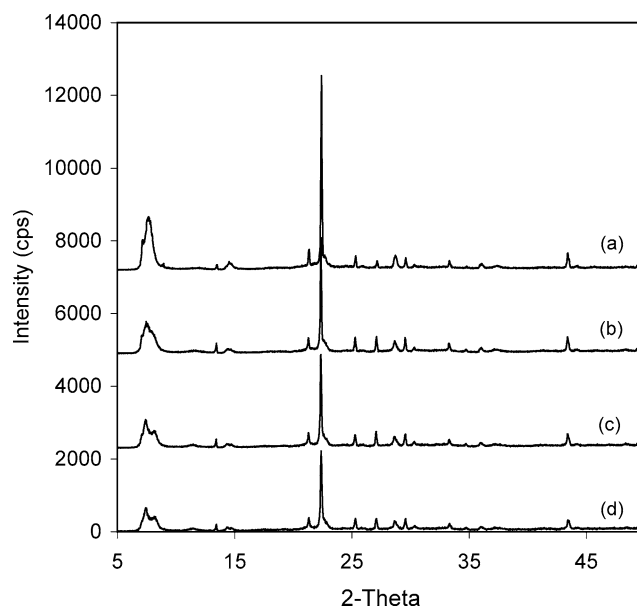


Fig. 1. XRD of (a) Si-beta, (b) Zr200, (c) Zr100, and (d) Zr75 zeolite beta.

acids and bases was investigated by adding 0.37–0.52 mmol of acetic acid, benzoic acid, or pyridine to the reaction mixture.

3. Results and discussion

3.1. Catalyst characterization

The physical properties of the catalysts used are summarized in Table 1. All the samples possess large specific surface area, > 400 m^2/g . The crystal size of the unseeded pure Si-beta was in the range of 10–15 μm , while the seeded samples were much smaller (1–2 μm). It was difficult to determine the crystal size for the Al-zeolite beta (Si/Al 12.5) synthesized according to Wadlinger et al. [20] due to aggregation of particles and the rather small crystal size.

Table 1
Physical properties of catalysts

Catalyst	Si/ metal	Surface area (m^2/g)	Crystal size (μm)	Microporous pore volume (cm^3/g)	Total pore volume (cm^3/g)
Si-beta	–	487	10–15	0.23	0.26
Zr-beta (im) ^a	95	308	10–15	0.13	0.18
Zr75	84	499	~ 1	0.24	0.27
Zr100	107	490	~ 1	0.23	0.27
Zr200	194	474	1–2	0.22	0.26
Sn125	125	500	1–2	0.23	0.31
Al100	100	451	~ 1	0.22	0.24
Ti100	100	468	~ 1	0.22	0.25
Al-beta-500 ^b	12.5	522	–	0.25	0.27
Al-beta-700 ^b	12.5	508	–	0.25	0.27

^a $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ impregnated on Si-zeolite beta.

^b Ion-exchanged with NH_4NO_3 and calcined at 500 and 700 °C, respectively.

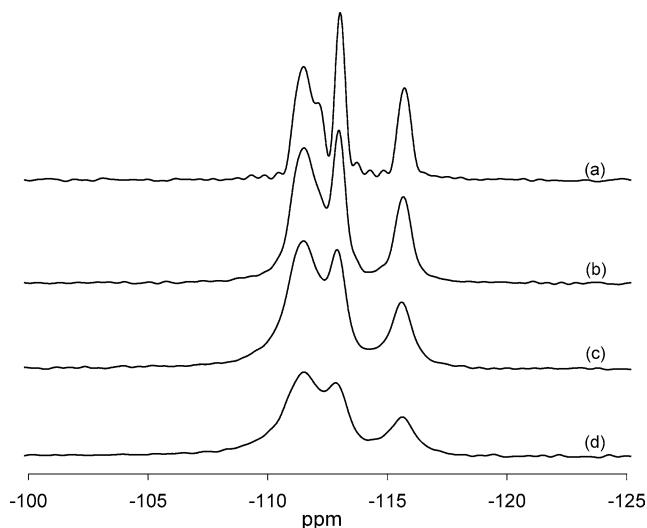


Fig. 2. ^{29}Si NMR spectra of (a) Si-beta, (b) Zr200, (c) Zr100, and (d) Zr75.

The incorporation of Zr into the silica framework was deduced from powder XRD and XPS measurements. The powder XRD patterns of the pure Si-zeolite beta and Zr-zeolite beta with Si/Zr of 75, 100, and 200 are typical for well-crystallized zeolite beta (Fig. 1). There is a loss of crystallinity with Zr substitution together with a change in the line profile at $2\theta = 7^\circ\text{--}9^\circ$. The asymmetry in this peak indicates the presence of two isostructures of zeolite beta. In the pure Si-zeolite beta, the bigger maximum at $\sim 8^\circ$ with a shoulder at $\sim 7^\circ$ indicates that the polymorph A constitutes more than 60% of the phase [21]. With increasing Zr-substitution, the change in the line profile indicates the preferential formation of polymorph B. No peaks due to ZrO_2 or any other crystalline impurity phases are seen. From the XPS measurements, the observed binding energy of $\text{Zr}3d_{5/2}$ (183 eV) is significantly higher than that of ZrO_2 (182.2 eV), but close to that of Zr in ZrSiO_4 (183.3 eV). The position of the lines is very similar to that observed for Zr in the MFI structure [22], where it had been shown that the Zr is incorporated into the framework of the zeolite structure.

^{29}Si MAS NMR spectra of the calcined pure Si- and Zr-zeolite beta (Fig. 2) show resolved signals at -111.5 , -112.3 , -113.0 , and -115.8 ppm, all in the range of Q^4 (Si with four O–Si connectivities). No Q^3 -resonance indicative of $(\text{OH})\text{Si}(\text{O}-\text{Si})_3$ or structural defects of connectivity was observed. This is further proof of the high quality of the material with very few broken connectivities in the framework. The lines broaden as the amount of Zr in the zeolite increases, which resulted in a loss of resolution. It has been reported that for pure siliceous zeolite beta synthesized in fluoride medium, only the resonance lines corresponding to Q^4 species occupying different crystallographic sites were detected in the ^{29}Si MAS NMR spectrum [18]. In comparison, zeolite beta synthesized in basic medium show two resonances, one at -110.9 ppm assigned to Q^4 and the other, assigned to Q^3 , at -101.6 ppm [23].

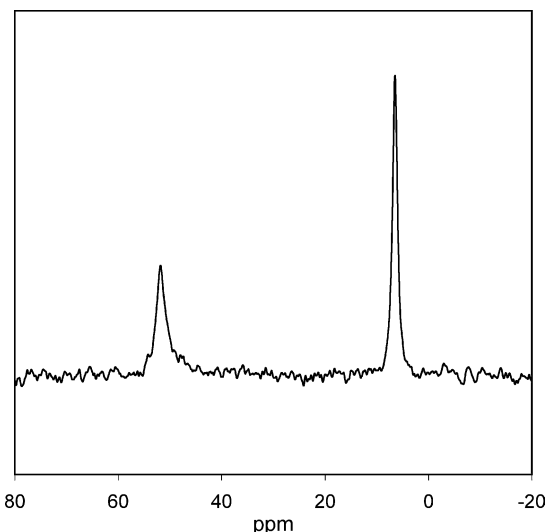


Fig. 3. ^{13}C NMR spectrum of Zr100.

Thermogravimetric analysis and ^{13}C CP MAS NMR were performed to determine the chemical state of organic materials filling the pores. The ^{13}C CP MAS NMR spectrum of the as-synthesised Zr100 is given in Fig. 3. Two peaks were observed, one at 51.9 ppm assigned to the methylene groups and the other at 6.5 ppm due to the methyl groups of the TEA cations. A comparison of the chemical shifts with those of aqueous TEAOH confirms the presence of TEA cations in the zeolite pores. The TGA curves for Zr-zeolite beta show three main weight losses occurring in the following temperature ranges: (i) $185\text{--}320^\circ\text{C}$, (ii) $320\text{--}380^\circ\text{C}$, (iii) $380\text{--}500^\circ\text{C}$ (Fig. 4). A similar decomposition pattern has been observed by zeolite beta synthesized in fluoride media [18,24]. The first two weight losses can be attributed to the degradation of TEA^+ balancing the F^- ions and the oxidation of the organic materials. The third weight loss can be assigned to TEA^+ balancing framework Zr charges. Indeed, it is found that as the Zr content increased, the weight loss at the high temperature range also increased proportionally.

The acidic properties of the metal-containing zeolites were determined by IR spectroscopy following adsorption of pyridine at room temperature and desorption at 100°C (Fig. 5). The pyridine adsorption spectra showed the presence of only Lewis acid sites on Sn- and Ti-zeolite beta. Due to the very low metal content, the IR spectra of these zeolites were very similar to that of silica. However, the band at $\sim 1442\text{ cm}^{-1}$, indicative of H-bonded and Lewis-acid bonded pyridine, was shifted to higher wavelength for Zr100 as compared to Ti- and Sn-zeolite beta. In addition to the bands at 1445 cm^{-1} and 1490 cm^{-1} (the latter is assigned to coordinately bonded pyridine and pyridinium ion), a small band at 1545 cm^{-1} indicates the presence of some Brønsted acid sites [25].

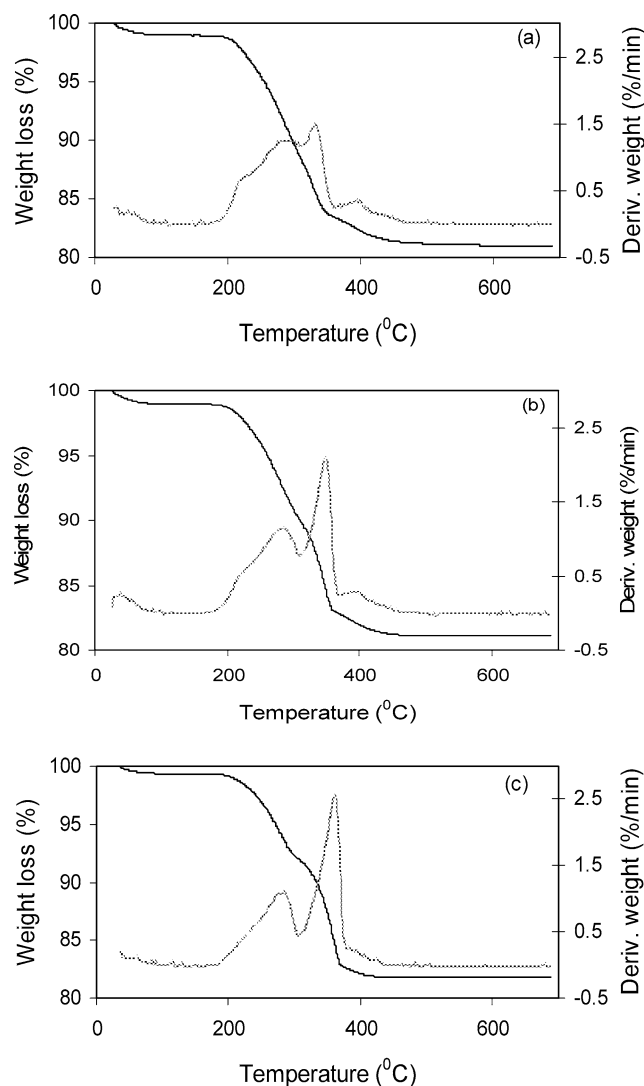


Fig. 4. TGA of (a) Zr75, (b) Zr100, and (c) Zr200.

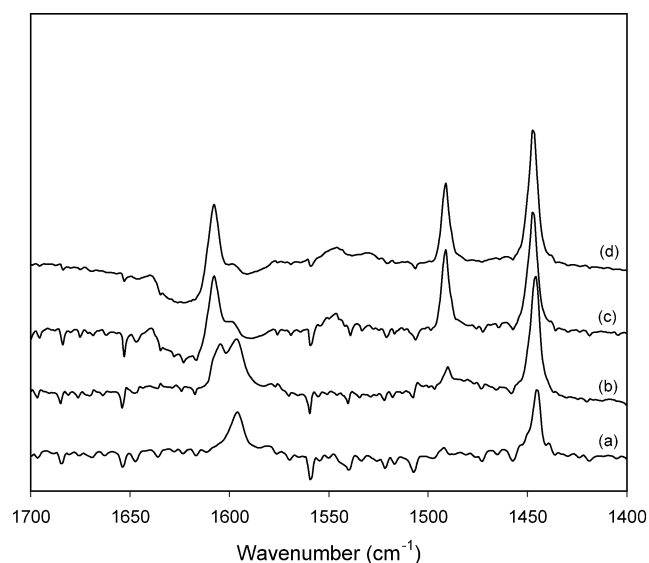


Fig. 5. IR spectra after pyridine desorption at 100 °C over (a) Sn125, (b) Ti100, (c) Zr100, and (d) Zr75.

Table 2

MPV reduction of 4-*tert*-butylcyclohexanone over various zeolite beta catalysts

Catalyst	Conversion ^a (%)	Selectivity ^b (%)	<i>cis:trans</i>
Si-beta	0	–	–
Zr-beta (im)	0	–	–
Zr75	97.3	> 99	99:1
Zr100	95.2	> 99	99:1
Zr200	72.8	> 99	98:2
Sn125	70.6	> 99	98:2
Ti100	2.9 ^c	> 99	100:0
Al100	< 0.5 ^c	–	–
Al-beta-500	16.0 ^c	98	84:16
Al-beta-700	65.4 ^c	> 99	89:11

Reaction conditions: 5.2 mmol 4-*tert*-butylcyclohexanone, 83 mmol 2-propanol, 100 mg catalyst, under reflux and stirring at 82 °C.

^a Conversion after 60 min.

^b Selectivity to the corresponding alcohol.

^c 1.3 mmol 4-*tert*-butylcyclohexanone used.

3.2. Catalytic activity

Zr-zeolite beta was highly active in the MPV reduction of 4-*tert*-butylcyclohexanone (Table 2). The only product formed was the 4-*tert*-butylcyclohexanol. After 60 min, > 95% conversion was achieved over Zr75 and Zr100. Sn-zeolite beta (Si/Sn 125) was also active with 70.6% conversion. However, both Ti-zeolite beta (Si/Ti 100) and Al-zeolite beta (Si/Al 100) were rather inactive, with conversions of 2.9% and < 0.5%, respectively. Al-zeolite beta with a higher Al content (Si/Al 12.5) was also not very active; the conversion being 16% for the 500 °C-calcined sample and 65.4% for the 700 °C sample. Of the two possible isomers for the product, the thermodynamically less favored *cis*-4-*tert*-butylcyclohexanol was formed with very high selectivity. Over Zr-zeolite beta, the *cis:trans* alcohol was 99:1, while over Al-zeolite beta, the ratio was slightly lower. The high regioselectivity of the reduction proves that the reaction proceeds in the channels of the zeolite structure, where steric constraints force the reaction to proceed via the less bulky transition state, as proposed by Creighton et al. [10] for Al-zeolite beta. The presence of the metal atom is important as Si-zeolite beta was inactive for the reaction. Impregnation of the Si-zeolite beta with zirconium oxychloride to give Si/Zr 100 did not result in an active material, indicating that isolated Zr atoms in the framework of zeolite beta are important for activity. Further support comes from a comparison of the activity of Zr-zeolite beta with that of grafted Zr propoxide/SBA-15 containing non-monomeric Zr species [15]. Despite the higher Zr loading, 10 wt%, for the grafted catalyst, only 60% conversion of 4-*tert*-butylcyclohexanone was achieved after 30 min as compared to 5 min over Zr-zeolite beta.

Corma et al. [12] demonstrated that the Sn atoms in the zeolitic framework were most likely the catalytically active sites in Sn-zeolite beta as they were able to coordinate cyclohexanone and polarize the carbonyl group. Likewise, using 4-methylcyclohexanone as probing molecule, the IR

Table 3
Activity of Zr-zeolite beta after 8 cycles of MPV reduction

Catalyst	Si/Zr		Conversion (%)	<i>cis:trans</i>
	Before	After		
Zr100	107	108	98.3	99:1
Zr100 ^a	108	110	99.0	99:1
Zr100 ^b	107	110	95.6	98.2

Reaction conditions: 1.3 mmol 4-*tert*-butylcyclohexanone, 83 mmol 2-propanol, 50 mg catalyst, under reflux and stirring at 82 °C.

^a Regenerated by calcination at 580 °C.

^b Washed with 2-propanol and reused without calcination.

spectrum of adsorbed 4-methylcyclohexanone on Zr100 revealed a strong interaction with the substrate [16]. Besides the unperturbed carbonyl vibration at 1719 cm⁻¹, a second signal appeared at 1675 cm⁻¹. Upon desorption at 200 °C, the former signal disappeared completely, whereas the latter still had substantial intensity, indicating a strong dative bond from the carbonyl oxygen to the Zr-centers in the zeolite. The shift of 45 cm⁻¹ is comparable to that reported for Sn-zeolite beta [12] and is considerably larger than that observed for Ti-zeolite beta.

3.3. Reuse of Zr-zeolite beta

The Zr-zeolite beta retained good activity over several rounds of catalytic testing (Table 3). The used catalyst was isolated from the reaction mixture by filtration and reactivated at 580 °C. The activity of the catalyst was found to be slightly improved after reactivation, which can be explained by the exposure of some active sites originally being blocked by coke. Interestingly, the catalyst could be regenerated by just thorough washing with 2-propanol. The conversion to 4-*tert*-butylcyclohexanol was still as high as 95.6% even after eight recycle runs. From the weight of the recovered catalyst after the testing, the slight drop in activity is not due to the leaching of the zirconium active sites but the loss of the catalyst during washing process. ICP analysis showed that the Si/Zr remained the same as in the original catalyst, within the experimental uncertainty. Furthermore, the filtrate obtained from refluxing Zr100 in 2-propanol was inactive. These results indicate that zirconium did not leach out during reaction.

3.4. Effect of different substrates and reducing agents

Different reducing agents were tested using the MPV reduction of 4-*tert*-butylcyclohexanone over Zr100 (Table 4). The linear alcohols were more effective than branched or cyclic alcohols. The rate of reaction was fastest using 2-propanol, followed by 2-butanol and 2-pentanol. The rate of reaction was slower with cyclopentanol and cyclohexanol. In the latter case, some cyclohexene, formed by dehydration of cyclohexanol, was detected. The lower activity achieved with bulkier alcohols such as cyclopentanol, cyclohexanol, and 4-methyl-2-pentanol may be due to hindered diffusion

Table 4
Reduction of 4-*tert*-butylcyclohexanone over Zr100 with various secondary alcohols

Alcohol	Conversion ^a (%)	Selectivity (%)	<i>cis:trans</i>
2-Propanol	98.8	> 99	99:1
2-Butanol	98.5	> 99	99:1
2-Pentanol	90.5	> 99	99:1
Cyclopentanol	27.3	98.2	99:1
Cyclohexanol	32.4	82.8	100:0
4-Methyl-2-pentanol	52.9	> 99	100:0

Reaction conditions: 1.3 mmol 4-*tert*-butylcyclohexanone, 83 mmol alcohol, 100 mg catalyst, under reflux and stirring at 82 °C.

^a After 30 min reaction.

of these alcohols in the pores of the zeolite as well as steric hindrance in the formation of the transition state between 4-*tert*-butylcyclohexanone and the alcohol.

The position of the methyl substituent in cyclohexanone has considerable influence on the rate of MPV reduction. The rate of reaction was fastest for cyclohexanone, followed by 4-methylcyclohexanone, 3-methylcyclohexanone, and 2-methylcyclohexanone. As with Sn-zeolite beta [12], Zr-zeolite beta was able to catalyze the reduction of 2-methylcyclohexanone, unlike Al-zeolite beta, where it was observed that the reaction did not proceed [10]. This may be due to the bigger size of the Zr⁴⁺ and Sn⁴⁺ ions as compared to Al³⁺, leading to greater “exposure” of the ions in oxygen framework atoms. The variation in reaction rate with position of the methyl group on the cyclohexanone ring may be explained by steric hindrance posed by the methyl group in the coordination of the carbonyl to the active site. It was expected that when cyclohexanone has a smaller substituent group such as methyl instead of *tert*-butyl, the pore constraints limiting the formation of the axially oriented transition state would be minimized. However, the results showed that 4-methylcyclohexanone is reduced almost exclusively to the *cis*-alcohol (*cis:trans* > 99:1). This has been observed for Ti-zeolite beta [24] and Sn-zeolite beta [12]. The results suggest that the solvent may participate in the intracrystalline pore channels, restricting the volume so that the more aligned *cis*-transition state is favored. The use of zeolite catalysts in the liquid phase leads to confinement of molecules in the intracrystalline volume, a subject that has been covered well by Derouane et al. [26,27].

The *cis*- and *trans*-isomers of 3-methylcyclohexanol could not be separated by gas chromatography. To ascertain if only one or both isomers were formed, ¹H NMR of the products was measured. The results show that *trans*-3-methylcyclohexanol was the major isomer, with a *cis:trans* ratio of 29:71. *Trans*-3-methylcyclohexanol, with axial hydroxyl, is more linear and can align better with the pore channels of zeolite beta than the 3-*cis* isomer. However, *cis*-3-methylcyclohexanol with both hydroxyl and methyl groups in equatorial position is the thermodynamically stable isomer. More *trans*-3-methylcyclohexanol was formed (*cis:trans* 21:79) when a bulkier alcohol such as 4-methyl-2-pentanol was used as the reductant instead of 2-propanol,

Table 5
MPV reduction of alkyl cyclohexanones with 2-propanol over Zr100 and grafted Zr propoxide/SBA-15

Substrate	Catalyst	Conversion ^a (%)	<i>cis:trans</i> ^c
Cyclohexanone	Zr100	94.5	–
	Zr(OPr)/SBA-15	59.5	–
2-Methylcyclohexanone	Zr100	6.1	55:45
	Zr(OPr)/SBA-15	3.6 ^b	42:58
3-Methylcyclohexanone	Zr100	54.4	29:71
	Zr(OPr)/SBA-15	94.1 ^b	75:25
4-Methylcyclohexanone	Zr100	81.7	99:1
	Zr(OPr)/SBA-15	98.7 ^b	19:81
4- <i>tert</i> -Butylcyclohexanone	Zr100	98.8	99:1
	Zr(OPr)/SBA-15	59.8	16:84

Reaction conditions: 1.3 mmol ketone, 83 mmol 2-propanol, 50 mg catalyst, under reflux and stirring at 82 °C.

^a After 30 min reaction time.

^b After 360 min reaction time.

^c Only product was corresponding alcohol.














again suggesting that the size of the channels in microporous materials plays a very important role in the stereoselectivity of the reaction. For 2-methylcyclohexanone, where the rate of reaction was the slowest of the substituted cyclohexanones, more of the thermodynamically stable *trans*-alcohol was formed, with a *cis:trans* ratio of 45:55.

For comparison, the MPV reduction of methylcyclohexanones was carried out over grafted Zr(1-propoxide)/SBA-15 containing 10 wt% Zr. Details of this catalyst have been reported previously [15]. The grafted Zr catalyst was less active than Zr-zeolite beta despite its higher Zr loading (Table 5). As the mean pore diameter in this catalyst is ~ 6.5 nm, the effect of pore constraints affecting the stereoselectivity of the products is expected to be small so that the thermodynamically stable isomer should be formed in each case. Indeed, the main isomer for the MPV reduction of 4-methylcyclohexanol over grafted Zr(propoxide)/SBA-15 is the thermodynamically stable *trans*-4-methylcyclohexanol with a *cis:trans* ratio of 19:81. The reduction of 3-methylcyclohexanone also led a higher proportion of the thermodynamically stable isomer, i.e., *cis*-3-methylcyclohexanol (*cis:trans* ratio of 75:25). Furthermore, in the MPV reduction of 2-methylcyclohexanone, slightly more *trans*-2-methylcyclohexanol was formed than *cis*-alcohol as compared with Zr-zeolite beta.

The regiospecificity over Zr-zeolite beta was also observed in the Oppenauer oxidation of 4-*tert*-butylcyclohexanol using 2-butanone as the oxidant. Starting with a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanol (*cis:trans* ≈ 27:73), the *cis*-isomer was almost exclusively converted to the corresponding ketone within 1 h, while the *trans*-isomer remained essentially unreacted even after 2 h (Fig. 6). This again indicates that the constrained pore space of Zr-zeolite beta hinders the formation of the transition state involving the *trans*-alcohol.

In addition to alkyl-substituted cyclohexanones, a variety of other ketones were also tested over Zr-beta with 2-propanol as reducing agent (Table 6). Cyclopentanone is

Table 6
MPV reduction of different substrates over Zr100

Entry	Substrate	Time (h)	Conversion (%)	Selectivity ^a (%)
1	 Cyclopentanone	6	92.1	> 99
2	 2-Cyclopenten-1-one	6	0	–
3	 Cyclohexanone	0.5	94.5	> 99
4	 2-Cyclohexen-1-one	6	31.2	56.5
5	 4- <i>tert</i> -Butylcyclohexanone	0.5	98.8	> 99
6	 1,4-Benzoquinone	6	90	> 99
8	 Dihydrocarvone	24	0	–
9	 Acetophenone	24	67.8	> 99
10	 Benzyl methyl ketone	24	84.1	97.6
11	 4-Chloroacetophenone	24	89.1	> 99
12	 4-Methylacetophenone	24	81.2	66.9 ^b
13	 4-Methoxyacetophenone	24	63.1	< 1 ^b
14	 Benzoylcyclohexane	24	0	–

^a Selectivity to alcohol.

^b Corresponding isopropyl ether was the main byproduct.

less easily reduced than cyclohexanone. Conjugation between the carbonyl bond and the C=C double bond in 2-cyclohexene-1-one and 2-cyclopenten-1-one makes these compounds more difficult to reduce than saturated ketones. An aryl substituent as in acetophenone slowed down the reduction compared to ketones with alkyl substituents. In benzyl methyl ketone, a CH₂ group separates the benzene ring from the carbonyl group; this substrate was more easily

reduced than acetophenone. The increased flexibility leads to a reduction of steric constraints around the carbonyl. Substituents in the aromatic ring have an effect on the conversion and selectivity of the reaction due to inductive and resonance effects. The incorporation of an electron-withdrawing group with lone pair electrons such as Cl in the benzene ring resulted in an enhanced rate of reaction compared to the unsubstituted acetophenone. The only product was the reduced alcohol, 1-(4-chlorophenyl)ethanol. Although the rate of reduction of 4-methoxyacetophenone was similar to that for acetophenone, very little of the alcohol was detected and the major product was 1-(1-isopropoxyethyl)-4-methoxy benzene, which resulted from the etherification of the formed alcohol with 2-propanol. For the electron-donating methyl substituent, the rate of reaction was enhanced over acetophenone but the selectivity to the alcohol was only 68% with the other products being due to etherification of 1-(4-methylphenyl) ethanol and 2-propanol and dehydration of the formed alcohol. The formation of ethers and dehydration products can be attributed to the more acidic nature of Zr-zeolite beta as similar products were not observed over (Zr propoxide)/SBA-15 catalyst [15].

Dihydrocarvone and benzoylcyclohexane were not reduced over Zr-zeolite beta which may be due to the rigid and bulky structure of the molecules posing steric hindrance in the formation of the transition state.

3.5. Influence of acid, base, and moisture on the catalyst activity

The activity of Zr-zeolite beta for the MPV reduction of 4-*tert*-butylcyclohexanone decreased by 30% in the presence of benzoic acid but was only slightly suppressed when pyridine was added to the reaction medium (Fig. 7). Acetic acid also decreased the activity of the catalyst. A similar effect had been observed over zirconium 1-propoxide grafted on SBA-15 where the activity decreased to one-ninth that of the fresh catalyst [15]. However, unlike the grafted catalyst, the effect of poisoning was completely reversible over Zr-zeolite beta, and full activity was recovered after washing the catalyst with 2-propanol. These results indicate that Zr-beta is very stable as neither base nor acid causes the leaching of zirconium active sites.

In addition, the Zr-zeolite beta was found to show good resistance to the presence of water (Fig. 8a) up to 9.1 wt%. Although the rate of reaction was decreased, the conversion of 4-*tert*-butylcyclohexanone was ~98% after 60 min. The turnover numbers calculated from the first 5 min of reaction showed that Zr-zeolite beta retained almost 50% of its activity in the presence of as much as 9.1% water. In contrast, Al- and Ti-zeolite beta were completely inactivated by the presence of water. The activity of Sn-zeolite beta (Si/Sn 125) was more adversely affected by the presence of water (Fig. 8b). With 9.1 wt% water in the reaction mixture, the conversion was ~10% after 60 min as compared to over 95% under moisture-free conditions. This observation

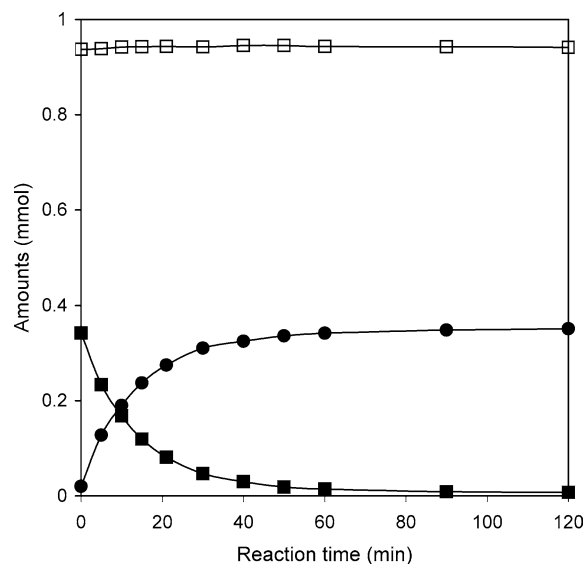


Fig. 6. Oppenauer oxidation of 4-*tert*-butylcyclohexanol with 2-butanone over Zr100: (□) *trans*-4-*tert*-butylcyclohexanol, (■) *cis*-4-*tert*-butylcyclohexanol, and (●) 4-*tert*-butylcyclohexanone.

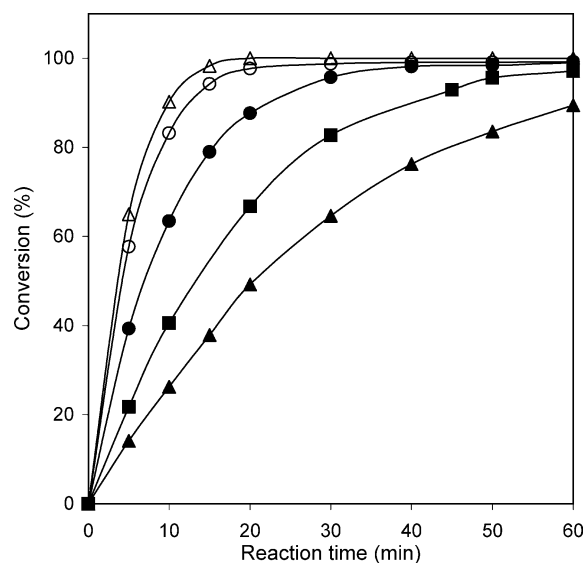


Fig. 7. Conversion of 4-*tert*-butylcyclohexanone with added base and acids: (○) pure reactants, (●) 0.37 mmol pyridine, (■) 0.52 mmol acetic acid, (▲) 0.37 mmol benzoic acid, and (△) after benzoic acid and washing with 2-propanol.

agrees with the result of Corma et al. [12] who found that the turnover number dropped from 109 to 3.8 upon exposure to about 10% water content. The authors reported that the water resistance of their Sn catalyst could be considerably improved by hydrophobizing the surface in a postsynthesis silylation step with hexamethyldisilazane. The activity of the modified material at 10% water content was 48 mol per mol h, or about 45% of the activity under dry conditions. The Zr-zeolite beta synthesized for this study retained this level of activity in the presence of water, without requiring additional surface modification.

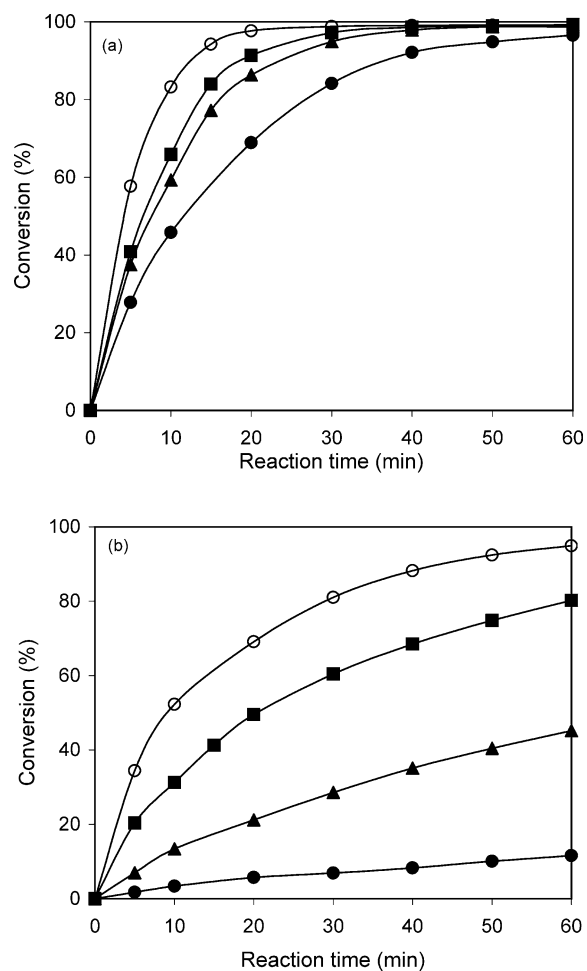


Fig. 8. Conversion of 4-*tert*-butylcyclohexanone over (a) Zr100 and (b) Sn125—(○) without water and in the presence of added water: (■) 0.6 wt%, (▲) 2.9 wt%, and (●) 9.1 wt%.

Zeolites synthesized in the fluoride medium is reported to be relatively free of connectivity defects, making it more hydrophobic [19]. Furthermore, the high water tolerance of Zr-beta may be due to the facile ligand exchange at the Zr active center within the zeolite framework. The retention of activity in the presence of water suggests that adsorbed water at the Zr centers can be exchanged for 2-propanol under reaction conditions so that the MPV activity is relatively unaffected. Water is not irreversibly adsorbed at the Lewis acidic Zr sites. Indeed, we have shown that hydroxyl groups in hydrous zirconia play an important role in its activity as an MPV catalyst [14]. In contrast, aluminum-containing catalysts such as aluminum 2-propoxide, aluminum alkoxides grafted on MCM-41, and Al-zeolite beta are generally moisture-sensitive. Even traces of water can dramatically reduce their activity. This feature limits their practical applicability. Sn-zeolite beta is water-resistant to some extent, indicating that the ligand exchange is not as facile as for Zr-zeolite beta.

4. Conclusion

Well-crystallized Al-free Zr-zeolite beta can be obtained in a fluoride medium using nanocrystalline zeolite seeds. Framework substitution of Zr in the zeolite beta structure is possible up to about 1.3% (Si/Zr 75) in a seeded synthesis in fluoride medium. The incorporation of Zr into zeolite beta resulted in an active catalyst for the MPV reduction of several ketones. The high catalytic ability of Zr-beta zeolite for the MPV reaction can be attributed to the presence of Lewis acid sites with appropriate acid strength and to the ease of ligand exchangeability of Zr. Zr-zeolite beta has predominantly Lewis acidity with higher Lewis acid strength than that of Ti- and Sn-zeolite beta. This appropriate medium Lewis acidity enables Zr-zeolite beta to bind the carbonyl group effectively. An insight into the ease of ligand exchangeability of Zr-zeolite beta may be drawn from the retention of activity with addition of acids, base or moisture. Regeneration of the catalyst after poisoning by benzoic acid can be effected by thorough washing with 2-propanol. The sample showed good tolerance to the presence of water and pyridine.

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