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Selective Meerwein–Ponndorf–Verley reduction of α, β-unsaturated aldehydes over Zr-zeolite beta

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Abstract

Zr-zeolite beta with Si/Zr ratio of 75–200, as well as zeolite beta with both Zr (Si/Zr ratio of 100) and Al (Si/Al ratios of 100 and 25), were synthesized in a seeded synthesis using HF as the mineralizer. The Al-free Zr-zeolite beta was found to catalyse the MPV reduction of α, β-unsaturated aldehydes to the corresponding alcohols with high selectivity. In the reduction of cinnamaldehyde to cinnamyl alcohol, TONs of 55–77 $\mathrm{mol\,mol_{Zr}^{-1}\,h^{-1}}$ were obtained with selectivity >98%. Zr-zeolite beta maintained good activity and selectivity in the presence of water and benzoic acid. Reuse of the catalyst by washing with 2-propanol or recalcination led to recovery of activity. For the Al-containing Zr-zeolite beta, ^{27}Al NMR spectra showed that Al was incorporated into the zeolitic framework. This is in agreement with pyridine adsorption studies in which Brønsted acidity was detected. However, the increased acidity decreased the selectivity in the MPV reduction of cinnamaldehyde as a significant amount of 1-cinnamyl 2-propyl ether was formed as a byproduct. Hence, Al-free Zr-zeolite beta is a useful chemoselective catalyst for the MPV reduction of α, β-unsaturated aldehydes.

Keywords: Zr-zeolite beta; Meerwein–Ponndorf–Verley reduction; Cinnamaldehyde; α, β-Unsaturated aldehydes; Chemoselectivity

1. Introduction

α, β-Unsaturated alcohols are of industrial interest because many are important intermediates in the production of pharmaceuticals, agrochemicals, and fragrances. They may be produced by oxidation of olefins [1] or alkylation of unsaturated aldehydes [2]. A more general route is the chemoselective reduction of unsaturated ketones and aldehydes. On a laboratory scale, stoichiometric reductions with borohydride, in combination with $CeCl_3$, or with oxazaborolidines lead to satisfactory results, but cheaper reducing agents are desirable for larger-scale reactions [3,4]. In homogeneous catalysis, a major breakthrough was the discovery of chemoselective reduction with H_2 and a Ru-phosphine-diamine catalyst [5,6]. However, this catalyst requires extra base for its activation, is not easily recovered from the reaction mixture, and may lose its activity in the recycling. To overcome these problems, the selective reduction of α, β-unsaturated aldehydes using heterogeneous catalysis has been the focus of much research.

Catalysts based on supported metals, such as osmium, iridium, ruthenium, rhodium, platinum, palladium, nickel, and cobalt, have been extensively studied for the hydrogenation of α, β-unsaturated aldehydes [7–15]. The hydrogenation of α, β-unsaturated aldehydes into saturated carbonyls is comparatively easy to achieve. However, the selective hydrogenation of the C=O group is much more difficult in the presence of a C=C bond, because the hydrogenation of the C=C bond is thermodynamically more favored (Scheme 1). To selectively hydrogenate C=O groups, different approaches to modify the intrinsic catalytic properties of metal oxide catalysts have been adopted. The addition of promoters, such as Fe(III), Sn(II), and Ge(IV), and the selection of specific supports, such as zeolites, have been found to be the most effective methods [7].

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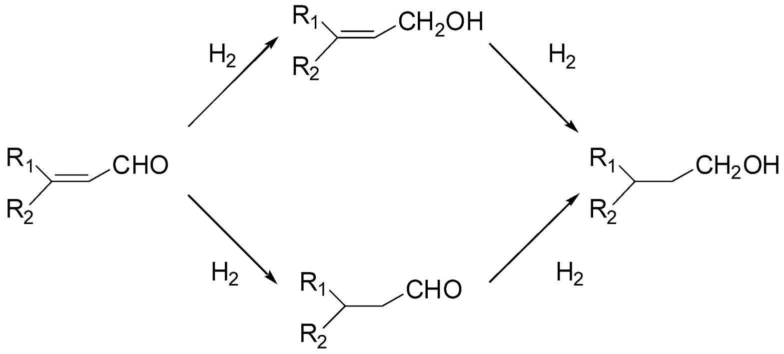


Scheme 1. Reaction pathways in the hydrogenation of α,β-unsaturated aldehydes.

An alternative way to selectively reduce α,β-unsaturated aldehydes to the corresponding unsaturated alcohols is offered by the Meerwein–Ponndorf–Verley (MPV) hydrogen-transfer reaction [16]. The reductant is usually an easily oxidizable secondary alcohol, such as 2-propanol. Only the carbonyl group is reduced; other reducible groups, such as C=C double bonds and C–halogen bonds, are not affected. This feature makes it very appropriate for the production of α,β-unsaturated alcohols. The reaction is usually catalysed by metal alkoxides. The homogeneously catalysed MPV reactions usually require stoichiometric amounts of catalyst, and there is subsequently a need to neutralize the residual catalyst in the medium with a strong acid at the end of the reaction. Furthermore, because the process takes place in a homogeneous phase, isolating the products is very often a labor-intensive and time-consuming task.

To overcome these problems, the MPV reaction has been investigated over different heterogeneous catalysts, including metal oxides [17], hydrous zirconia [18–20], hydrotalcites [21–26], zeolites [27–34], and even metal alkoxides immobilized on mesoporous materials [35–40]. Many of these catalysts have been applied in reactions of saturated ketones (e.g., substituted cyclohexanones), which are much easier to reduce than unsaturated aldehydes. Only a few heterogeneous catalysts were applied in the MPV reduction of α,β-unsaturated aldehydes. We previously reported that suitably pretreated hydrous zirconia was an active catalyst in the MPV reduction of an important α,β-unsaturated aldehyde, cinnamaldehyde [20]. The calcination temperature of the hydrous zirconia was found to be an important parameter because it affects the surface density of hydroxyl groups that are necessary for ligand exchange with the reductant, 2-propanol. Mg–Al mixed oxides could also catalyze the MPV reduction of various α,β-unsaturated aldehydes, but with only moderate activity [26].

We have found that Zr-zeolite beta is a very efficient catalyst for the reduction of alkyl- and aryl-saturated ketones [41]. Lewis acid sites resulting from the incorporation of Zr into the zeolite framework were considered the active centers of the zeolite. In the present work, we investigated the use of Zr-zeolite beta in the MPV reduction of α,β-unsaturated aldehydes. We also studied the effect of Al on the activity and selectivity of zeolite Zr-beta.

2. Experimental

2.1. *Preparation of Zr- and (Zr,Al)-zeolite beta*

The preparation of Zr-zeolite beta has been reported previously [41]. Basically, Al-free Zr-zeolite beta (Si/Zr ratio of 75–200), was prepared in a seeded synthesis using HF as the mineralizer. The samples are denoted as Zr(n), where n denotes the Si/Zr ratio. Two Al-containing Zr-beta samples, ZrAl(100) (Si/Zr ratio of 100, Si/Al ratio of 100) and ZrAl(25) (Si/Zr ratio of 100, Si/Al ratio of 25), were synthesized in an analogous way to the synthesis of Al-free Zr-beta. After hydrolyzing tetraethyl orthosilicate (TEOS) with tetraethylammonium hydroxide (TEAOH), a solution of $ZrOCl_2 \cdot 8H_2O$ (Merck, 99%) and $Al(NO_3)_3 \cdot 9H_2O$ (Merck, 99%) in water was added, and the mixture was stirred until all ethanol formed by the hydrolysis of TEOS was evaporated. HF and dealuminated zeolite beta seed crystals were added. The final gel composition was 1.0 SiO_2:0.01 ZrO_2:x Al_2O_3:0.56 TEAOH:7.5 H_2O:0.56 HF, where x was 0.005 and 0.02. The crystallization was carried out in a Teflon-lined stainless steel autoclave at 140 °C for 20 days. The solid product obtained was filtered, washed with deionized water, dried at 100 °C, and activated at 580 °C for 4 h.

2.2. *Catalyst characterization*

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 (XRD). 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 wafers were 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 the wafers were cooled to room temperature, a background spectrum was recorded. Pyridine was introduced for 15 min before the system was evacuated for 1 h; then 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 wide-bore solid-state spectrometer with 4-mm rotors, operating at a resonance frequency of 79.46 MHz with a spinning rate of 12 kHz, pulse length of 3 µs, and recycle time of 20 s. The ^{29}Si chemical shifts are reported relative to TMS. The ^{27}Al MAS NMR spectra were acquired at 104.26 MHz, with a pulse width of 1.7 µs and a recycle time of 5 s. The Al chemical shifts are referenced to aqueous $Al(NO_3)_3$. The elemental composition of the samples was determined by ICP-AES analysis after the sample was dissolved in HF. A JEOL JSM-5200 scanning electron microscope was used to determine crystal size and morphology.

2.3. Catalytic reactions

The MPV reduction was carried out in a 25-cm^3 round-bottomed flask equipped with a septum port, reflux condenser, and guard tube. The reaction mixture containing 1.3 mmol of the aldehyde substrate and 5 g (83 mmol) of 2-propanol were placed in the flask and heated to 82 °C. Then 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 those of authentic samples.

3. Results and discussions

3.1. Catalyst characterization

The chemical and textural properties of the catalysts are given in Table 1. Zirconium could be incorporated into zeolite beta down to a Si/Zr ratio of 84. The efficiency of incorporation decreased with increasing zirconium content, so that the discrepancy between expected and measured Si/Zr ratio became larger. Therefore, the Al-containing zeolite beta catalysts were synthesized at a Si/Zr ratio of 100. All the samples had surface areas in the range of 470–530 m^2/g, with those containing aluminium having the higher surface areas. Scanning electron microscopy measurements showed that these samples had a smaller crystallite size than the pure Zr-zeolite beta; this can be explained by a faster nucleation rate induced by the aluminum in the latter samples.

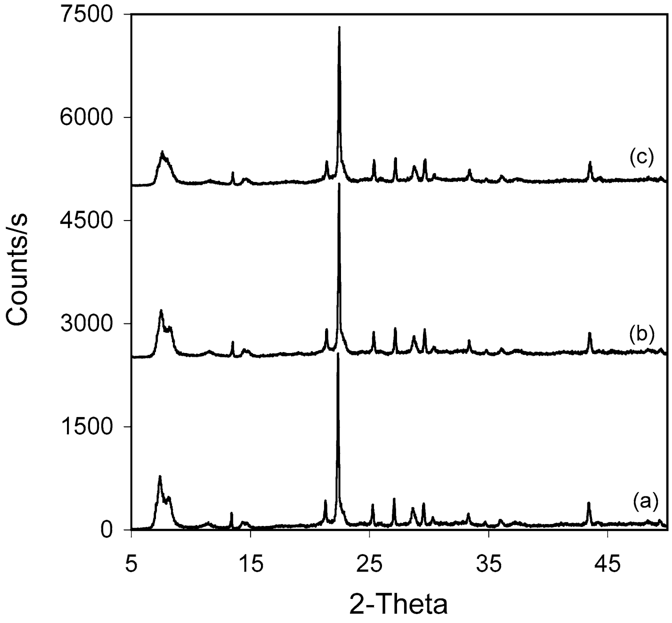


Fig. 1. XRD patterns of (a) Zr(100), (b) ZrAl(100), and (c) ZrAl(25).

The XRD patterns of Zr(100), ZrAl(100), and ZrAl(25) showed the typical features of zeolite beta with sharp and broad reflections, indicative of stacking disorders resulting from the intergrown hybrid of two distinct but closely related polymorphs, A and B (Fig. 1). In particular, the 2-theta peak at ~8° is asymmetric due to the relative proportions of the polymorphs [42]. In the Al-free sample, Zr(100), and the low Al-sample, ZrAl(100), one large peak appeared at $2\theta \approx 7.5°$ with a shoulder at $2\theta \approx 8.3°$, indicating the preferential formation of polymorph B. However, in ZrAl(25), only one broad peak was observed at $2\theta \approx 8°$. The results demonstrate that aluminum can influence the stacking sequence of Zr-zeolite beta with the formation of more polymorph A.

The acidic properties of Al-free and Al-containing Zr-zeolite beta samples were determined by IR spectroscopy after the adsorption of pyridine at room temperature and desorption at 200 °C. The appearance of the band corresponding to Lewis acid sites in the IR spectra (1450 cm^{-1}) was clearly observed for all samples (Fig. 2). With increasing aluminium content in the samples, the bands at 1545 and 1620–1640 cm^{-1} increased in intensity. These bands are due to the formation of pyridinium ions and indicate the existence of Brønsted acid sites. The absorption band at 1490 cm^{-1} has been assigned to the presence of coordinated pyridine as well as pyridine chemisorbed at pro-

Table 1
Chemical and textural properties of Zr(Al)-zeolite beta samples tested in MPV reactions

Catalyst	Si/Me ratio[a]		BET surface area (m^2/g)	Crystal size (µm)	Microporous pore volume (cm^3/g)	Total pore volume (cm^3/g)
	Si/Zr	Si/Al				
Zr(75)	84	>4000	499	~1	0.24	0.27
Zr(100)	107	>4000	490	~1	0.23	0.27
Zr(200)	194	>4000	474	1–2	0.22	0.26
ZrAl(100)	104	103	510	0.5–1	0.23	0.31
ZrAl(25)	105	27	533	0.5–1	0.21	0.24

[a] Determined by ICP.

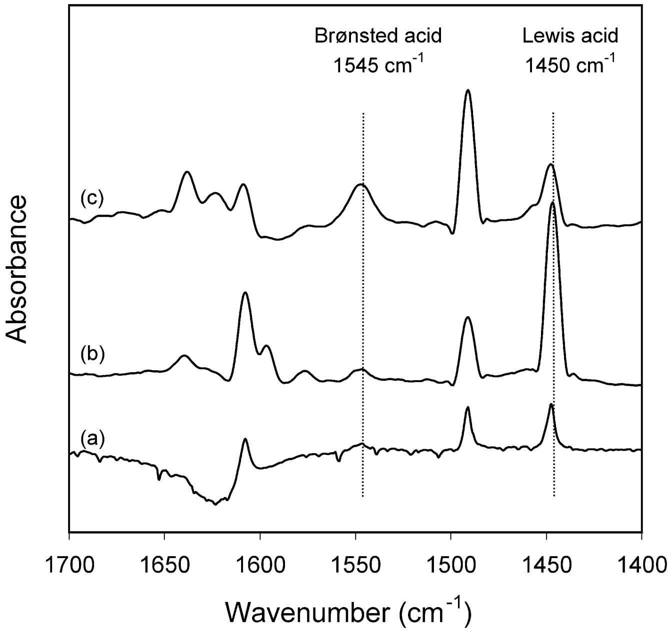


Fig. 2. IR spectra of pyridine adsorption at 25 °C and desorption at 100 °C over (a) Zr(100), (b) ZrAl(100), and (c) ZrAl(25).

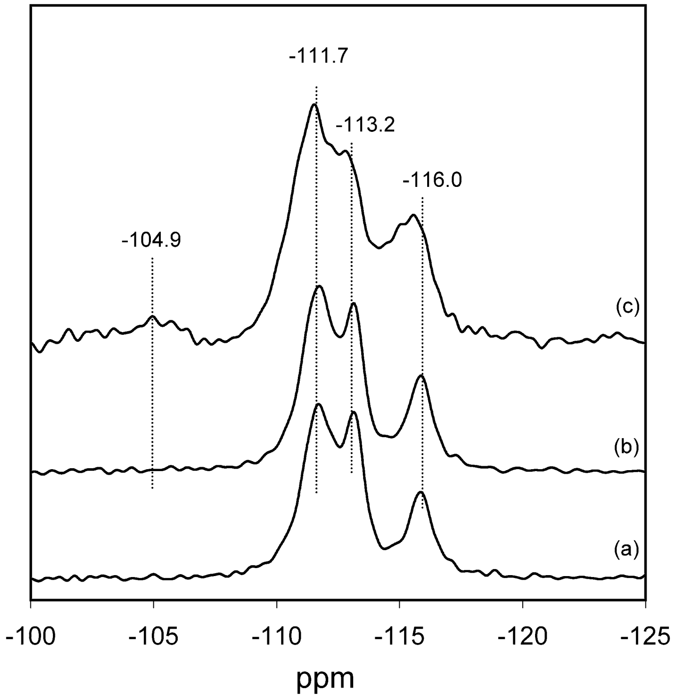


Fig. 3. ^{29}Si MAS NMR of calcined (a) Zr(100), (b) ZrAl(100), and (c) ZrAl(25).

tonic acid sites. Its intensity also increased with increasing aluminium content in the samples.

From the ^{29}Si MAS NMR spectra of calcined Zr(100), ZrAl(100), and ZrAl(25), three bands at $\delta \approx -116.0$, -113.2, and -111.7 ppm could be resolved (Fig. 3). These bands are all in the range of Q^4 and can be assigned to Si(4Si) species occupying different crystallographic sites. In addition, a very weak band at 104.9 ppm was also present in ZrAl(25), which can be due to both Si(3Si, Al) and Si(3Si, OH) species. The bands broadened as the amount of aluminium in the Zr-zeolite beta samples increased. This is similar to the observations by Camblor et al. [43] for Al-zeolite beta synthesized in the fluoride media. The observed band broadening was attributed to the presence of connectivity defects generated by dealumination during calcinations, as well as a decrease in local order due to a higher concentration of aluminium.

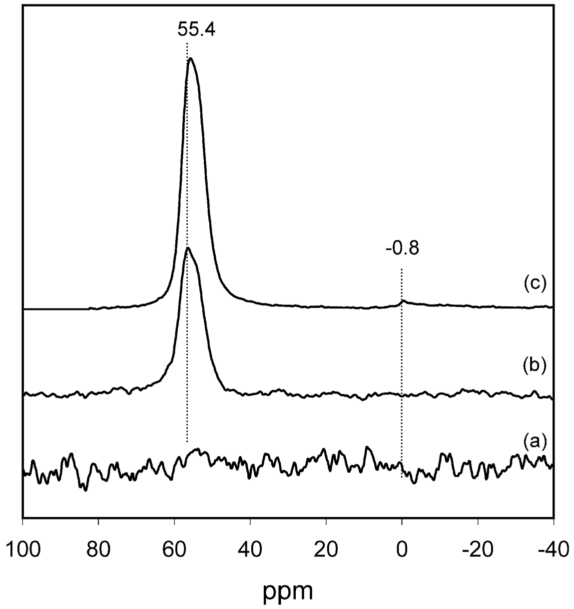


Fig. 4. ^{27}Al MAS NMR of calcined (a) Zr(100), (b) ZrAl(100), and (c) ZrAl(25).

^{27}Al MAS NMR spectra of calcined Zr(100), ZrAl(100), and ZrAl(25) are shown in Fig. 4. Not surprisingly, no signal related to aluminium could be detected in the Al-free Zr-zeolite beta sample. In the case of ZrAl(100) and ZrAl(25), a well-resolved band appeared at 55.4 ppm. This resonance band can be assigned to aluminium in the tetrahedral coordination environment that results when aluminium is incorporated into the zeolite lattice. In the ZrAl(25) sample, which has a high aluminium content, an additional weak band at -0.8 ppm was observed. This is attributed to octahedral aluminium species, possibly extra-framework aluminium that formed during calcination. However, it has also been proposed that a fraction of the aluminium can reversibly change its coordination from tetrahedral to octahedral without leaving its framework sites [44].

3.2. *MPV of cinnamaldehyde over Zr-zeolite beta*

Cinnamaldehyde (3-phenyl-2-propenal, C_9H_8O) is an α,β-unsaturated aldehyde used in the fragrance industry to give spicy and “Oriental” notes [45]. It is also an important intermediate in the synthesis of cinnamyl alcohol and dihydrocinnamyl alcohol, both of which are also used in the perfume industry. Particularly, the reduced unsaturated product, cinnamyl alcohol, is valuable in perfumery for its odor and fixative properties. Furthermore, it is a starting material for cinnamyl esters, several of which are valuable fragrance compounds. In addition, cinnamyl alcohol has applications in the formulation of animal repellant compositions, insect attractants, photosensitive poly-

Table 2
MPV reduction of cinnamaldehyde over various catalysts

Entry	Catalyst	Conversion[a] (%)	TOF[b]	Selectivity[a] (%)
1	Zr(75)	69.9	57.3	>98
2	Zr(100)	80.6	74.7	>98
3	Zr(155)	61.7	77.2	>98
4	Zr(200)	40.5	67.7	>98
5	ZrAl(100)	59.1	54.7[c]	95.0
6	ZrAl(25)	41.8	38.8[c]	64.1
7	Zr-SBA-15	20.3	2.4	100
8	Zr-beta (im)[d]	No reaction	–	–
9	Si-beta	No reaction	–	–
10	Ti(100)	No reaction	–	–
11	Sn(125)	No reaction	–	–

Reaction conditions: 1.3 mmol cinnamaldehyde, 83 mmol 2-propanol, 100 mg catalyst, under reflux and stirring at 82 °C.

[a] Conversion and selectivity after 1 h.

[b] Turnover frequency in mol $\text{mol}_{\text{Zr}}^{-1}$ h^{-1} calculated after 1 h.

[c] Al was not considered when calculating TOF.

[d] $ZrOCl_2$ impregnated on Si-beta.

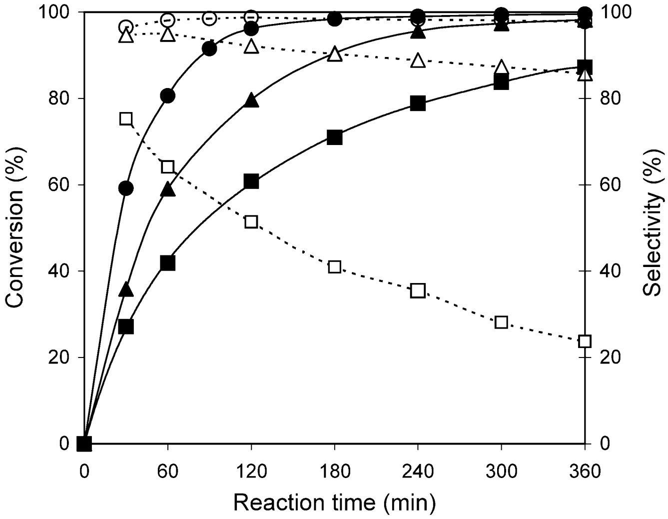
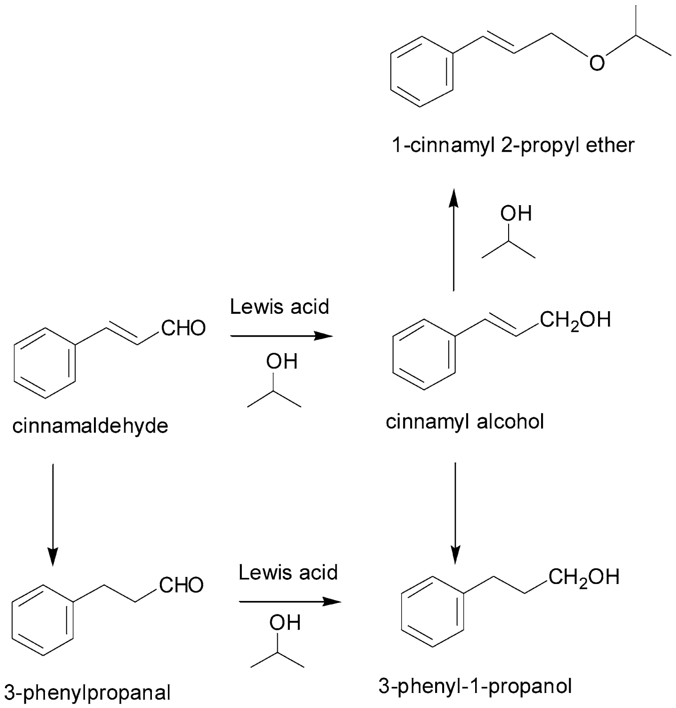


Fig. 5. MPV reduction of cinnamaldehyde over (●) Zr(100), (▲) ZrAl(100), and (■) ZrAl(25). Dashed lines and open symbols refer to selectivity. Reaction conditions: 1.3 mmol cinnamaldehyde, 83 mmol 2-propanol, 100 mg catalyst, under reflux and stirring at 82 °C.

mers, and multicolor inks. Consequently, the selective reduction of cinnamaldehyde to cinnamyl alcohol is important both academically and industrially.

Al-free Zr-zeolite beta is a very selective catalyst for the MPV reduction of cinnamaldehyde (Table 2). The selectivity to the desired cinnamyl alcohol was >98% and remained high throughout the reaction (Fig. 5). The only byproduct detected was 1-cinnamyl 2-propyl ether. The rate of conversion of cinnamaldehyde was also very high and was found to be related to the Si/Zr ratio. Zr(100) exhibited the best activity, with nearly all cinnamaldehyde reduced to cinnamyl alcohol after 4 h of reaction. Zr(75) had the lowest turnover frequency (TOF) of all of the Al-free Zr-zeolite beta samples. This observation indicates that zirconium in zeolite beta is not equally efficient. At low loading, zirconium is incorporated in the zeolite framework; as the zirconium loading increases, extra framework zirconium species may be formed. The extra-framework zirconium species are less active than the framework zirconium species, leading to the observed lower TOF over Zr(75). A similar observation was reported by Renz et al. in their studies of Baeyer–Villiger oxidation over zeolite Sn-beta [46].

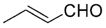
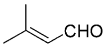
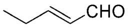
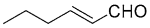
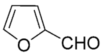
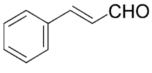
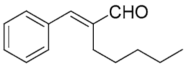
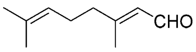


Scheme 2. MPV reduction of cinnamaldehyde over Zr(Al)-beta leading to cinnamyl alcohol and other side products.

The conversion and selectivity in the MPV reduction of cinnamaldehyde were greatly influenced by the presence of aluminium in Zr-zeolite beta (entries 5 and 6 in Table 2). After 1 h, the conversion was only 59% over ZrAl(100) and 42% over ZrAl(25), compared with 80% over Zr(100). The selectivity to the desired product, cinnamyl alcohol, was only 64% over ZrAl(25) and decreased further to <25% after 6 h (Fig. 5). Besides the main byproduct, 1-cinnamyl 2-propyl ether, two hydrogenated saturated products, 3-phenylpropanal and 3-phenyl-1-propanol, were also detected. No aldol condensation products were observed in any of the experiments, probably due to the high excess of 2-propanol used in the reaction mixture.

The formation of the byproduct 1-cinnamyl 2-propyl ether can be explained by a Brønsted-catalysed etherification of the formed cinnamyl alcohol with 2-propanol (Scheme 2). Whereas Zr-zeolite beta contains predominantly Lewis acid sites, substituting Zr^{4+} for Si^{4+} in the silica framework can result in Brønsted acidity at the bridging oxygen due to differences in the charge density of the two ions. The presence of Brønsted acid sites was detected by pyridine IR studies. Brønsted acidic sites have also been detected after the substitution of zirconium into silica MCM-41 [47]. Where a large numbers of Brønsted acid sites are present, another route to the formation of ethers is through the formation of hemiacetals followed by dehydration. This process has been observed during the MPV reduction of a number of substituted cyclohexanones over H-MCM-22 [48].

Table 3
MPV reduction of various α,β-unsaturated aldehydes over Zr(100)

Entry	Substrate	Time (h)	Conversion (%)	Selectivity (%)	TOF[a]
1	 crotonaldehyde	6	95.2	100	44.4
2	 3-methylcrotonaldehyde	6	87.7	93.7	29.0
	 *trans*-2-pentenal				
4	 *trans*-2-hexenal	6	97.4	100	53.8
5	 2-furfural	1	96.3	93.4	89.2
6	 cinnamaldehyde	3	98.4	>98	74.7
7	 α-pentylcinnamaldehyde	24	33.2	>98	2.6
8	 citral(E/Z)	6	92.8	72.4	53.2

Reaction conditions: 1.3 mmol substrate, 83 mmol 2-propanol, 100 mg Zr(100), under reflux and stirring at 82 °C.

[a] Turnover frequency in $\text{mol}\,\text{mol}_{\text{Zr}}^{-1}\,\text{h}^{-1}$ calculated after 1 h reaction.

The Brønsted acid-catalysed reaction competes with the Lewis acid-catalysed MPV reduction, resulting in low selectivity to alcohols; however, no ether formation was observed in the MPV reduction of substrates other than cinnamldehyde. We have also observed the formation of 1-cinnamyl 2-propyl ether when zirconium hydroxide was used as a catalyst; the selectivity to this byproduct was 7.8% at close to 100% conversion [20]. It is postulated that cinnamyl alcohol is susceptible to etherification with the excess 2-propanol. The presence of conjugated double bonds coupled to the benzene ring stabilizes the carbocation formed by the abstraction of the OH group over a Brønsted acid site. Hence, the increased aluminium content in ZrAl(100) and ZrAl(25) results in more Brønsted acid sites and, consequently, a lower selectivity in the MPV reduction of cinnamaldehyde.

The presence of the metal atom is essential for the reaction; no reaction was observed over pure Si-beta. Impregnation of the Si-beta with zirconium oxychloride to give a Si/Zr ratio of 100 also did not result in an active material, indicating that isolated zirconium atoms in the framework of zeolite beta are important for activity. A zirconium 1-propoxide-grafted Zr-SBA-15 sample with about 10 wt% Zr was also active for the MPV reduction of cinnamaldehyde. This catalyst exhibited good selectivity and moderate activity. Its selectivity to cinnamyl alcohol was close to 100%, but the TOF of 2.4 $\text{mol}\,\text{mol}_{\text{Zr}}^{-1}\,\text{h}^{-1}$ was considerably smaller than that for Zr-zeolite beta. This suggests that the supported zirconium is not as efficient in Zr-SBA-15 as it is in Zr-zeolite beta.

Ti-zeolite beta (Si/Ti ratio of 100) and Sn-zeolite beta (Si/Sn ratio of 125), prepared similarly to Zr-zeolite beta by fluoride-assisted synthesis, were totally inactive for the MPV reduction of cinnamaldehyde. Even after 6 h, no cinnamyl alcohol could be detected. This is surprising, because these two catalysts were active for the MPV reduction of 4-*tert*-butylcyclohexanone [31,33]. The poor performance of these catalysts may be caused by two factors: (1) too-weak Lewis acidity of Ti-beta and Sn-beta and (2) the not-easily reduced conjugated carbonyl group in cinnamaldehyde.

3.3. Selective reduction of other α,β-unsaturated aldehydes

Besides cinnamaldehyde, various other α,β-unsaturated aldehydes were also tested over Zr-zeolite beta with 2-propanol as the reducing agent. Typical results are summarized in Table 3. Linear substrates, such as crotonaldehyde, *trans*-2-hexenal, and *trans*-2-pentenal, could be easily reduced to the corresponding α,β-unsaturated alcohol with high conversion and selectivity. The rate of reaction was somewhat slower with branched substrates, however, such as 3-methylcrotonaldehyde and citral (entries 2 and 8). 2-Furfural had the highest TOF of all of the substrates tested; however, its selectivity to the alcohol, 93%, was slightly low. The relatively small molecule size and electronic effect derived from the oxygen atom in the cyclic ring could contribute to its higher activity. The drop in selectivity is due to the formation of a condensation by-product, 1,2-di(furan-2-yl)-2-hydroxyethanone. Cinnamaldehyde reacted much faster than α-pentylcinnamaldehyde. Considering the larger molecular size of α-pentylcinnamaldehyde, its slower rate of reaction is probably due to the steric hindrance

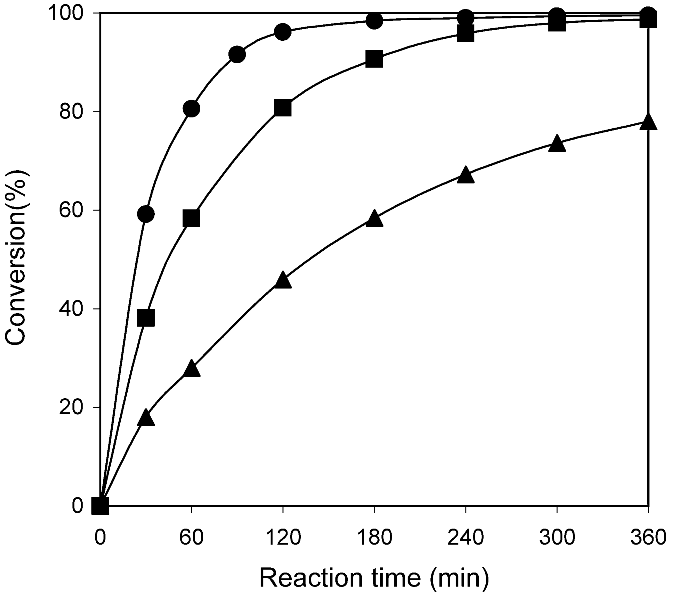


Fig. 6. Influence of water on the MPV reduction of cinnamaldehyde over Zr(100): (●) without water, (■) 0.6 wt% water, (▲) 3.0 wt% water. Reaction conditions: 1.3 mmol cinnamaldehyde, 83 mmol 2-propanol, 100 mg Zr(100), under reflux and stirring at 82 °C.

effect. Indeed, when a zirconium 1-propoxide-grafted Zr-SBA-15 (which has large pores) was used as catalyst, up to 80% conversion after 24 h was achieved for α-pentylcinnamaldehyde, justifying the foregoing hypothesis. Most importantly, except for citral, for which dehydration of the formed alcohols led to lower selectivity, all other substrates tested could be reduced with high selectivity to the unsaturated alcohol. The corresponding saturated products were not detected. All of these results indicate that Zr-zeolite beta is an effective and chemoselective catalyst for the MPV reduction of α,β-unsaturated aldehydes.

3.4. Poisoning test and catalyst stability

Aluminium-containing MPV catalysts, such as aluminium 2-propoxide, metal alkoxide-grafted MCM-41, and H-beta, are generally moisture-sensitive; even trace amounts of water can dramatically decrease their activity. This limits their practical applications to some extent. Zeolites synthesized in fluoride medium are reportedly relatively free of connectivity defects and hence are more hydrophobic [43,49]. Some claim that hydrophobic zeolites containing Lewis acids are more suitable for the MPVO reaction when water is present [33]. Previously, we showed that Zr-zeolite beta is a highly water-resistant MPV catalyst in the reduction of 4-*tert*-butylcyclohexanone [41]. Similarly, we investigated the influence of water on the MPV reduction of cinnamaldehyde by adding different amounts of water to the reaction mixture. The activity of Zr-zeolite beta was only slightly influenced in the presence of 0.6 wt% of water, and nearly all cinnamaldehyde was converted after 6 h of reaction time (Fig. 6). However, the activity dropped significantly in the presence of 3.0 wt% water; the conversion of cinnamaldehyde was <80% even after 6 h of reaction time.

Table 4
Influence of water, base, and acid on the catalytic activity of Zr(100) in the MPV reduction of cinnamaldehyde

	Conversion[a] (%)	TOF[b]	Selectivity[a] (%)
No addition	80.6	74.7	>98
Water (0.6 wt%)	63.3	58.6	>98
Water (3.0 wt%)	25.6	23.7	>98
Pyridine (0.37 mmol)	28.0	25.9	>98
Benzoic acid (0.37 mmol)	58.4	54.1	>98

Reaction conditions: 1.3 mmol cinnamaldehyde, 83 mmol 2-propanol, 100 mg Zr(100), under reflux and stirring at 82 °C.
[a] Conversion and selectivity after 1 h.
[b] Turnover frequency in mol $\text{mol}_{\text{Zr}}^{-1}\,\text{h}^{-1}$ calculated after 1 h.

The activity of Zr-zeolite beta for the MPV reduction of cinnamaldehyde decreased significantly in the presence of pyridine but was only slightly suppressed when benzoic acid was added to the reaction medium (Table 4). The reduced activity can be explained by the adsorption of pyridine at the Lewis acid sites. However, unlike the total loss in activity observed over Al- and Ti-zeolite beta [50], the interaction between Zr-zeolite beta and pyridine is less strong, so that some of the coordinated pyridine could be displaced by 2-propanol. Therefore, the activity of Zr-zeolite beta is only partially suppressed by pyridine. In the case of benzoic acid, the activity of Zr-zeolite beta was only slightly affected. The poisoning effect appears to be substrate-specific; we had previously observed that for the MPV reduction of 4-*tert*-butylcyclohexanone, the activity of Zr-zeolite beta was significantly decreased in the presence of benzoic acid but only slightly affected by pyridine. These results suggest that the high resistance of Zr-zeolite beta to acid poisoning in the MPV reduction of cinnamaldehyde may be due to the α,β-unsaturated nature of the molecule where the presence of conjugated double bonds coupled to the benzene ring facilitates the coordination of the carbonyl group to Lewis acid centers. Therefore, competitive binding is less affected by the presence of benzoic acid compared with that of 4-*tert*-butylcyclohexanone. The effects of poisoning could be reversed by washing the catalyst with 2-propanol. In conclusion, the activity of Zr-zeolite beta for the MPV reduction of cinnamaldehyde is not severely affected by the poisoning of water, base, and acid.

3.5. Catalyst deactivation and recycling

One advantage of heterogeneous catalysts over homogeneous catalysts is their potential reusability. To check whether Zr-zeolite beta could be reused, Zr(100) was recovered and used for five consecutive MPV reductions of cinnamaldehyde (Fig. 7). After each run, the catalyst was filtered and washed with 2-propanol, then submitted to a new reaction batch. Some loss in activity occurred during the reaction, and the conversion was lowered to 75% after five cycles; however, the selectivity was still as high as 95%. The loss of activity could be due to the adsorption of cinnamaldehyde or cinnamyl alcohol on the catalyst after the reaction. Indeed, the originally white catalyst became a little yellow after the reaction, indicative of some ad-

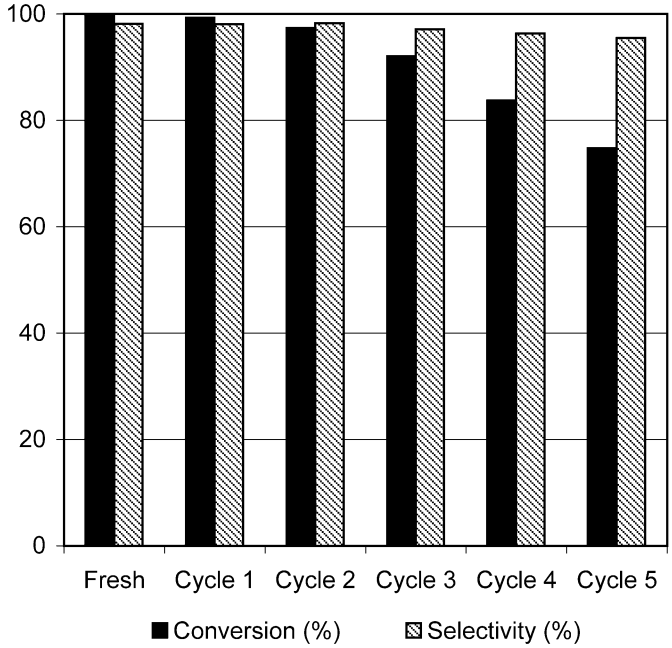


Fig. 7. Recycling tests of Zr(100) in the MPV reduction of cinnamaldehyde. Reaction conditions: 1.3 mmol cinnamaldehyde, 83 mmol 2-propanol, 100 mg Zr(100), under reflux and stirring at 82 °C. Reused catalyst was simply recovered by washing with 2-propanol.

sorbate on it. After five cycles, the used catalyst was recalcined, and this treatment almost restored the initial activity. In a subsequent run, the catalyst again had about 90% of its initial activity. These results indicate that Zr-zeolite beta is very stable and can be reused.

4. Conclusion

Zr-zeolite beta was found to be an active and chemoselective catalyst for the MPV reduction of cinnamaldehyde. A high initial TOF of 50–80 $\text{mol}\,\text{mol}_{\text{Zr}}^{-1}\,\text{h}^{-1}$ was obtained over Al-free Zr-zeolite beta samples. The selectivity to cinnamyl alcohol was $>98\%$ throughout the reaction. In contrast, Al-containing Zr-zeolite beta samples were less active and selective than Zr-zeolite beta in the MPV reduction of cinnamaldehyde. The presence of Brønsted acid sites in the Al-containing samples catalysed the formation of 1-cinnamyl 2-propyl ether from cinnamyl alcohol and 2-propanol.

Besides cinnamaldehyde, various other α,β-unsaturated aldehydes can be effectively reduced to allylic alcohols over Zr-zeolite beta through the MPV reaction. Excellent conversions were always paired with high selectivities. The activity of Zr-zeolite beta was only slightly affected by adding water and benzoic acid to the reaction medium, but pyridine led to more severe deactivation; however, this deactivation could be reversed by removing the poison. The catalyst could be reused by mere washing with solvent or by recalcination. Therefore, Zr-zeolite beta is a promising heterogeneous catalyst for selective reduction of α,β-unsaturated aldehydes.

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References

[1] W. Adam, M. Prein, Acc. Chem. Res. 29 (1996) 275.
[2] M.J. Viaplana, P. Molina, A. Arques, C. Andres, R. Pedrosa, Tetrahedron: Asymmetry 13 (2002) 5.
[3] J.-L. Luche, L. Rodriguza-Hahn, P. Crabbé, Chem. Commun. (1978) 601.
[4] E.J. Corey, C.J. Helal, Angew. Chem. Int. Ed. Engl. 37 (1998) 1986.
[5] T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 120 (1998) 13529.
[6] T. Ohkuma, H. Takeno, Y. Honda, R. Noyori, Adv. Synth. Catal. 102 (1986) 190.
[7] P. Gallezot, D. Richard, Catal. Rev.-Sci. Eng. 40 (1, 2) (1998) 81.
[8] M. Arai, H. Takahashi, M. Shirai, Y. Nishiyama, T. Ebina, Appl. Catal. A 176 (1999) 229.
[9] A.A. Wismeijer, A.P.G. Kieboom, H. van Bekkum, Appl. Catal. A 25 (1986) 181.
[10] U.K. Singh, M.A. Vannice, J. Catal. 191 (2000) 165.
[11] M. Shirai, T. Tanaka, M. Arai, J. Mol. Catal. A 168 (2001) 99.
[12] C. Ando, H. Kurokawa, H. Miura, Appl. Catal. A 185 (1999) L181.
[13] F. Salman, C. Park, R.T.K. Baker, Catal. Today 53 (1999) 385.
[14] F. Coloma, J. Llorca, N. Homs, P.R. de la Piscina, F. Rodríguez-Reinoso, A. Sepúlveda-Escribano, Phys. Chem. Chem. Phys. 2 (2000) 3063.
[15] B. Bachiller-Baeza, I. Rodríguez-Ramos, A. Guerrero-Ruiz, Appl. Catal. A 205 (2001) 227.
[16] C.F. de Graauw, J.A. Peters, H. van Bekkum, J. Huskens, Synthesis 10 (1994) 1007.
[17] V.A. Ivanov, J. Bachelier, F. Audry, J.C. Lavalley, J. Mol. Catal. 91 (1994) 45.
[18] M. Shibagaki, K. Takahashi, J. Matsushita, Bull. Chem. Soc. Jpn. 61 (1988) 3283.
[19] H. Kuno, M. Shibagaki, K. Takahashi, H. Matsushita, US Patent 5 210317 (1993), to Japan Tobacco Inc.
[20] S.H. Liu, S. Jaenicke, G.K. Chuah, J. Catal. 206 (2002) 321.
[21] P.S. Kumbhar, J. Sanchez-Valente, J. Lopez, F. Figueras, Chem. Commun. (1998) 535.
[22] T.M. Jyothi, T. Raja, M.B. Talawar, K. Sreekumar, R. Rajagopal, B.S. Rao, Bull. Chem. Soc. Jpn. 73 (2000) 1425.
[23] T.M. Jyothi, T. Raja, K. Sreekumar, M.B. Talawar, B.S. Rao, J. Mol. Catal. A 157 (2000) 193.
[24] T.M. Jyothi, T. Raja, B.S. Rao, J. Mol. Catal. A 168 (2001) 187.
[25] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F. Urbano, Appl. Catal. A 206 (2001) 95.
[26] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F. Urbano, Appl. Catal. A 249 (2003) 1.
[27] J. Shabtai, R. Lazar, E. Biron, J. Mol. Catal. 27 (1984) 25.
[28] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, Chem. Commun. (1995) 1859.
[29] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, J. Mol. Catal. 115 (1997) 457.
[30] J.C. van der Waal, K. Tan, H. van Bekkum, Catal. Lett. 41 (1996) 63.
[31] J.C. van der Waal, P.J. Kunkeler, K. Tan, H. van Bekkum, J. Catal. 173 (1998) 74.
[32] A. Corma, M.E. Domine, L. Nemeth, S. Valencia, J. Am. Chem. Soc. 124 (2002) 3194.
[33] A. Corma, M.E. Domine, S. Valencia, J. Catal. 215 (2003) 294.
[34] Y.Z. Zhu, G.K. Chuah, S. Jaenicke, Chem. Commun. (2003) 2734.
[35] R. Anwander, C. Palm, G. Gerstberger, O. Groeger, G. Engelhardt, Chem. Commun. (1998) 1811.

[36] P. Leyrit, C. McGill, F. Quignard, A. Choplin, J. Mol. Catal. A 112 (1996) 395.

[37] K. Inada, M. Shibagaki, Y. Nakanishi, H. Matsushita, Chem. Lett. (1993) 1795.

[38] F. Quignard, O. Graziani, A. Choplin, Appl. Catal. A 182 (1999) 29.

[39] Y.Z. Zhu, S. Jaenicke, G.K. Chuah, J. Catal. 218 (2003) 396.

[40] M.D. Bruyn, M. Limbourg, J. Denayer, G.V. Baron, V. Parvulescu, P.J. Grobet, D.E. De Vos, P.A. Jacobs, Appl. Catal. A 254 (2003) 189.

[41] Y.Z. Zhu, G.K. Chuah, S. Jaenicke, J. Catal. 227 (2004) 1.

[42] J.M. Newsam, M.M.J. Treacy, W.T. Koetsier, C.B. de Gruyter, Proc. R. Soc. London, Ser. A 420 (1988) 375.

[43] M.A. Camblor, A. Corma, S. Valencia, J. Mater. Chem. 8 (1998) 2137.

[44] E. Bourgeat-Lami, P. Massiani, F. Di Renzo, P. Espiau, F. Fajula, Appl. Catal. A 72 (1991) 139.

[45] K. Bauer, L. Garbe, in: W. Gerhertz (Ed.), Ullmann's Encyclopedia of Industrial Chemistry, vol. A11, VCH, Weinheim, 1988, p. 185.

[46] M. Renz, T. Blasco, A. Corma, V. Fornés, R. Jensen, L. Nemeth, Chem. Eur. J. 8 (2002) 4708.

[47] X.X. Wang, F. Lefebvre, J. Patarin, J.-M. Basset, Microporous Mesoporous Mater. 42 (2001) 269.

[48] M.J. Verhoef, E.J. Creyghton, J.A. Peters, H. van Bekkum, Chem. Commun. (1997) 1989.

[49] M.A. Camblor, A. Corma, S. Valencia, Chem. Commun. (1996) 2365.

[50] J.C. van der Waal, E.J. Creyghton, P.J. Kunkeler, K. Tan, H. van Bekkum, Top. Catal. 4 (1997) 261.