Al-free Zr-zeolite beta as a regioselective catalyst in the Meerwein–Ponndorf–Verley reaction†

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Al-free Zr-zeolite beta catalyzes the transfer reduction of ketones to the corresponding alcohols in high yield and with exceptional stereocontrol. Notably, the catalyst is very robust and gives good results even with 10% water content in the reaction mixture.

The Meerwein–Ponndorf–Verley (MPV) transfer reduction of ketones with simple secondary alcohols such as 2-propanol or 2-butanol allows for the chemoselective reduction of the keto functionality even in the presence of other unsaturated bonds. Because of the mild reaction conditions it is widely used in the synthesis of natural products, and finds industrial applications particularly in the chemical manufacture of flavor agents. The reaction has been known since 1925, and in the classical form, uses $Al(O-iPr)_3$ in almost stoichiometric amounts as the catalyst.[1] Recently, several attempts have been made to conduct the MPV reduction in a truly catalytic way,[2–4] and to find heterogeneous catalysts for the reaction.[5–11] The catalytic activity of zirconium compounds for this reaction was first described by Ooi *et al.*[2] Choplin and collaborators[5] immobilized zirconium 2-propoxide on a silica support and found that the grafted material had much increased activity for the MPV reduction. Anwander *et al.*[7] also reported high activity for a grafted Al-catalyst, but this catalyst was very moisture sensitive. Other recent breakthroughs were the use of layered magnesia-alumina oxides,[8] SBA-supported zirconium 1-propoxide,[9] hydrous zirconia,[10] and Al-free Sn-zeolite beta.[11] While the Mg-Al-oxide catalyst required careful exclusion of moisture for good catalytic activity, the Sn-BEA catalyst was reported to have high activity in the presence of some water if its surface was hydrophobized in a post-synthesis silylation step.

Zirconium is increasingly used in catalysis due to its moderate acidity and oxidising properties.[12] The incorporation of zirconium into zeolite beta allows these properties to be manifested in a shape selective catalyst. The synthesis of Zr-zeolite beta is difficult in a conventional basic medium and requires the presence of Al. We want to report here the preparation of aluminium-free Zr-zeolite beta catalysts (Zr75, Zr100 and Zr200) that have superior performance for the stereoselective MPV reduction of 4-*tert*-butylcylclohexanone. The catalyst was prepared in a fluoride-assisted hydrothermal synthesis with the addition of seeds from dealuminated zeolite beta, similar to the procedure described by Corma *et al.*[11] for the preparation of Al-free Sn-beta. Typically, tetraethyl orthosilicate (TEOS) was hydrolyzed in a solution of tetraethylammonium hydroxide (TEAOH) under stirring. A solution of $ZrOCl_2 \cdot 8H_2O$ in water was added, and the mixture was stirred until the ethanol formed during the hydrolysis of TEOS was evaporated. HF and an aqueous suspension of seeds of dealuminated nanocrystalline zeolite beta (*ca.* 50 nm as determined by TEM) was added. The final gel had the composition $1\ SiO_2 : 0.005–0.02\ ZrO_2 : 0.56\ TEAOH : 0.56\ HF : 7.5\ H_2O$. Crystallization was carried out in a static Teflon-lined stainless steel autoclave at 140 – 170 °C for 5–30 days. It was necessary to substantially increase the crystallization time

with increasing Zr-content. Higher zirconium content than 1.3 mol% leads to incompletely crystallized material even after 30 days of hydrothermal treatment.

The powder XRD spectra of the unsubstituted Si-beta and Zr-beta with Si/Zr of 75, 100, and 200 are typical for well crystallized zeolite beta. A pronounced asymmetry in the broad peak at $2\theta \sim 8°$ indicates the presence of the two iso-structures of zeolite beta. In the Zr-free material, the bigger peak at $\sim 8°$ relative to the shoulder at $7°$ indicates that the polymorph A is present at more than 60%. The change in line profile with increasing Zr-substitution may be interpreted as a Zr-induced preference for the stacking sequence of polymorph B.

X-ray photoelectron spectroscopy (XPS) was used to obtain information on the oxidation state and the co-ordination of the Zr in the framework. The observed binding energy of 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,[13] where it had been shown that the Zr is incorporated into the framework of the zeolite structure. In our study, the Zr $3d_{3/2}$ and $3d_{5/2}$ peaks are better resolved, and the full width at half maximum of the peaks is narrower (1.6 eV), indicating less spread in the nature of the chemical environment around the Zr^{4+} ions.

The ^{29}Si MAS-NMR shows resolved signals at -111.5, -112.3, -113.0 and -115.8 ppm (relative to TMS), all in the range of Q^4 (Si with four O–Si connectivities). The lines broaden and the resolution decreases with increasing Zr content. A similar phenomenon had been observed by Blasco *et al.*[14] for the case of low-level Ti-substitution in zeolite beta prepared by fluoride-assisted synthesis. The line broadening is attributed to the fact that the ^{29}Si $(O–Si)_4$ and the ^{29}Si $(O–Si)_3(O–Ti)$ signals appear at a very similar chemical shift.

IR of adsorbed 4-methylcyclohexanone on Zr100 revealed a strong interaction with the substrate (Fig. 1). Besides the
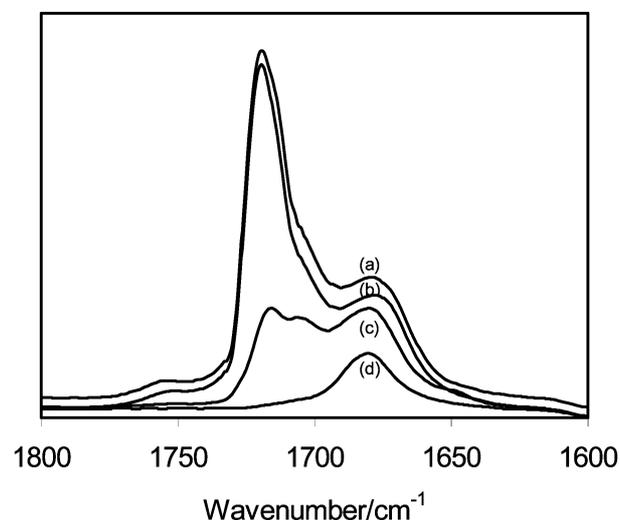
Fig. 1 Infrared spectra of 4-methylcyclohexanone adsorbed on Zr100 at (a) 25 °C (b) 50 °C (c) 100 °C and (d) 200 °C

† Electronic supplementary information (ESI) available: ^{29}Si MAS NMR spectra. See http://www.rsc.org/suppdata/cc/b3/b309191k/

carbonyl vibration of the keto group 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-substituted zeolite beta[11] and larger than that observed for Ti-substituted zeolite.

Some structural data and catalytic activities of the various zeolite beta catalysts for the MPV reduction of 4-*tert*-butylcyclohexanone are given in Table 1. Zr-beta catalysts were much more active than the Al- and Ti-zeolite beta catalysts. They performed even better than a Sn-zeolite beta. 4-*tert*-butylcyclohexanol was the only reaction product. The thermo-dynamically less favored *cis*-isomer was formed with 99% selectivity. This 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.[6,15] Si-beta impregnated with zirconium oxychloride was inactive indicating that isolated Zr atoms in the framework of zeolite beta are important for activity. The appropriate acidity and ligand exchangeability of Zr-beta may be the cause of the high activity. IR spectra of adsorbed pyridine showed that Lewis acid sites are predominant in Zr-beta, Ti-beta, and Sn-beta, with essentially no Brønsted acid sites.

Of particular interest is the high tolerance of the new material towards moisture. Table 2 compares the turnover numbers measured over the Zr-zeolite beta catalyst and a Sn-zeolite beta synthesized following Corma's procedure.[11] The turnover frequency has been calculated from the integral reaction rate over the first 5 minutes of reaction. Zr-beta retained almost 50% of its activity in the presence of 9.1% water. In contrast, Sn125 was drastically affected by the presence of water. This observation agrees with the result of Corma *et al.* who found that the TON 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

Table 1 MPV reduction of 4-*tert*-butylcyclohexanone over various substituted zeolite beta catalysts

Catalyst	Si/M	Surf. Area (m^2 g^{-1})	Conv. (%)^a	*cis* : *trans*^{b}
Si-beta	—	487	0	—
Zr-beta^c	95	308	0	—
Zr75	84	499	97.3	>99 : 1
Zr100	107	490	95.2	>99 : 1
Zr200	194	474	72.8	>99 : 1
Sn125	125	500	70.6	98 : 2
Ti100	100	468	2.9^d	100 : 0
Al100	100	451	<0.25^d	—

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} 4-*tert*-butylcyclohexanol only product formed. ^{c} ZrOCl$_2$ impregnated on Si-beta. ^{d} 1.3 mmol substrate.

Table 2 Activity over Zr- and Sn-beta in the presence of water

Water added (wt.%)	Zr100		Sn125	
	TOF^a	Conv.^{b} (%)	TOF^a	Conv.^{b} (%)
0	632	99	425	81
0.6	447	97	251	60
2.9	410	95	86	29
9.1	304	84	21	7

Reaction conditions: 1.3 mmol of 4-*tert*-butylcyclohexanone in 83 mmol 2-propanol, 100 mg catalyst under reflux and stirring 82 °C.^{a} Turn-over frequency after initial 5 min reaction: mol per mol·h ^{b} Conversion after 30 min.

by hydrophobizing the surface in a post-synthesis silylation step with hexamethyldisilazane. The activity of the modified material at 10% water content was 48 mol per mol·h, or about 50% of the activity under dry conditions. The Zr-beta synthesized for this study retained this level of activity in the presence of water, without requiring additional surface mod-ification. The catalyst can be easily recovered by filtration and could be re-used after washing with 2-propanol. Even after the eighth cycle, the activity of the catalyst was essentially unchanged.

In conclusion, we have shown that framework substitution with Zr in the zeolite beta structure is possible to a level of 1.3% (Si/Zr = 75). Well crystallized Al-free Zr-zeolite beta can be obtained in a seeded synthesis in fluoride medium. The material is an excellent catalyst for the MPV reduction, and is particularly valuable because of its tolerance to moisture.

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