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Supported zirconium propoxide—a versatile heterogeneous catalyst for the Meerwein–Ponndorf–Verley reduction

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Abstract

Grafting of zirconium 1-propoxide on SBA-15 resulted in highly active catalysts for the MPV reduction. The activity increased with zirconium loading up to a monolayer coverage. In most cases, there were no side products other than the desired alcohol. Electron-donating groups adjacent to the carbonyl group in the substrate facilitate the reaction. The grafted zirconium catalysts did not lose their activity in the presence of moisture or on exposure to ambient atmosphere, making them easy to handle and reuse. No leaching of the grafted zirconium 1-propoxide into the reaction mixture was observed. The addition of pyridine and water to the reaction medium had only a small effect on its activity while benzoic acid led to severe deactivation. The deactivation is attributed to strong adsorption of benzoic acid at the Zr metal centres which could be reversed on removal of the poison. Aluminum 2-propoxide grafted on SBA-15 resulted in a less active catalyst than the zirconium catalysts. The good resistance to hydrolysis of the zirconium catalysts makes them superior to the aluminum 2-propoxide catalysts.

Keywords: Zirconium 1-propoxide; Aluminum 2-propoxide; Grafted catalysts; MPV reduction; 4-*tert*-Butylcyclohexanone; Poisoning; Water resistance

1. Introduction

The Meerwein–Ponndorf–Verley (MPV) reduction of aldehydes and ketones provides a convenient access to the corresponding alcohols under mild conditions. The hydride donor is usually a secondary alcohol such as 2-propanol. The reaction is chemoselective: under the conditions of the MPV reduction, unsaturated aldehydes and ketones are not reduced to the saturated alcohols [1]. Hence, the MPV reduction offers a convenient synthesis route to α,β-unsaturated alcohols, many of which are important starting materials for the production of fine chemicals [2]. Traditionally, the reaction is catalyzed homogeneously by aluminum alkoxides such as aluminum 2-propoxide. Recently, a number of other aluminum complexes have been reported to be highly active for the MPV reduction of carbonyl substrates [3,4]. Precatalysts such as dimethylaluminum chloride or trimethylaluminum were shown to give superior yields in the reaction [5]. Besides aluminum complexes, the zirconium complex, bis(cyclopentadienyl)zirconium dihydride, has also been reported to be active in the MPV reaction [6].

In order to hetereogenise the complexes used in MPV reductions, grafting onto inorganic supports has been carried out. Heterogeneous catalysts offer the advantage of ease of separation and reusability. Anwander et al. [7] used MCM-41 as a support material for grafting aluminum propoxide. The hybrid system was found to be very active in the MPV reduction of 4-*tert*-butylcyclohexanone. However, the solvent 2-propanol must be carefully dried to observe good catalytic activity. The enhanced activity was ascribed to the formation of surface complexes involving four- or five-coordinated geometrically distorted aluminum. Leyrit et al. [8] reported that tetra-neopentylzirconium anchors to the surface of silica via a covalent bond, giving mononuclear and well-dispersed (siloxy)tris(neopentyl)zirconium. The heterogeneous complex was found to be an effective catalyst for the MPVO reactions of a number of ketones and alcohols.

We have found that suitably pretreated hydrous zirconia is an active catalyst in the MPV reduction such as the formation of cinnamyl alcohol from cinnamaldehyde [9]. The calcination temperature of the hydrous zirconia was found to be an important parameter as it affects the density of

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hydroxyl groups, necessary for ligand exchange with the reductant, 2-propanol. In this work, we extend our studies to the use of zirconium 1-propoxide grafted on a number of high surface area supports with a range of well-defined pores. Zirconium propoxide is less moisture sensitive than aluminum 2-propoxide and this property makes it easier to handle. Grafting on high surface area supports offers good dispersion of zirconium propoxide. For the present study, we evaluated various mesoporous silicas as support, namely SBA-15, MCM41, MCM-48, and a commercial silica gel. SBA-15 has hexagonal mesopores of 50–90 Å, depending on the preparation conditions [10] while MCM-41 has mesopores of 30–40 Å [11]. MCM-48 has a cubic structure of interconnected channels with average pore diameter of 20–30 Å and a very high surface area of 1600 m^2/g [12,13]. The commercial silica gel 60 has a wider pore size distribution centered around 60 Å. The grafted catalysts were tested toward the chemoselective MPV reduction of a number of ketones and aldehydes. Some of the substrates and the reduced products are used in the fragrance industry [14]. For example, citral and its reduction products, geraniol, citronellol, and 3,7-dimethyloctan-1-ol are used as fragrance and flavour chemicals. Upon reduction, 4-*tert*-butylcyclohexanone is reduced to *cis*- and *trans*-4-*tert*-butylcylcohexanol which can be further acetylated to yield 4-*tert*-butylcyclohexyl acetate, used in soap perfumes.

2. Experimental

2.1. Synthesis of supports

Silica MCM-41 was synthesised by dissolving 2.1 g of tetraethylammonium hydroxide (TEAOH, 40%, Fluka) and 2.95 g cetyltrimethylammonium bromide (CTMAB, Merck) in 12.2 g of deionised water with heating and stirring until a clear solution was obtained. Fumed silica (1.8 g) was added to the solution with stirring for another 2 h. The gel was aged for 24 h at room temperature. The molar composition of the final gel mixture was 1.0 SiO_2:0.19 TEAOH:0.27 CTMAB:40 H_2O. The mixture was placed in a Teflon-lined stainless-steel autoclave and kept at 150 °C for 48 h under autogeneous pressure. The product was filtered, washed with deionised water, dried at 100 °C, and calcined at 550 °C for 12 h.

Silica MCM-48 was synthesised following Ref. [12]. In a typical synthesis, 10 cm^3 of tetraethoxysilane (TEOS, Fluka) was added to an aqueous solution containing 8.8 g of a 10% CTMAB solution and 10 cm^3 of 2 M NaOH. The molar composition of the final gel mixture was 1.0 SiO_2:0.46 NaOH:0.55 CTMAB:112 H_2O. The mixture was stirred for 30 min before it was left for crystallisation in a Teflon-lined stainless-steel autoclave at 100 °C for 72 h. The product was washed and calcined as above.

Silica SBA-15 was synthesised according to the procedure described in Ref. [10]. Typically, 2 g of Pluronic P123 (Aldrich) was added to 75 cm^3 of 1.6 M HCl solution. The mixture was stirred at 40 °C for 3 h until all P123 had dissolved. Next, 4.25 g of TEOS was added to the solution and the mixture stirred for another 24 h. The composition of the mixture was 1.0 TEOS:5.71 HCl:158 H_2O. The resulting gel was placed in a Teflon-lined autoclave and heated at 100 °C for 24 h. The solid product was filtered, washed, and calcined as above.

2.2. Preparation of catalysts

The grafting of zirconium 1-propoxide (Alfa) onto the supports was carried out following Ref. [15]. Prior to grafting, the support (1.0 g) was dried at 300 °C for 4 h before cooling down to 100 °C. It was then added to a solution of zirconium 1-propoxide in dry hexane (30 mL). The suspension was refluxed at 69 °C for 12 h. The concentration of zirconium 1-propoxide in hexane was varied to give 5, 7, 11, and 14 wt% Zr in the grafted sample. The product was recovered by filtration and washed with hexane to remove any unreacted precursor. It was transferred to a vacuum desiccator and dried under vacuum for 6 h. Aluminum 2-propoxide (Fluka) was similarly grafted onto SBA-15 to give 3.74 wt% Al. This Al loading should result in the same molar content of active sites as found in the 11 wt% Zr-grafted sample (1.4 mmol/g support). The samples are referred to as wM-S where w is the wt% Zr or Al (M) and S is the support SBA-15, MCM-41, MCM-48, or silica gel 60 (Merck).

2.3. Characterisation

The surface area, pore size distribution, and pore volume were determined by nitrogen adsorption using a Quantachrome NOVA 2000. The crystalline phase of the samples was determined by powder X-ray diffraction. A Siemens D5005 diffractometer (Cu anode operated at 40 kV and 40 mA) equipped with variable slits was used for wide-angle measurements of all materials except SBA-15. The crystallinity of SBA-15 was determined with a Bruker D8 GADDS at a sample-to-detector distance of 30 cm using Cu radiation. FT-IR spectra were made to ascertain that zirconium 1-propoxide had been grafted onto the support. SBA-15 and the grafted samples were pressed into self-supporting wafers of $\sim$ 8–10 mg. The wafer was mounted in a Pyrex IR cell with NaCl windows. The sample was dried by evacuating under vacuum (10^{-3} mbar) for 2 h at 200 °C. Subsequently, the sample was cooled to room temperature before making an IR measurement. A Bruker Equinox 55 spectrometer was used with a resolution of 2 cm^{-1}. The elemental compositions of the grafted catalysts were determined by AES-ICP after dissolution of the solid in HF.

2.4. Catalytic activity

The reaction mixture containing 1.3 mmol of the aldehyde or ketone and 5 g (83 mmol) of 2-propanol was placed in a round-bottomed flask equipped with a septum port, reflux condensor, and a guard tube. To this mixture was added 100 mg of freshly vacuum-dried catalyst. The MPV reduction was carried out under reflux at 82 °C. Aliquots were removed at different reaction times and the products were analyzed by gas chromatography (HP5, 0.25 mm, 30 m). The identity of the products was verified by comparing the retention times and GCMS spectra with authentic samples.

To test for any leaching, about 100 mg of the grafted catalyst was refluxed in 5 g of 2-propanol at 82 °C for 6 h. The solution was filtered and the filtrate was tested for activity in the MPV reduction of 4-*tert*-butylcyclohexanone. The reuse of catalyst was also tested by washing the used catalyst with 2-propanol and testing it in further rounds of reaction. Poisoning of the grafted catalyst was investigated by adding 0.1098 mmol (equivalent to the Zr content in 100 mg of 11Zr-SBA-15) of water, pyridine, or benzoic acid to the reaction medium. The "poisoned" catalyst was filtered after the reaction, washed with 2-propanol, and tested for any recovery of activity in a subsequent MPV reaction.

The moisture sensitivity of the grafted zirconium 1-propoxide and aluminum 2-propoxide was investigated by exposing the samples to ambient environment (humidity ~ 80%) for 48 h before testing for their activity in the MPV reduction of 4-*tert*-butylcyclohexanone. Homogeneous catalysis by zirconium 1-propoxide and aluminum 2-propoxide was carried out to compare the activity with the grafted catalysts. Forty-nine microliters of 70% zirconium 1-propoxide (containing 0.1098 mmol Zr) or 0.0238 g of aluminum 2-propoxide (0.1386 mmol) was added to the reaction medium of 4-*tert*-butylcyclohexanone and 2-propanol. At different reaction times, an aliquot was removed, water was added to precipitate the catalyst, and the filtrate was analysed by gas chromatography.

3. Results and discussion

3.1. Textural properties

The experimentally determined zirconium loading on the SBA-15-grafted samples was between 75 and 92% of the intended values (Table 1). The slightly lower than expected values can be due to limited accessibility of some of the surface hydroxyl groups during the grafting reaction. Fig. 1 shows the nitrogen adsorption-desorption isotherms for SBA-grafted samples with different loading of zirconium 1-propoxide. The isotherms were all of IUPAC type IV. The H1 hysteresis loop is indicative for agglomerates or compacts of spheroidal particles of fairly uniform size and array [16]. The mean pore diameter of SBA-15 was 73 Å, while that of the grafted SBA samples was around 58–70 Å. The reduced pore diameter together with the retention of the uniform pore distribution shows that there is an even dispersion of zirconium 1-propoxide on the pore surface. The total pore volume decreased from 1.20 cm^3/g in SBA-15 to 0.70 cm^3/g in 14Zr-SBA-15. Silica gel has a wide pore diameter of 64 Å (Fig. 2). After grafting, the mean pore dimension in 11Zr-SiO$_2$ was 57 Å, and the total pore volume decreased from 0.77 to 0.62 cm^3/g.

Table 1
Chemical and textural properties of the catalysts used in the study

Sample	Zr or Al [%]		Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore Ø (Å)
	Expected[a]	Measured			
SBA-15	–	–	816	1.20	73
5Zr-SBA-15	5	3.8	764	1.13	70
7Zr-SBA-15	7	5.0	630	0.92	65
11Zr-SBA-15	11	10.0	606	0.82	60
14Zr-SBA-15	14	11.4	570	0.70	58
3.7Al-SBA-15	4	3.75	545	0.90	65
MCM-41	–	–	1136	1.01	33
11Zr-MCM-41	11	11.0	784	0.63	31
MCM-48	–	–	1630	1.24	26
11Zr-MCM-48	11	10.5	1342	0.71	22
SiO$_2$	–	–	307	0.77	64
11Zr-SiO$_2$	11	5.5	295	0.62	57

[a] From alkoxide used in grafting.

In contrast to SBA-15 and silica gel supports, the reduction in the pore volume of zirconium 1-propoxide grafted on MCM-41 and MCM-48 was bigger, ~ 40%. Based on a trimeric structure for zirconium 1-propoxide, a molecular mechanics (MM+; Hyperchem) calculation gives a kinetic diameter of about 17.9 Å. The size of the zirconium 1-propoxide complex could hinder its penetration into smaller pores; at the same time, bigger pores could be completely filled up or considerably reduced in size after grafting. Hence, the loss in pore volume is more drastic than for bigger pore material, such as SBA-15 or silica gel.

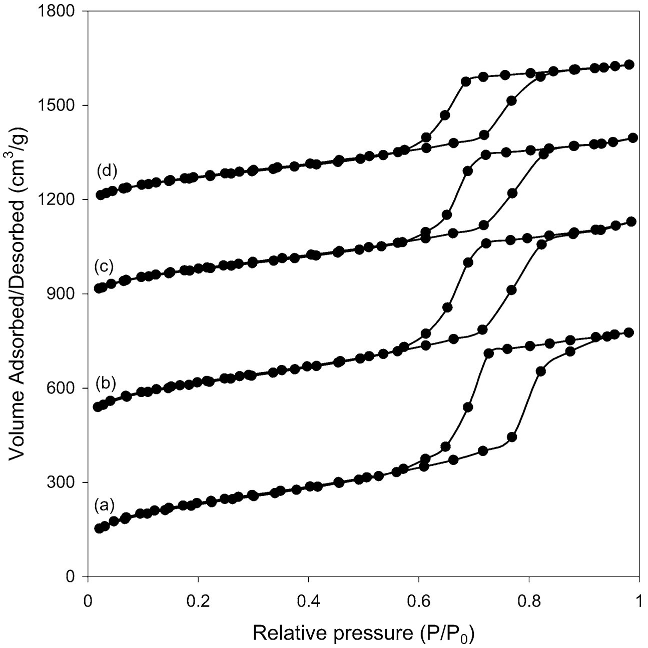


Fig. 1. Nitrogen adsorption/desorption isotherms for (a) SBA-15, (b) 5Zr-SBA-14, (c) 7Zr-SBA-15, and (d) 11Zr-SBA-15.

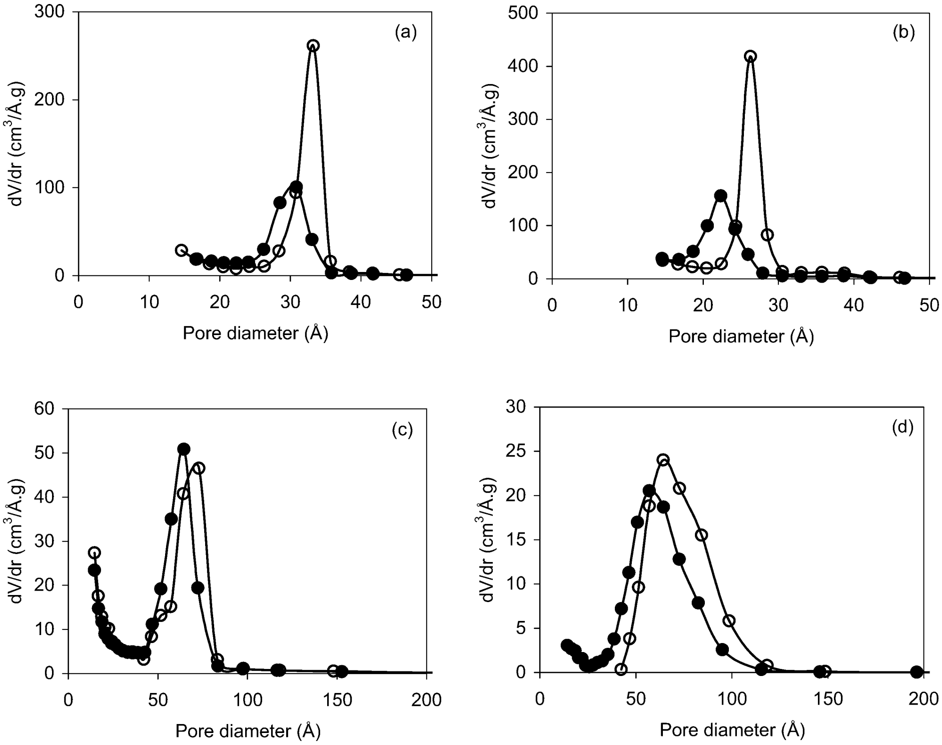


Fig. 2. Pore-size distribution for (○) support and (●) 11 wt% Zr-grafted catalysts on (a) MCM-41, (b) MCM-48, (c) SBA-15, and (d) SiO_2.

X-ray powder diffraction was used to confirm the crystalline phase of the different supports. The X-ray powder diffraction patterns for pure silica SBA-15 support and the grafted samples are shown in Fig. 3. SBA-15 shows one strong primary peak at $2\theta \sim 0.85°$ corresponding to the (100) reflection, and two smaller higher order peaks indexed as the (110) and (200) reflections at 1.5 and 1.75°. The presence of these reflections indicates a high degree of order in the arrangement of the pore network. The X-ray diffractograms of the grafted samples were nearly identical to that of the support, verifying the retention of the pore structure even after grafting.

The IR spectra of the pure silica SBA-15 and MCM-41 have a broad absorption band in the OH stretching range from 3200 to 3800 cm^{-1} (Fig. 4). The sharp peak at 3741 cm^{-1} originates from terminal silanol groups, and the

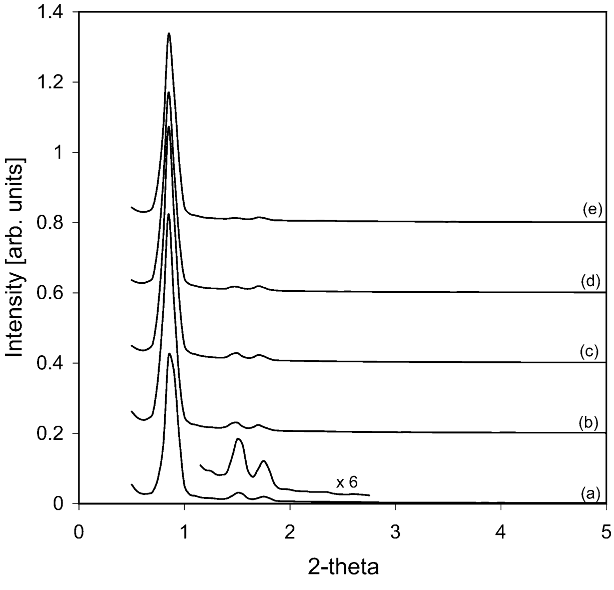


Fig. 3. XRD diffractograms of (a) SBA-15, (b) 5Zr-SBA-15, (c) 7Zr-SBA-15, (d) 11Zr-SBA-15, and (e) 14Zr-SBA-15.

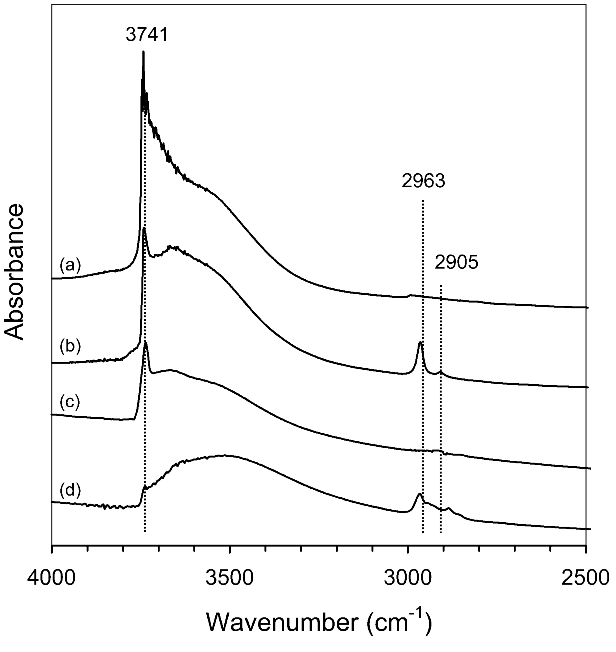


Fig. 4. IR spectra of (a) SBA-15, (b) 7Zr-SBA-15, (c) MCM-41, and (d) 11Zr-MCM-41.

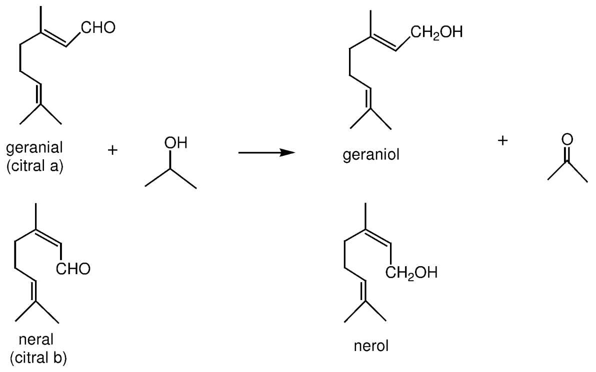
broad shoulder at the low frequency side is assigned to OH groups located at defect sites [17]. Upon grafting of zirconium 1-propoxide onto the support, the vibration band due to silanols at 3741 cm^{-1} was reduced in intensity. This clearly points to the role of surface silanols in reacting with the zirconium 1-propoxide. The grafted samples show additional peaks at 2963 and 2905 cm^{-1}, which can be assigned to C–H stretching of the propoxide.

3.2. *Catalytic activity*

Unmodified SBA-15 was not active in the MPV reduction of 4-*tert*-butylcylcohexanone. However, once zirconium 1-propoxide was grafted onto SBA-15, the heterogenised material showed good activity (Fig. 5). Almost all 4-*tert*-butylcyclohexanone was reduced within 100–250 min, depending on the catalyst. The rate of reaction increased with zirconium propoxide loading; however, the most highly loaded samples, 11Zr-SBA and 14Zr-SBA, had very similar activity.

4-*tert*-butylcyclohexanone was reduced to the corresponding *trans*- and *cis*-alcohol. The *trans*:*cis* ratio was 84:16. No other reduction products were detected, showing the high selectivity of the reaction. 1-Propanol was also detected in the reaction mixture immediately after the start of the reaction, indicating that the 1-propoxide ligand was readily exchanged with excess 2-propanol. Based on the Zr loading (from ICP results) and the 1-propanol detected (by GC), a Zr:1-propanol ratio of 1:2 was obtained. Hence, zirconium 1-propoxide was immobilised to the surface via reaction with two OH groups, leaving two propoxide groups at the metal centre.

The reaction was also carried out at lower temperatures. At 25 and 60 °C, the conversion after 300 min over 11Zr-SBA was 15.8 and 80.1%, respectively. From the temperature dependence, the activation energy was calculated to be 59.5 kJ/mol. This compares well with the value of 51.7 kJ/mol reported by Shibagaki et al. for cyclohexanone reduction [18].



Scheme 1. MPV reduction of citral (a and b) to geraniol and nerol.

For comparison, the activity of the homogeneously catalysed reaction was tested using an equivalent amount of zirconium 1-propoxide as found in 11Zr-SBA-15. Here, the conversion of 4-*tert*-butylcyclohexanone was 32% after 120 min. The rate of reaction over the supported catalyst was faster: the conversion reached 96% in the same time. The selectivity to the *trans*-alcohol in the homogeneously-catalysed reaction was very high, 91% as compared to 84% in the grafted catalyst.

Citral occurs as *cis*- and *trans*-isomers, known as neral and geranial, respectively. Scheme 1 outlines the reduction of citral to the corresponding alcohols using 2-propanol as reductant. Although the rate of reaction was slower in the reduction of citral, a similar trend to that of 4-*tert*-butylcyclohexanone was observed (Fig. 6). The rate increased with Zr loading up to a limit with both 11Zr-SBA-15

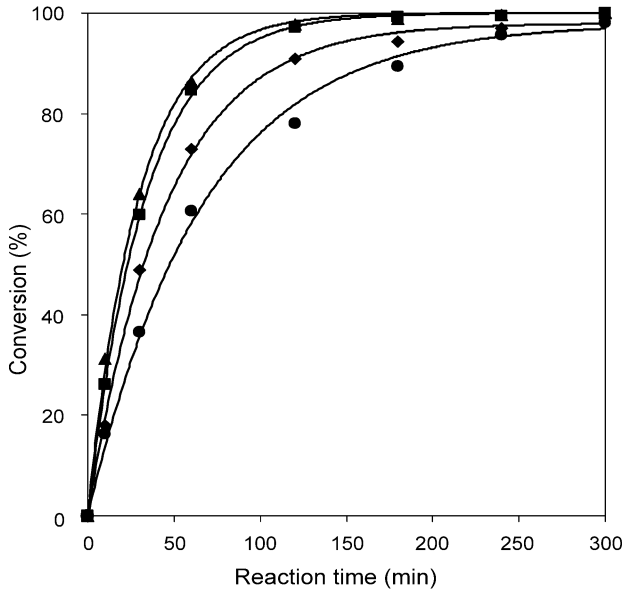


Fig. 5. Conversion of 4-*tert*-butylcyclohexanone over (●) 5Zr-SBA-15, (◆) 7Zr-SBA-15, (■) 11Zr-SBA-15, and (▲) 14Zr-SBA-15.

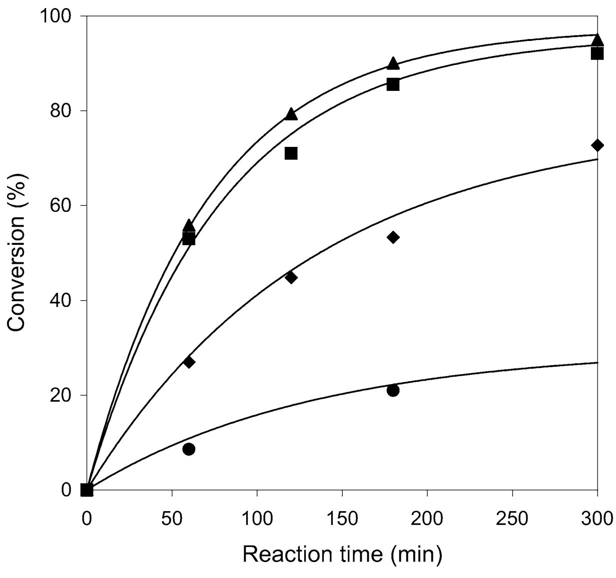


Fig. 6. Conversion of citral over (●) 5Zr-SBA-15, (◆) 7Zr-SBA-15, (■) 11Zr-SBA-15, and (▲) 14Zr-SBA-15.

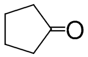
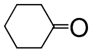
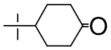
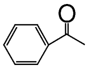
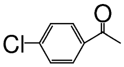
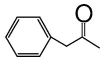
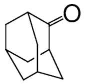
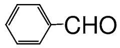
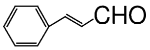
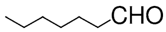
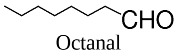
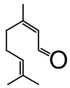
and 14Zr-SBA-15 having a similar reaction rate. Further increase in Zr loading does not lead to significant increase in the rate. Over the catalysts, the selectivity to nerol and geraniol was more than 90%. Some isomerisation of the formed alcohols occurred, leading to the by-products, 3,7-dimethyl 1,6-octadien-3-ol and 2,7-dimethyl 2,6-octadien-1-ol, as detected by GCMS.

The observation that the activity of the catalysts increases with zirconium loading to a limiting value suggests that the surface coverage of zirconium 1-propoxide approached a monolayer at 10–11.4 wt% Zr. Based on the Zr loading and the BET surface area (816 m^2/g), the surface coverage works out to be 1.11–0.96 nm^2/Zr propoxide. From the calculated kinetic diameter for trimeric zirconium 1-propoxide of 1.79 nm, a value of 0.84 nm^2/Zr propoxide is obtained. The good fit of the experimental and calculated values strongly supports the assumption that a monolayer is attained at these Zr loadings. Once a monolayer is formed in a grafting process, the loading can only be increased if the sample is calcined to regenerate hydroxyl groups for the grafting reaction [19].

The results from the MPV reduction of a number of aldehydes and ketones over 11Zr-SBA catalyst are given in Table 2. Cyclopentanone was less easily reduced than cyclohexanone. Cyclohexanone was reduced at the same rate as 4-*tert*-butylcyclohexanone despite the bulky tertiary butyl group on the latter. The pore size of the supported catalyst did obviously not restrict site accessibility for the 4-*tert*-butylcyclohexanone. However, both adamantone and benzyl methyl ketone were not reduced to the corresponding alcohols under the reaction conditions. Steric hindrance due to the polycyclic rings of adamantone could contribute to its low activity. The low activity of benzyl methyl ketone as compared to acetophenone and benzaldehyde may indicate that the benzene ring is involved in binding to the active site. If the benzene ring binds planar to the surface, the C=O group in benzaldehyde and acetophenone will be aligned parallel to the surface. However, this is not possible in benzyl methyl ketone. The conversion of acetophenone (18.3% after 5 h) is slightly lower than that of 4-chloroacetophenone (23.8%). The *para*-substituted chlorine is too far away to influence the electron density at the keto group as indicated by the ^{13}C NMR shift. Hence, the slightly higher activity for chloroacetophenone may be due to a resonance effect.

Aldehydes were efficiently reduced by 2-propanol with very high selectivity. Benzaldehyde was almost completely reduced within 1 h, while a conversion of 55.6% was measured for cinnamaldehyde after 5 h. Cinnamyl alcohol was the only product in the MPV reduction of cinnamaldehyde over the grafted catalysts. The conversion of heptanal and octanal reached more than 95% within 5 h.

Table 2
Substrates used for the MPV reduction with 2-propanol over 11Zr-SBA-15

Entry	Substrate	Time (h)	Conversion (%)	Selectivity (%)
1	 Cyclopentanone	5	16.9	100
2	 Cyclohexanone	5	98.1	100
3	 4-*tert*-Butylcyclohexanone	5	100	100
4	 Acetophenone	5	18.3	100
5	 4-Chloroacetophenone	5	23.8	100
6	 Benzyl methyl ketone	24	< 1	–
7	 Adamantone	24	< 1	–
8	 Benzaldehyde	1	99	100
9	 Cinnamaldehyde	5	55.6	100
10	 Heptanal	5	95.8	100
11	 Octanal	5	94.4	100
12	 Citral	1	53.0	> 90

1.3 mmol of substrate, 5 g of 2-propanol, 100 mg catalyst.

3.3. Poisoning experiments

In the presence of pyridine, the rate of reduction of 4-*tert*-butylcyclohexanone was only a little reduced (Fig. 7). However, the addition of benzoic acid drastically decreased the rate to about one-ninth. The poisoning effect can be reversed to some extent. Removal of the catalyst from the reaction mixture and washing with 2-propanol caused a recovery of the activity to about one-third that of the fresh catalyst. From the results, it can be inferred that the benzoic acid did not cause leaching of zirconium 1-propoxide from the support. This was confirmed by FTIR measurements of the used catalyst where the C–H absorption band of the propoxide groups was still present. The addition of small amounts of water also did not significantly reduce the activity of the catalyst. The good resistance of the catalyst to the presence of moisture was also verified by exposing the catalyst, 11Zr-SBA-15, to the ambient environment for 48 h prior to catalyst testing. The conversion of 4-*tert*-butylcyclohexanone after 300 min was 97.5% as compared to 100% over the unexposed catalyst (Table 3).

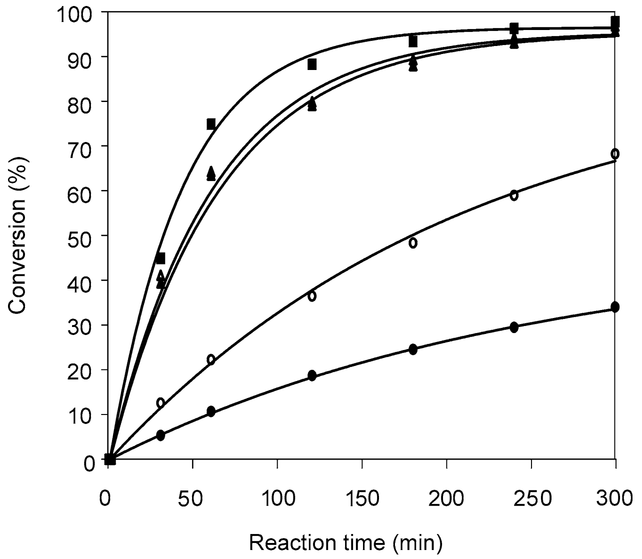


Fig. 7. Conversion of 4-*tert*-butylcyclohexanone over 11Zr-SBA-15 in (■) pure reaction medium, after addition of (▲) pyridine, (△) water, (●) benzoic acid, and (○) after removal of benzoic acid.

Table 3
Activity of grafted aluminum- and zirconium-propoxide catalysts before and after exposure to air

Catalyst	Conversion[a] (%)	Selectivity (%)	*trans*:*cis*
11Zr-SBA-15	100	100	84:16
11Zr-SBA-15[b]	97.5	100	84:16
3.7Al-SBA-15	38.1	100	78:22
3.7Al-SBA-15[b]	10.5[c]	100	78:22

[a] After 300 min.
[b] After exposure to air for 48 h.
[c] After 24 h.

Table 4
Recycling test of 11Zr-SBA-15 in the MPV reduction of 4-*tert*-butylcyclohexanone

Cycle	Conversion[a] (%)	Selectivity (%)	*Trans*:*cis*
1	100	100	84:16
2	100	100	84:16
3	100	100	85:15
4	100	100	84:16
5	99.5	100	85:15
6	99.3	100	85:15

[a] After 300 min.

Table 5
Conversion of 4-*tert*-butylcyclohexanone over grafted zirconium 1-propoxide on different supports

Catalyst	Conversion[a] (%)	*trans*:*cis* ratio of product
11Zr-MCM-41	86.6	80:20
11Zr-MCM-48	74.3	79:21
11Zr-SBA-15	59.8	84:16
11Zr-SiO_2	57.3	89:11

[a] Reaction time: 30 min.

3.4. Reuse of grafted catalysts

The filtrate obtained after refluxing the grafted catalyst in 2-propanol was not active for the MPV reduction of 4-*tert*-butylcyclohexanone, showing the absence of leaching into the reaction medium. The grafted catalyst could be reused with good activity and selectivity. After each round of reaction, the catalyst was washed with 2-propanol and tested in another batch reaction. Table 4 shows that in the MPV reduction of 4-*tert*-butylcyclohexanone, the activity of the catalyst, 11Zr-SBA-15, remained high even after six rounds of reaction. The selectivity to the 4-*tert*-butylcyclohexanol was 100% in each round.

3.5. Comparison of supports for grafting

The catalytic activity at the same loading, 10–11 wt% Zr, was compared for MCM-41, MCM-48, and SBA-15 (Table 5). All catalysts showed high activity in the reaction. 11Zr-SiO_2 showed the slowest rate of reaction. This may be explained by its lower Zr loading, 5.5 wt%, compared to the other samples. This loading corresponds to a monolayer of Zr 1-propoxide. Based on the diameter of zirconium 1-propoxide (1.79 nm), a monolayer on the smaller surface area silica should be reached at 5.26 wt% Zr. This result lends support to the role of surface hydroxyl groups in limiting the grafting to no more than a monolayer. We did not expect that the mesoporous supports would have an effect on the stereoselectivity of the reaction. However, the *trans*:*cis* ratio was highest for the SiO_2-supported catalyst, 89:11. The *trans*:*cis* ratio of 4-*tert*-butylcyclohexanol decreased to 79:21 for 11Zr-MCM-48 which had the narrowest pore size of the supports used. These results must to be compared to the ratio 91:9 observed for the reaction in the homogeneous phase.

3.6. Grafted aluminum 2-propoxide on SBA-15

Aluminum 2-propoxide is established as homogeneous catalyst for MPV reactions [2]. For the comparison with zirconium 1-propoxide, both homogeneous and heterogeneous forms of aluminum 2-propoxide were tested for the reduction of 4-*tert*-butylcyclohexanone. As a homogeneous catalyst, aluminum 2-propoxide (0.1386 mmol) was less active than zirconium 1-propoxide when compared on an equivalent molar basis. The conversion of 4-*tert*-butylcyclohexanone after 120 min was only 7.2%, increasing to 15.2% after 300 min. The *trans*:*cis* selectivity of the alcohol was very similar to that over zirconium 1-propoxide, 91:9. After grafting aluminum 2-propoxide onto the SBA-15 support, the conversion increased to 38.1% after 300 min (Table 3). The *trans*:*cis* ratio of the products was 78:22. However, the activity of the grafted aluminum 2-propoxide was still well below that of 11Zr-SBA-15 where the substrate was almost completely converted in the same time.

One explanation for the lower activity observed here could be hydrolysis of the aluminum 2-propoxide during handling or under reaction conditions. To verify this, 3.7Al-

SBA-15 was also exposed to ambient environment for 48 h before catalytic testing as for 11Zr-SBA-15. The activity of the exposed 3.7Al-SBA-15 decreased tremendously; after 24 h, the conversion was only 10.5%. In contrast, 11Zr-SBA-15 remained active at 97.5% conversion. This shows the advantage of grafted zirconium propoxide for practical applications.

4. Discussion

The MPV reaction is usually catalysed by metal alkoxides, such as aluminum 2-propoxide. In this study, it is found that for the homongeneously catalysed MPV reduction of 4-*tert*-butylcyclohexanone, zirconium 1-propoxide has a higher activity than aluminum 2-propoxide. Heterogenisation of the metal alkoxides leads to an increase in the catalytic activity when compared on a molar basis with the homogeneous catalysts. High surface area mesoporous materials like SBA-15, MCM-41, MCM-48, and silica gel provide a useful support for the heterogenisation of zirconium 1-propoxide. Surface hydroxyl groups are involved in the grafting reaction, allowing the zirconium 1-propoxide to build up to a monolayer.

The immobilised zirconium 1-propoxide is resistant to leaching under reaction conditions. In addition, grafted zirconium 1-propoxide does not lose its catalytic activity following long exposure to ambient environment or water in the reaction medium. This is in contrast to the grafted aluminum 2-propoxide. The high activity of the zirconium 1-propoxide even in the presence of water may be related to the good activity of zirconium hydroxide. We have previously reported that zirconium hydroxide is a good catalyst for the MPV reduction of cinnamaldehyde. We postulated that the hydroxyl groups on the hydroxide are involved in ligand exchange with 2-propanol. Indeed, facile exchange between ligands and the reductant has been demonstrated to be important in the MPV reaction. The efficiency of the MPV reaction was found not to depend on the ligands [5]. Indeed, alkylaluminum such as $Al(CH_3)_3$ or $Al(CH_3)_2Cl$ was found to convert under reaction conditions to aluminum 2-proproxide while in bis(cyclpentadienyl)zirconium dihydride, the cyclopentadienyl groups were found to split off when reacted with 2-propanol resulting in zirconium 2-propoxide [6]. Campbell et al. [5] attributed the high activity of the catalysts formed from these alkylaluminum reagents to a lower aggregation state with fewer bridging alkoxides than in bulk aluminum 2-propoxide. It was further postulated that only the nonbridging alkoxy group is involved in the hydride transfer to the carbonyl group during the MPV reduction.

It has been proposed that the MPV mechanism for heterogeneous catalysts involves basic or acidic sites. In zeolites, aluminum Lewis acid sites are believed to be the active centres [20], while in MgO and hydrotalcites, the activity seems to be linked to basic sites [21–23]. The reductant, 2-propanol, chemisorbs either at an acidic or a basic site to form the surface propoxide. In the grafted catalysts used in this study, the chemisorption of a secondary alcohol and the ketone or aldehyde occurs at the Zr metal centre [1]. The poisoning experiments with pyridine and benzoic acid indicated that only the latter hindered the reaction. This may be explained by a displacement of 2-propanol by benzoic acid at the Zr centre. Lopez et al. [24] reported that the adsorption coefficient of benzoic acid was 860 times higher than that of 2-propanol. The strongly adsorbed benzoate will interfere with the binding of the keto-compound to the metal centre and the formation of the cyclic transition state required for the hydride transfer.

As zirconium 1-propoxide was used as reagent for grafting zirconium onto the support, ligand exchange between the 1-propoxide group and 2-propanol has to occur before reduction of the substrate becomes possible. For the ketone or aldehyde, the presence of electron-donating groups adjacent to the C=O bond facilitates the adsorption, as can be deduced from the increasing rate of conversion in the series from benzyl methyl ketone, acetophenone to 4-chloroacetophenone. Bulky molecules like adamantone and benzyl methyl ketone have very low reactivity. The MPV reduction of a number of unsaturated aldehydes and ketones was highly selective toward the corresponding alcohols. Cinnamaldehyde was reduced to cinnamyl alcohol.

Comparing the activity of grafted zirconium 1-propoxide on supports with smaller pores than SBA-15, it was found that the pore structure has little effect on the rate of reaction. Although MCM-48 with its 3-dimensional network of channels would be expected to allow more facile diffusion of reactants and products, the rate of reaction was fastest over zirconium 1-propoxide supported on MCM-41, which has uniform one-dimensional channels. A slight influence of the nature of the support on the *cis*:*trans* ratio of the 4-*tert*-butylcyclohexanol was observed. The highest selectivity toward *cis*-4-*tert*-butylcyclohexanol was observed over 11Zr-MCM-48 which has the smallest pore diameter of the materials studied. This indicates some shape-selective effect within the pore space and can be rationalised by the less bulky transition state for the formation of *cis*- rather than the *trans*-alcohol. This had also been observed in the group of van Bekkum over zeolite beta [20]. In line with this interpretation is the fact that the *trans*:*cis* ratio for 4-*tert*-butylcyclohexanol was very high when the reaction was homogeneously catalysed by zirconium 1-propoxide or aluminum 2-propoxide, but the ratio decreased when the catalyst was immobilized onto a support.

5. Conclusion

Grafted zirconium 1-propoxide supported on SBA-15 was particularly active in the selective reduction of a number of aldehydes and ketones. The selectivity to the desired alcohols was in most cases 100%. The activity of the catalysts increased with zirconium 1-propoxide loading to reach a limit at a monolayer coverage. Further loading did not lead to a significant increase in activity. Although zirconium propoxide easily undergoes hydrolysis, the grafted zirconium 1-propoxide catalysts were not deactivated by the presence of water and showed good stability despite exposure to ambient environment. In contrast to grafted zirconium 1-propoxide catalysts, grafted aluminum 2-propoxide showed lower activity and was very sensitive to humidity or moisture in the reaction medium. The turnover frequency of the surface-immobilised zirconium 1-propoxide was higher than that of the free complex, an indication of the importance of the reduction in dimensionality in a surface-mediated reaction.

References

[1] C.F. de Graauw, J.A. Peters, H. van Bekkum, J. Huskens, Synthesis 10 (1994) 1007.
[2] E.J. Creyghton, J. Huskens, J.C. van der Waal, H. van Bekkum, in: H.U. Blaser, A. Baiker, R. Prins (Eds.), Heterogeneous Catalysis and Fine Chemicals IV, Elsevier, Amsterdam, 1997, p. 531.
[3] T. Ooi, T. Miura, K. Maruoka, Angew. Chem., Int. Ed. 37 (1998) 2347.
[4] T. Ooi, Y. Itagaki, T. Miura, K. Maruoka, Tetrahedron Lett. 40 (1999) 2137.
[5] E.J. Campbell, H. Zhou, S.T. Nguyen, Organic Lett. 3 (2001) 2391.
[6] Y. Ishii, T. Nakano, A. Inada, Y. Kishigami, K. Sakurai, M. Ogawa, J. Org. Chem. 51 (1986) 240.
[7] R. Anwander, C. Palm, G. Gerstberger, O. Groeger, G. Engelhardt, Chem. Commun. (1998) 1811.
[8] P. Leyrit, C. McGill, F. Quignard, A. Choplin, J. Mol. Catal. A 112 (1996) 395.
[9] S.H. Liu, S. Jaenicke, G.K. Chuah, J. Catal. 206 (2002) 321.
[10] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.
[11] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[12] J. Xu, Z. Luan, H. He, W. Zhou, L. Kevan, Chem. Mater. 10 (1998) 3690.
[13] K. Schumacher, M. Grün, K.K. Unger, Micropor. Mesopor. Mater. 27 (1999) 201.
[14] K. Bauer, D. Garbe, H. Surburg, in: W. Gerhertz (Ed.), Ullmann's Enclyclopedia of Industrial Chemistry, Vol. A11, VCH, Weinheim, 1988, p. 141.
[15] M.S. Morey, G.D. Stucky, S. Schwarz, M. Fröba, J. Phys. Chem. B 103 (1999) 2037.
[16] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, New York, 1982.
[17] A. Jentys, N.H. Pham, H. Vinek, J. Chem. Soc., Faraday Trans. 92 (1996) 3287.
[18] M. Shibagaki, K. Takahashi, H. Matsushita, Bull. Chem. Soc. Jpn. 61 (1988) 3283.
[19] J. Ma, G.K. Chuah, S. Jaenicke, R. Gopalakrishnan, K.L. Tan, Ber. Bunsen.-Gesellschaft Phys. Chem. 99 (1995) 184.
[20] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, J. Mol. Catal. A 115 (1997) 457.
[21] P.S. Kumbhar, J. Sanchez-Valente, J. Lopez, F. Figueras, Chem. Commun. (1998) 535.
[22] T.M. Jyothi, T. Raja, K. Sreekurma, M.B. Talawar, S. Rao, J. Mol. Catal. A 157 (2000) 193.
[23] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marina, J.R. Ruiz, F.J. Urabano, Appl. Catal. A 206 (2001) 95.
[24] J. Lopez, J. Sanchez Valente, J.-M. Clacens, F. Figueras, J. Catal. 208 (2002) 30.