

Liquid-phase Oppenauer oxidation of primary allylic and benzylic alcohols to corresponding aldehydes by solid zirconia catalysts

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Abstract

Hydrous zirconia and grafted zirconium 1-propoxide catalysts were found active in the Oppenauer oxidation of cinnamyl alcohol, geraniol and 4-*tert*-butylcyclohexanol (*cis*- and *trans*-). The most active hydrous zirconia catalysts were formed by calcining at 250–300 °C. Grafted zirconium 1-propoxide on silica gel and MCM-41 were active in the Oppenauer oxidation of geraniol with high selectivity to the desired citral product. However, over an acidic support such as AlMCM, the grafted zirconium 1-propoxide catalysed the dehydration and isomerisation of the alcohol, leading to low yield to citral. Also, furfural was found to be an efficient oxidant for the titled Oppenauer oxidation. Other solid catalysts such as γ -Al₂O₃, Na–Al₂O₃, zeolite beta and Mg/Al hydrotalcite showed only moderate catalytic activity and selectivity in the Oppenauer oxidation of geraniol. As compared to other solid catalysts, hydrous zirconia solid catalysts used in this work are active and selective towards the formation of desired carbonyl oxidation products; additionally, these solid zirconia catalysts are easy to prepare and recycle, and applicable to different alcohol substrates.

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1. Introduction

The oxidation of primary alcohols to aldehydes or secondary alcohols to ketones can be carried out under Oppenauer oxidation [1]. The reaction avoids overoxidation to carboxylic acids. Like the MPV reaction, Oppenauer oxidation proceeds via a complex in which both the oxidant and the alcohol are bound to the metal ion [2]. The alcohol reactant is coordinated as the alkoxide. Hydride transfer occurs from the alcoholate to the carbonyl group via a six-membered transition state. Aluminium alkoxide catalysts such as aluminium 2-propoxide and *tert*-butoxide are commonly used because of their ease of preparation and good solubility in alcohols and hydrocarbons. However, a stoichiometric amount is often required.

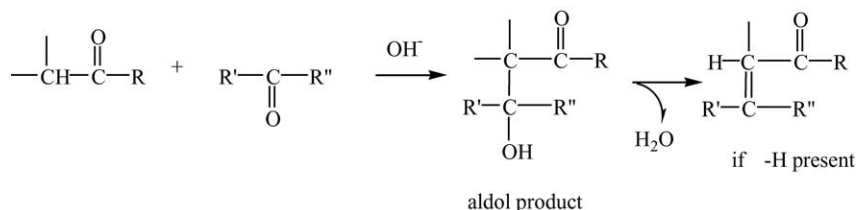
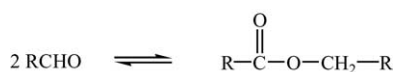
Side reactions may occur during the Oppenauer oxidation of primary alcohols [3]. Aldol condensation may take place when the aldehydes formed from the oxidation of primary alcohols contain an α -hydrogen (Scheme 1). Aldol condensation is more extensive for aldehydes than ketones as the equilibrium lies far to the right for the former. The aldol undergoes further dehydration as the new double bond will be in conjugation with the carbonyl bond.

Aldehydes, which lack an α -hydrogen, like benzaldehyde, may undergo the Tishchenko reaction forming carboxylic esters (Scheme 2).

The oxidants in Oppenauer oxidation are usually carbonyl compounds with high oxidation potentials, like aromatic and aliphatic aldehydes. Acetaldehyde, acrolein, acetophenone, acetone, benzaldehyde, *p*-benzoquinone, benzophenone, cyclohexanone, etc. have been used as the oxidant. Although acetone has a low oxidation potential, it is commonly used in the Oppenauer oxidation reaction. Being inexpensive, it can be used in large excess to shift the equilibrium towards the desired direction [4]. Although *p*-benzoquinone

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Scheme 1. Aldol condensation of aldehydes containing α -hydrogen.Scheme 2. Tishchenko reaction between two aldehydes without α -hydrogen.

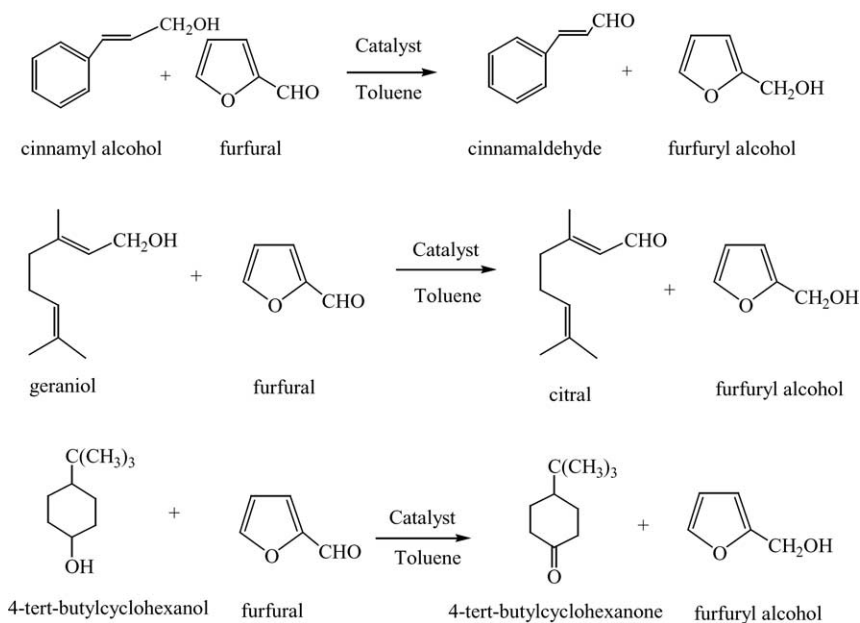
and benzophenone were found to be very efficient as oxidants, they both have very high boiling points (180 °C and 305 °C, respectively). The high temperatures may cause side reactions with heat-sensitive aldehydes, e.g. citral. Furfural has a lower boiling point (162 °C) and was found to be very efficient for the homogeneous Oppenauer oxidation of several important allylic alcohol substrates, including geraniol, cinnamyl alcohol, prenol and coniferyl alcohol, etc. [3]. The reaction could be carried out under very mild conditions. Furfuryl alcohol formed has a relatively low boiling point (170 °C), allowing its convenient separation from the aldehyde products (citral with a b.p. 220 °C) and recovery by distillation. Furfuryl alcohol is, itself, a useful product which is used in the making of resins.

Various heterogeneous catalysts have been used in the Oppenauer oxidation of alcohols to aldehydes [1,5]. Hydrous zirconia [6–8], MgO [9], hydrotalcite [10], zirconia-based

catalysts [11], Al₂O₃ [12] and silica-supported zirconium alkoxide [13,14] had been found to be efficient solid catalysts for the Oppenauer oxidation of various primary alcohol substrates.

Citral is a mixture of citral-a (geranial) and citral-b (neral). It is a highly useful intermediate in the synthesis of several products, such as ionones and methyl ionones. The condensation of citral with acetone leads to pseudoionone, which in turn can be converted into α -ionone and β -ionone. The latter is a key intermediate in the production of Vitamin A. Pseudoionone itself is useful in the production of Vitamin E [15].

Both cinnamaldehyde and 4-*tert*-butylcyclohexanone are used in the fragrance industry. *trans*-Cinnamaldehyde has a strong spicy odour characteristic of cinnamon. 4-*tert*-butylcyclohexanol is used to form 4-*tert*-butylcyclohexyl acetate. 4-*tert*-butylcyclohexanol exists in the *cis*- and *trans*-forms. The *trans*-isomer has a rich, woody odour while the *cis*-isomer has a more intense flowery smell. The conversion of 4-*tert*-butylcyclohexanol to the corresponding 4-*tert*-butylcyclohexanone via Oppenauer oxidation had been reported over zeolite beta where the *cis*-isomer is preferentially converted due to the shape-selectivity of the catalyst [16].

Scheme 3. Oppenauer oxidation of cinnamyl alcohol, geraniol and 4-*tert*-butylcyclohexanol by furfural.

Recently, we found that suitably pretreated hydrous zirconia [17] and grafted zirconium 1-propoxide on a number of high surface supports (e.g. SBA-15) [18] are active catalysts in the MPV reduction of a series of carbonyl substrates. In this paper, the reverse liquid-phase Oppenauer oxidation of (a) cinnamyl alcohol to cinnamaldehyde, and (b) geraniol to citral using furfural as the oxidant was investigated (Scheme 3). For comparison, the Oppenauer oxidation of 4-*tert*-butylcyclohexanol (*cis*- and *trans*-) to 4-*tert*-butylcyclohexanone was also studied with furfural as the oxidant (Scheme 3). Hydrous zirconia and other solid acids were used as the catalysts.

2. Experimental

2.1. Catalyst preparation

The following catalysts were used in this study: a silica-free hydrous zirconia, ZrO_2-0 , was prepared by precipitation of $ZrCl_4$ with ammonia. Two silica-containing hydrous zirconia were prepared by digestion in a Pyrex flask for 2-days and 4-days, respectively. They contained 0.25% and 1.2 wt.% Si, respectively. The grafted zirconium propoxide catalysts were prepared following literature method [19]. $\gamma-Al_2O_3$ (Merck) was used as received. $Na-Al_2O_3$ was prepared by impregnating 1 g dried $\gamma-Al_2O_3$ in 100 mL 0.1 wt.% NaOH solution overnight followed by calcination at 500 °C for 12 h. Zeolite beta (Si/Al 13.1) and Mg/Al hydrotalcite were prepared according to reported methods, respectively [20,21].

2.2. Catalyst characterization

The surface area, pore size distribution, and pore volume were determined using a Quantachrome NOVA 2000. Different degassing conditions were used to dry the samples. Hydrous zirconia samples were degassed at 120 °C in a flow of nitrogen for 4 h prior to measurements. Supports (silica gel, MCM-41 and Al-MCM) and zeolite beta were dried under nitrogen at 300 °C. For the grafted catalysts, a number of procedures were used to remove water and any remaining solvent without destroying the grafted zirconium propoxide. These include drying under vacuum at room temperature and heating at 100 °C and 250 °C under nitrogen flow. The crystalline phase of the samples was determined by powder X-ray diffraction using a Siemens D5005 diffractometer (Cu anode) equipped with variable primary and secondary beam slits.

2.3. Catalytic testings

In the Oppenauer oxidation of cinnamyl alcohol, the reaction mixture containing 8 mmol (1.074 g) of cinnamyl alcohol (Fluka, >97%), 16 mmol oxidant, 15 mL toluene as solvent and 200 mg overnight-dried catalyst was heated under reflux (110 °C) with stirring. The oxidants used were furfural (1.536 g, Lancaster, 98%) and citral (2.461 g, Fluka, 97%).

The molar ratio of oxidant to reductant was 2:1. In addition, acetone was investigated as an oxidant; in this case, no toluene was added as the solvent. Instead, 15 mL acetone was used both as the solvent and oxidant.

In the Oppenauer oxidation of geraniol, 3.25 mmol (500 mg) of geraniol (Alfa, >99%), 3.25 mmol (312 mg) furfural or 3.25 mmol (345 mg) benzaldehyde (Fluka, >99%), 15 mL toluene and 250 mg catalyst were placed in the reaction flask. The catalyst was dried at 100 °C prior to reaction. The reaction mixture was heated under reflux with stirring. Different ratios of oxidant to reductant were investigated.

In the Oppenauer oxidation of 4-*tert*-butylcyclohexanol, the reaction mixture contained 3.85 mmol (593 mg) of 4-*tert*-butylcyclohexanol (Aldrich, 99%, *cis*- and *trans*-), 11.6 mmol (1.114 g) of furfural (Lancaster, 98%), 15 mL toluene as solvent and 100 mg overnight-dried catalyst. The reaction mixture was heated under reflux with stirring. The oxidant:reductant was 3:1.

3. Results

3.1. Textural properties

Table 1 shows the textural properties of the silica-free and silica-containing hydrous zirconia used in the oxidation of cinnamyl alcohol. The hydrous zirconia contained various amounts of Si, ranging from 0 wt.% to 1.2 wt.% Si. The presence of Si led to a stabilization of surface area and porosity. After calcination at 300 °C, the silica-containing hydrous zirconia catalysts had higher surface area and pore volume than the silica-free sample. However, all the samples were still X-ray amorphous, irrespective of the silica content.

The characterization results for grafted zirconium alkoxide and other solid catalysts can be found in our previous paper [17].

3.2. Oppenauer oxidation of cinnamyl alcohol to cinnamaldehyde

3.2.1. Effect of oxidant

The effect of different oxidants was investigated. Acetone, in large excess, is commonly used as the oxidant in the Oppenauer oxidation under homogeneous catalysis. However, no conversion was observed even after 24 h when acetone was used both as the oxidant and solvent in the oxidation of cinnamyl alcohol. This could be due to the lower oxidation temperature of 56 °C. Use of citral was more successful

Table 1
Textural properties of hydrous zirconia catalysts used in the Oppenauer oxidation of cinnamyl alcohol

Catalyst code	Surface area (m ² /g)	Pore volume (mL/g)
ZrO ₂ -0-300	186	0.15
ZrO ₂ -0.25Si-300	286	0.75
ZrO ₂ -1.2Si-300	316	0.74

Table 2
Catalytic activity for Oppenauer oxidation of cinnamyl alcohol over different oxidants with $\text{ZrO}_2\text{-1.2Si-300}$ as catalyst

Reaction time (h)	Citral		Furfural	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
1	22.2	100	56.2	100
2	28.2	100	69.6	100
4	37.0	100	80.3	100
24	42.2	100	92.4	100

(Table 2). After 1 h reaction, a conversion of 22% was measured. The oxidation product was cinnamaldehyde. Furfural was the best of the three oxidants studied. The reaction rate was the highest and after 1 h, the conversion to cinnamaldehyde was 56.2%.

3.2.2. Effect of silica in hydrous zirconia

Silica-free hydrous zirconia, calcined at 300 °C, showed poor catalytic activity in the Oppenauer oxidation of cinnamyl alcohol, using furfural as the oxidant. Even after 24 h, the conversion was less than 20% (Fig. 1). Silica-containing hydrous zirconia, $\text{ZrO}_2\text{-0.25Si-300}$, was more active; the conversion was 60% after 4 h. The activity increased with Si content of the hydrous zirconia. Over $\text{ZrO}_2\text{-1.2Si-300}$, the conversion was 80% after 4 h.

3.3. Oppenauer oxidation of geraniol to citral

3.3.1. Effect of oxidant

A comparison of furfural and benzaldehyde as oxidant was carried out. The reaction was carried out at 110 °C. Both furfural and benzaldehyde are common tertiary aldehydes with no active $\alpha\text{-H}$ and they had been used in both homogeneous [3] and heterogeneous [6,13] catalytic systems for Oppenauer oxidation. Use of furfural resulted in better catalytic activity and selectivity than benzaldehyde (Table 3). The selectivity

Table 3
Effect of oxidant for geraniol oxidation with $\text{ZrO}_2\text{-1.2Si-250}$ as catalyst

Reaction time (h)	Furfural		Benzaldehyde	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
1	44.7	84.1	37.4	91.8
2	60.5	86.0	49.0	90.4
4	68.0	90.4	61.4	88.4
6	78.6	91.0	64.2	87.1
24	85.3	93.8	77.5	66.7

was between 84% and 94% when furfural was used as the oxidant. However, for benzaldehyde, the selectivity decreased with reaction time, from >90% (2 h) to <70% (24 h). GC-MS results showed that the some isomerization side-reactions occurred for the formed citral product.

3.3.2. Effect of ratio of furfural to geraniol

The study of the thermodynamics of Oppenauer oxidation revealed that the reaction can be described as a redox equilibrium [1]. In order to increase the conversion, one way is to use a larger amount of oxidant. In this study, three different furfural/geraniol ratios were applied. When the furfural/geraniol ratio was increased from stoichiometric amount to fourfold excess, the conversion of geraniol after 24 h increased from 70% to 90%. A higher furfural/geraniol ratio of 8 did not increase the conversion significantly (Fig. 2). This is unusual, since the MPVO reaction is a reversible one; if one increases the amount of oxidant (in our case, furfural), the alcohol substrate can be converted completely. The most possible explanation is that after long time reaction (24 h), the hydrous zirconia catalyst was deactivated to great extent, resulting in the incomplete conversion of geraniol.

3.3.3. Catalytic activity of hydrous zirconia

In this study, the furfural to geraniol ratio was fixed at 1:1. Silica-containing hydrous zirconia, $\text{ZrO}_2\text{-1.2Si-T}$, was

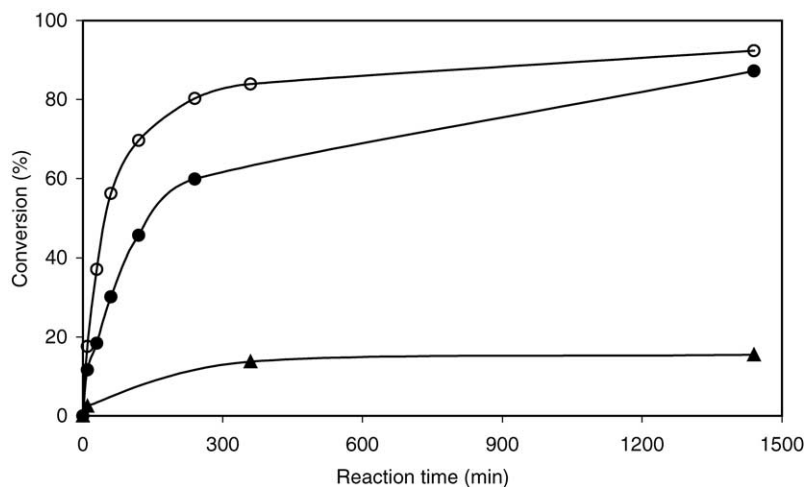


Fig. 1. Conversion of cinnamyl alcohol over hydrous zirconia catalysts (▲) $\text{ZrO}_2\text{-0-300}$, (●) $\text{ZrO}_2\text{-0.25Si-300}$ and (○) $\text{ZrO}_2\text{-1.2Si-300}$. Catalyst weight: 200 mg.

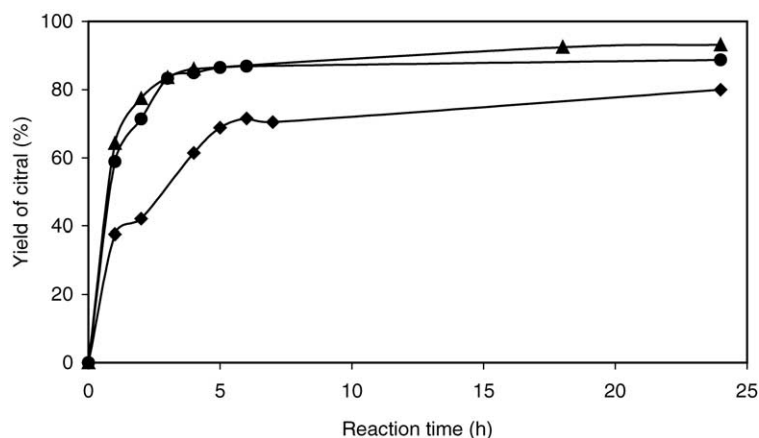


Fig. 2. Effect of ratio of furfural to geraniol in the Oppenauer oxidation of geraniol (◆) 1:1 (●) 4:1 and (▲) 8:1 with $ZrO_2-1.2Si-250$ as catalyst. Catalyst weight: 250 mg.

calcined at different temperatures to obtain a series of catalysts. Table 4 compares the conversion and selectivity after 1 h over these differently-calcined zirconia catalysts. The highest conversion (53%) was obtained in the catalysts calcined at 250–350 °C. Catalysts calcined at higher temperatures were less active. A conversion of 24% was obtained over the 500 °C-calcined sample. It is only after 24 h that the conversion increased to >70%. The selectivity towards citral was >90%. Side products were due to the isomerisation of geraniol where the double bond was shifted in position (e.g. linalool) and dehydration of the geraniol and the isomeric alcohols (e.g. 1,3,6-octatriene-3,7-dimethyl and 7-methyl-3-methylene-1,6-octadiene). The selectivity towards citral increased with calcination temperature of the hydrous zirconia so that citral was the only product detected over the 500 °C-calcined zirconia.

Silica-free hydrous zirconia catalysts, ZrO_2-0-T , were also tested for the Oppenauer oxidation of citral. The sample calcined at 250 °C was the most active for the oxidation and a conversion of 54.4% was obtained after 1 h (Table 5). After 24 h, the conversion reached almost 90% (Fig. 3). The activity of $ZrO_2-0-250$ is very similar to that of the silica-containing hydrous zirconia, $ZrO_2-1.2Si-250$. However, the influence of calcination temperature on the catalytic activity is more pronounced in the silica-free sample. The conver-

Table 4
Catalytic activity after 1 h for Oppenauer oxidation of geraniol over $ZrO_2-1.2Si-T$ vs. calcination temperature

Calcination temperature (°C)	Conversion (%)	Selectivity (%)
200	44.7	83.2
250	53.7	84.1
300	52.3	87.3
350	49.4	91.4
400	38.4	93.0
450	33.7	94.8
500	24.4	100

Catalyst weight: 250 mg.

sion decreased significantly for silica-free hydrous zirconia calcined at 350 °C and higher. After 1 h and 24 h reaction, $ZrO_2-0-350$ had a conversion of 40% and 59%, respectively. The 500 °C-calcined sample had an even lower activity with a conversion of 5.10% and 38% after 1 h and 24 h, respectively.

3.3.4. Catalytic activity of grafted zirconium propoxide

The grafted zirconium 1-propoxide catalysts were found to be very active towards the Oppenauer oxidation of geraniol.

Table 5
Catalytic activity of ZrO_2-0-T after 1 h for Oppenauer oxidation of geraniol vs. calcination temperature

Calcination temperature (°C)	Conversion (%)	Selectivity (%)
250	54.4	92.0
300	44.5	92.4
350	39.6	100
500	5.10	100

Catalyst weight: 250 mg.

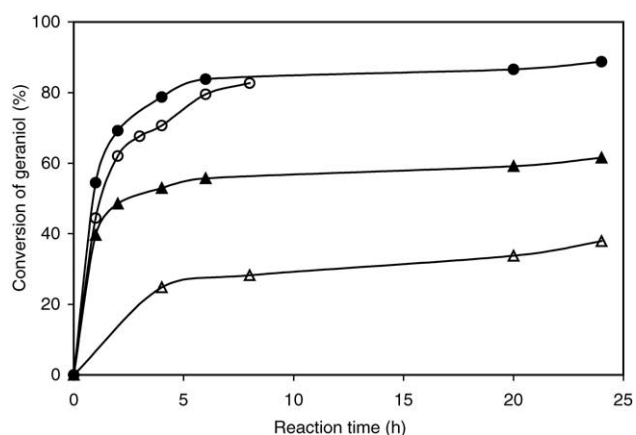


Fig. 3. Effect of calcination temperatures on the catalytic activity of ZrO_2-0-T in the Oppenauer oxidation of geraniol (●) 250 °C, (○) 300 °C, (▲) 350 °C and (△) 500 °C.

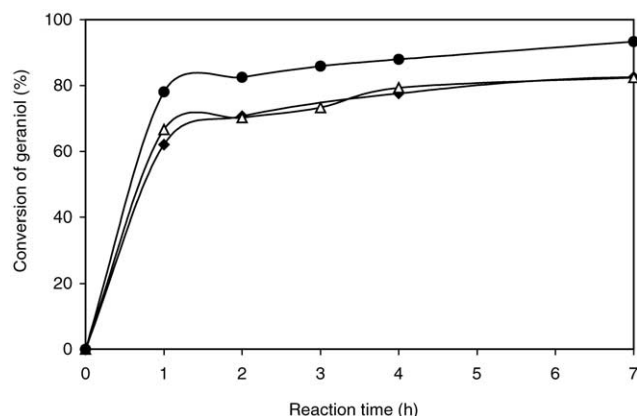


Fig. 4. Activity of grafted zirconium 1-propoxide catalysts in oxidation of geraniol (◆) $Zr(OR)_x/SiO_2$, (△) $Zr(OR)_x/MCM41$ and (●) $Zr(OR)_x/AlMCM$. Catalyst weight: 250 mg.

Within 1 h reaction, the conversion of geraniol reached >60% (Fig. 4). For both $Zr(OR)_x/SiO_2$ and $Zr(OR)_x/MCM41$, the conversion leveled off at 80% after 24 h reaction; while for $Zr(OR)_x/AlMCM41$ catalyst, the conversion leveled off at 90% after 24 h reaction (data not shown in Fig. 4). The possible reason for this conversion level-off is the catalyst deactivation at prolonged reaction (24 h). The selectivity to the citral product was 100% for $Zr(OR)_x/SiO_2$ (Fig. 5). However, over $Zr(OR)_x/MCM41$, the selectivity towards citral was initially 100% but decreased after 8 h to 68%, as the formed citral underwent further isomerisation and dehydration side-reactions. The side products were identified by GC–MS. The conversion over $Zr(OR)_x/AlMCM$ was >90% after 7 h. However, the selectivity to citral was only 40% after 1 h and decreased to 23% at longer time. Due to the acidic nature of the AlMCM support, the dehydration of geraniol was a competing reaction, resulting in higher conversion but lower selectivity towards citral.

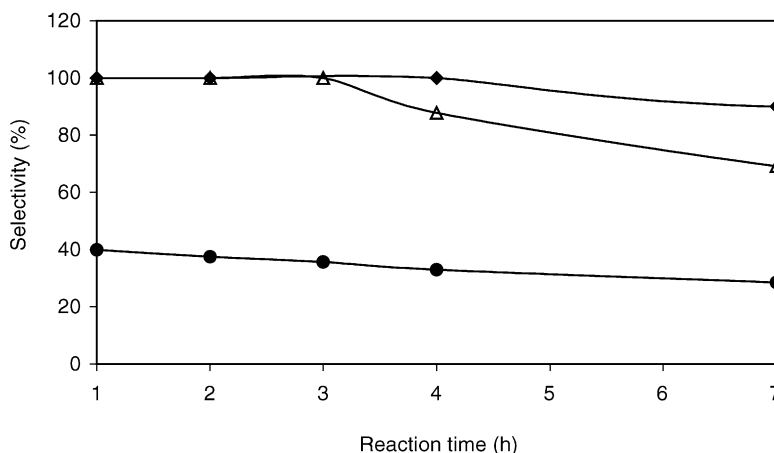


Fig. 5. Selectivity to citral for grafted zirconium 1-propoxide catalysts in oxidation of geraniol (◆) $Zr(OR)_x/SiO_2$, (△) $Zr(OR)_x/MCM41$ and (●) $Zr(OR)_x/AlMCM$. Catalyst weight: 250 mg.

Table 6
Catalytic activity of solid catalysts used in the Oppenauer oxidation of geraniol after 4 h

Catalyst (%)	Conversion (%)	Selectivity (%)
Zeolite beta (Si/Al 13.1)	28.4	0
Mg/Al hydrotalcite (Mg/Al 3)	29.0	92.2
$\gamma-Al_2O_3$	59.9	96.5
Na- Al_2O_3	52.3	100
$Zr(OR)_x/SiO_2$	77.6	100
$Zr(OR)_x/MCM41$	79.3	87.8
$Zr(OR)_x/AlMCM$	88.0	32.9

Catalyst weight: 250 mg.

3.3.5. Catalytic activity of other solid catalysts

Table 6 compares the activity and selectivity of several solid catalysts in the Oppenauer oxidation of geraniol to citral. Although zeolite beta was reported to be very efficient in the Oppenauer oxidation of 4-*tert*-butylcyclohexanol (*cis*- and *trans*-) to the corresponding ketone [16], it was found in this study that it could not efficiently catalyse the Oppenauer oxidation of geraniol to citral. The conversion was 28.4% after 4 h but no citral was formed over zeolite beta (Si/Al 13.1). Instead, over this acidic catalyst, the main products were the isomeric alcohols of geraniol and dehydration products of geraniol and its isomers.

Calcined layered double hydroxides (LDHs) were reported to be active in the hydrogenation of citral [21]. However, this study showed that it is less active in the reverse Oppenauer oxidation of geraniol. Hydrous zirconia and grafted zirconium propoxide catalysts were more active than the Mg/Al hydrotalcite (Table 6). The activity over Mg/Al hydrotalcite (Mg/Al 3) was rather limited with 29.0% conversion of geraniol and 92% selectivity to citral after 4 h reaction.

Over $\gamma-Al_2O_3$, a 60% conversion and a selectivity of 96% to citral were achieved after 4 h reaction. NaOH-impregnated $\gamma-Al_2O_3$, Na- Al_2O_3 , had a slightly lower conversion of 52% but a selectivity of 100% towards citral. This may be

Table 7
Catalytic activity for Oppenauer oxidation of 4-*tert*-butylcyclohexanol over different catalysts by using acetone and furfural as the oxidant

Catalyst	Conversion (selectivity) (%)			
	Acetone		Furfural	
	1 h	24 h	1 h	24 h
Zeolite beta-13.1	2.80 (100)	9.43 (100)	5.57 (100)	23.6 (100)
ZrO ₂ -1.2Si-300	1.60 (100)	7.61 (100)	25.1 (100)	60.9 (100)
Zr(OR) _x /SiO ₂	1.10 (100)	3.82 (100)	31.6 (100)	43.4 (100)

Catalyst weight: 100 mg.

explained by the removal of the acidic sites responsible for the dehydration side reactions when the γ -Al₂O₃ was treated by NaOH solution.

3.4. Oppenauer oxidation of 4-*tert*-butylcyclohexanol to 4-*tert*-butylcyclohexanone

The oxidation of 4-*tert*-butylcyclohexanol (*cis*- and *trans*-) was studied over three catalysts—zeolite beta (Si/Al 13.1), ZrO₂-1.2Si-300 and Zr(OR)_x/SiO₂. Both acetone and furfural were used as the oxidant (Table 7). A much higher conversion of 4-*tert*-butylcyclohexanol was obtained with furfural than acetone. This is not surprising, as the reaction temperature was higher when furfural was used instead of acetone. In addition, the oxidation potential of furfural is higher than that of acetone [1]. Both hydrous zirconia and Zr(OR)_x/SiO₂ were more active than zeolite beta. For the three catalysts, only 4-*tert*-butylcyclohexanone was formed.

4. Discussion

For Oppenauer oxidation in this work, the decrease in the activity of hydrous zirconia with calcination temperature suggests that the hydroxyl groups are important in the reaction. We once proposed that, in the MPV reduction of cinnamaldehyde, the hydroxyl groups on the surface of hydrous zirconia act as sites for ligand exchange with 2-propanol to form 2-propoxide species on the catalysts [17]. Similarly, in this work, the ligand exchange between surface hydroxyl groups and alcohol reactant to form alkoxide species is important. After being calcined at higher temperature, the hydroxyl groups on hydrous zirconia were removed irreversibly, thus resulting in lower catalytic activity. Therefore, the catalytic activity of hydrous zirconia can be correlated to the surface hydroxyl concentration (i.e. surface area). For both Si-free and Si-containing hydrous zirconia, the most active catalysts were formed by calcining at 250–300 °C (Tables 4 and 5), this corresponds to the maximum surface area of catalysts. With calcination temperature higher than 350 °C, the activity drops. However, this effect is more pronounced in the case of Si-free hydrous zirconia catalysts, which is in accordance with the change of surface area. For Si-free catalysts, the surface area suffers a more drastic drop with higher calcination

temperature, as compared to the Si-containing catalysts. Our previous work had showed that the incorporation of Si in hydrous zirconia, even at low concentration, is able to stabilize the surface area relative to the Si-free hydrous zirconia [17].

As demonstrated in the Oppenauer oxidation of both cinnamyl alcohol and geraniol, hydrous zirconia catalysts with higher Si contents are more active (Fig. 1, Tables 4 and 5), especially for catalysts calcined at high temperature (e.g. 500 °C). This can be attributed to the higher surface area (i.e. higher accessible surface hydroxyl binding sites) associated with the catalysts with higher Si content (Table 1).

The oxidation of allylic alcohols (cinnamyl alcohol and geraniol) was more facile than aliphatic alcohol (4-*tert*-butylcyclohexanol). The presence of a double bond adjacent to the hydroxyl group facilitates the formation of the alkoxide species with the surface hydroxyl groups because of the effect of electron delocalization.

The influence of the oxidant is also important. Furfural has an aromatic five-membered ring. It is less bulky than an aromatic six-membered ring as found in benzaldehyde. The bulky group in benzaldehyde is likely to hinder the formation of the six-membered transition state in the hydride transfer, as compared to furfural. Acetone showed rather low activity and this may be attributed to the rather low reaction temperature (refluxing temperature of 56 °C), its rather low oxidation potential [1,4] and bulkiness of the two methyl groups.

Different solid catalysts had been used for the Oppenauer oxidation of a variety of alcohols, especially primary alcohols [5–14]. Kuno et al. [6,7] used hydrous zirconia prepared from the precipitation method for the reaction. However, as compared to our thermally-stable and high surface area hydrous zirconia which was incorporated with a small amount of Si, our catalytic results are better. The catalytic activity of Si-free hydrous zirconia in our work is comparable to that in Kuno's report. Another difference is that we used furfural, a relatively lower-boiling-point oxidant, for the reaction. Although furfural had been found efficient for Oppenauer oxidation in homogeneous catalytic systems [3], it is only occasionally used in heterogeneous catalytic system [6,13]. We believe that the use of furfural as oxidant in hydrous zirconia-catalysed systems facilitates the products separation and makes the Oppenauer oxidation amenable to scale-up. When compared with the calcined layered double hydroxide catalysts, our hydrous zirconia is easy to prepare and recycle. As showed in Rao's report [10], the ratio of Mg/Al in calcined layered double hydroxides had to be adjusted carefully; in addition, the preparation and recycling procedures are somewhat tedious. With respect to Al₂O₃ catalyst [12], we found that a much larger amount of it had to be used for the reaction. Choplin and co-workers [13,14] demonstrated that the silica anchored mononuclear (tris)isopropoxyzirconium, (=SiO)Zr(Oi-Pr)₃, is an efficient catalyst for the Oppenauer oxidation of alcohols, and this grafted catalyst is very similar to our grafted zirconium 1-propoxide catalysts on silica

gel and pure-silica MCM-41. Through our work, we found that the supports used for grafting had great influence on the catalytic activity and especially the selectivity towards the desired aldehyde product. When pure siliceous supports, e.g. silica gel and pure-silica MCM-41, are used, the selectivity to the aldehyde products are much higher than that when acidic AIMCM support was used. Although zeolite beta had been reported to be efficient in the Oppenauer oxidation of 4-*tert*-butylcyclohexanol [16], we found that catalytic activity and selectivity of zeolite beta for Oppenauer oxidation are highly reactant-dependent. For instance, it is not efficient for the Oppenauer oxidation of cinnamyl alcohol (data not showed) and geraniol. For geraniol oxidation, although moderate conversion was measured, no any desired citral product was obtained, with all the consumed geraniol converting into side-products. By contrast, hydrous zirconia used in this work is applicable to a variety of alcohol substrates, including primary and secondary alcohols, allylic and aliphatic alcohols, etc.

5. Conclusions

Furfural was found to be an efficient oxidant in the Oppenauer oxidation of cinnamyl alcohol, geraniol and 4-*tert*-butylcyclohexanol. The most active hydrous zirconia catalysts were formed by calcining at 250–300 °C. Grafted zirconium 1-propoxide on silica gel and MCM-41 were active in the Oppenauer oxidation of geraniol. However, over an acidic support such as AIMCM, the grafted zirconium 1-propoxide catalysed the dehydration and isomerisation of the geraniol. Solid catalysts such as γ -Al₂O₃, Na–Al₂O₃, zeolite beta and Mg/Al hydrotalcite showed moderate catalytic activity and selectivity in the Oppenauer oxidation of geraniol. As compared to other solid catalysts, e.g. low-surface-area hydrous zirconia, Mg–Al hydrotalcite, Al₂O₃ and zeolite beta, thermally-stable and high-surface area hydrous zirconia used in this work is active and selective towards the formation of carbonyl oxidation products, easy to prepare and recycle, and applicable to a variety of alcohol substrates.

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