Available online at www.sciencedirect.com

Catalysis Today 97 (2004) 249–255

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Zirconia catalysts in Meerwein-Ponndorf-Verley reduction of citral

Yongzhong Zhu, Shuhua Liu, Stephan Jaenicke,
Gaikhuan Chuah*

[a]Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Singapore

Abstract

Zirconium-containing catalysts were found to be active in the Meerwein-Ponndorf-Verley (MPV) reduction of citral. Good activity and selectivity to the reduced alcohol, geraniol and nerol, were observed over hydrous zirconia and zirconium 1-propoxide supported on silica. In particular, hydrous zirconia calcined at temperatures below 300 °C was highly active. Hydrous zirconia catalysts modified by NaOH, NH_4F, PO_4^{3-} and SO_4^{2-} had lower activity. Surface hydroxyl groups are postulated to be involved in ligand exchange with the reductant, 2-propanol. Zr-zeolite beta showed high activity, but poorer selectivity than the other two samples, due to subsequent dehydration of the product formed. For all catalysts, the *trans*-isomer of citral was preferentially reduced over the *cis*-isomer.

Keywords: Hydrous zirconia; Grafted zirconium 1-propoxide; Zr-zeolite beta; MPV reduction of citral; Geraniol; Nerol

1. Introduction

Zirconium is an element which is increasingly used in catalysis due to its interesting and potentially useful catalytic properties. The addition of zirconium in catalysts has in many cases led to an improvement in activity, thermal stability or selectivity. One of the most important uses of zirconia is as an oxidation catalyst. Cerium–zirconium mixed oxide has been reported to be an excellent promoter for oxygen storage capacity in automotive three-way catalysts [1–3]. Furthermore, the addition of zirconia inhibits the sintering of cerium oxide resulting in better thermal stability of the catalyst. The presence of zirconium in supports used for hydrotreating heavy crudes increases the resistance to sintering, thus minimizing loss of activity during regeneration. Zirconia is found to be active in a number of reactions such as hydrogenation of aromatic carboxylic acid [4], Fischer–Tropsch synthesis of alkenes from carbon monoxide and hydrogen over zirconia supported nickel catalyst [5], methanol synthesis over zirconia supported copper catalyst [6], etc. Zirconia supported tungsten oxide functions as strong solid acids for the isomerization of light alkanes [7] and both sulfated and perchlorated zirconia have been shown to be highly acidic [8].

The Meerwein-Ponndorf-Verley (MPV) reduction of carbonyl compounds using secondary alcohols as hydrogen donor and the Oppenauer oxidation of alcohols, with oxidants such as furfural, benzophenone and cyclohexanone, are highly selective reactions [9]. Both reactions can be catalyzed using homogeneous catalysts such as metal alkoxides. Heterogeneous catalysts for the Meerwein-Ponndorf-Verley-Oppenauer (MPVO) reactions include zeolites [10–12], grafted alkoxides [13,14], metal oxides such as magnesium oxide, zirconia, silica, alumina [15], etc. Zeolite beta has been reported to show excellent activity for the Meerwein-Ponndorf-Verley-Oppenauer reaction [10]. Lewis acid sites were found to be the active centers [11]. In particular, the formation of thermodynamically less stable *cis*-4-*tert*-butylcyclohexanol from 4-*tert*-butylcyclohexanone occurs with a high stereoselectivity; the reverse Oppenauer oxidation occurred preferentially with the *cis*-alcohol rather than the *trans*-isomer. Corma et al. recently reported that Sn-beta zeolite showed excellent activity and selectivity in the MPV reduction of several ketones [12]. In addition, the Sn-zeolite beta was found to be more resistant to the

---

* Corresponding author. Fax: +65 6779 1691
E-mail address: chmcgk@nus.edu.sg (G. Chuah).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.07.002

presence of water in the reaction media than Ti- or Al-zeolite beta.

In this study, we investigate the use of zirconium-containing catalysts in the MPV reduction of citral (3,7-dimethyl-2,6-octadienal). This important aldehyde possesses an isolated C=C bond in addition to the conjugate C=C and C=O bonds. The C=C bond is more readily hydrogenated than the C=O bond. Compared to other unsaturated aldehydes, e.g., cinnamaldehyde, there have been few reports on the reduction of citral under MPV conditions [16–18]. Citral occurs as *cis*- and *trans*-isomers known as neral and geranial, respectively. The reduced alcohols, nerol and geraniol, are used in the fragrance industry for their pleasant roselike odour. Scheme 1 outlines the reduction of citral to the corresponding alcohols using 2-propanol. A comparison is carried out on the activity of hydrous zirconia, zirconium 1-propoxide grafted onto silica gel and Zr-zeolite beta for the MPV reduction of citral to nerol and geraniol.

2. Experimental

2.1. Materials

Hydrous zirconia was prepared by the precipitation of a 10 wt.% zirconium chloride solution with excess 5 M ammonium hydroxide. The precipitate was washed until free of chloride, dried at 100 °C and calcined from 200 °C to 500 °C for 12 h at each temperature. One percent NaOH-ZrO_2 was prepared by impregnating 1 g of hydrous zirconia in 100 cm^3 of 1.0% NaOH solution for 20 h. After drying at 100 °C overnight, the sample was calcined at 500 °C for 12 h. Similarly, 1.0% NH_4F-ZrO_2 and 1.0% PO_4-ZrO_2 were prepared by impregnating 1 g of hydrous zirconia in 100 cm^3 of 1.0% NH_4F and 1.0% $(NH_4)_2HPO_4$ solutions, respectively. The samples were calcined at 300 °C for 12 h. Sulfated zirconia was prepared by treating the dried hydrous zirconia in 0.25N H_2SO_4 for 1 h at room temperature using 5 cm^3 of solution per gram of solid. The resulting solid was filtered and dried at 100 °C. It was subsequently calcined at 600 °C for 12 h.

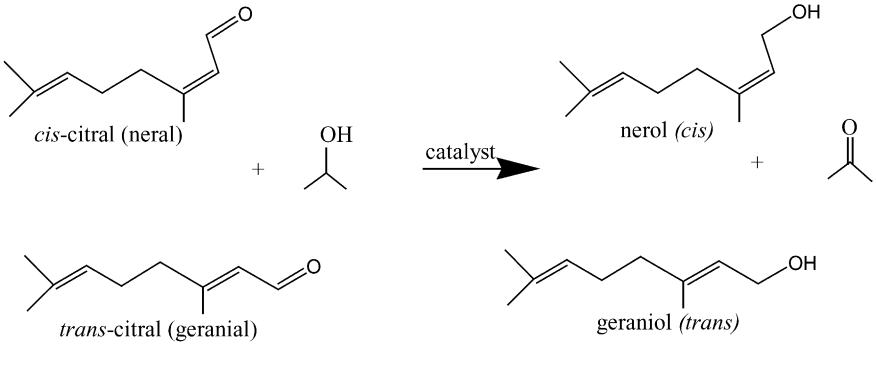
Grafted zirconium propoxide was prepared by first drying the silica support (silica gel 60) at 300 °C for 4 h under flowing nitrogen. It was then added to a solution of zirconium 1-propoxide in dry hexane. The suspension was refluxed at 69 °C for 12 h. The concentration of zirconium 1-propoxide in hexane was calculated to give slight stoichiometric excess based on an approximate surface hydroxyl group density of 1.4 OH/nm^2 [19]. 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-free Zr-zeolite beta catalyst containing Si/Zr 100 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. for the preparation of Al-free Sn-beta [12]. Typically, tetraethylorthosilicate (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) were added. The final gel had the composition 1 SiO_2: 0.01 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 °C for 20 days [20].

The BET surface area, pore volume and pore size distribution (BJH method) of the solid catalysts were measured with a Quantachrome NOVA 2000 instrument. Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer using a Cu anode operated at 40 kV and 40 mA. The zirconium content of the grafted catalyst and Zr-zeolite beta was determined by ICP-AES after dissolution of the solids in HF.

2.2. Catalytic MPV reduction of citral

The Meerwein-Ponndorf-Verley reaction was carried out in the liquid phase. The reaction mixture consisting of 3.25 mmol (500 mg) of citral (Fluka, 97% purity, *e*/*z* = 63/37), 196 mmol (15 cm^3) 2-propanol and 250 mg of dried catalyst were placed in a 25 cm^3 two-necked pear-shaped



Scheme 1. Meerwein-Ponndorf-Verley reduction of citral by 2-propanol.

Table 1
Textural properties of catalysts

Catalyst	Calcination temperature (°C)	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Zr content (wt.%)
$Zr(OH)_4$	200	283	0.49	–
$Zr(OH)_4$	250	257	0.46	–
$Zr(OH)_4$	300	237	0.45	–
$Zr(OH)_4$	350	176	0.44	–
$Zr(OH)_4$	400	104	0.42	–
$Zr(OH)_4$	450	79.6	0.41	–
ZrO_2	500	54.4	0.26	–
NaOH-ZrO_2-300	300	254	0.46	–
NH_4F-ZrO_2-300	300	194	0.40	–
PO_4-ZrO_2-300	300	296	0.48	–
NH_4F-ZrO_2-500	500	54.8	0.18	–
PO_4-ZrO_2-500	500	246	0.43	–
SO_4-ZrO_2-500	500	141	0.33	–
SiO_2	300	307	0.77	–
$Zr(OPr)_4/SiO_2$	–	295	0.62	5.5
Zr-beta zeolite	580	490	0.27	1.3

flask. The 2-propanol was dried over 4A molecular sieves prior to use. The reaction mixture was heated to reflux at 82 °C. Samples were withdrawn at regular intervals and analysed by GC (HP6890, HP 5 cross-linked 5% phenyl methyl siloxane, FID). The products were identified on the basis of their retention times by comparing with authentic samples and by GC-MS analysis (Shimadzu GCMS-QP5000). 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 citral.

3. Results

3.1. Textural properties

The surface area of the hydrous zirconia decreased from 283 $m^2 g^{-1}$ to 54.4 $m^2 g^{-1}$ when the calcination temperature was increased from 200 °C to 500 °C (Table 1). The pore volume also decreased from 0.49 $cm^3 g^{-1}$ to 0.26 $cm^3 g^{-1}$ in the same temperature range. Hydrous zirconia has a range of pore sizes from microporous to mesoporous (Fig. 1a). Calcination at 500 °C removed the micropores so that only pores in the range of 20–400 Å were present. Hydrous zirconias calcined below 400 °C were X-ray amorphous. Crystallinity was first observed after calcination at 450 °C. A mixture of tetragonal and monoclinic phases was observed. As hydrous zirconia is an amphoteric compound, impregnating cations or anions onto its surface will modify the acid–base property. The presence of F^-, PO_4^{3-} and SO_4^{2-} ions gives rise to enhanced acidity, while the incorporation of Na^+ leads to increased basicity. Besides affecting the chemical property of hydrous zirconia, the textural properties can also be influenced by the presence of the ions (Table 1). Hydrous zirconia impregnated with PO_4^{3-} and NaOH had higher surface area than the pure hydrous zirconia after heat treatment at 300 °C. The pore volume of PO_4-ZrO_2-300 and NaOH-ZrO_2-300 was also only slightly decreased from that of the hydrous zirconia support, ZrO_2-100. This shows that there was no pore blockage due to the impregnation of these ions. The incorporation of F^- led to a reduction in the surface area after calcination to 300 °C. After further calcination to 500 °C, the surface area of NH_4F-ZrO_2-500 was only 54.8 $m^2 g^{-1}$, similar to that of pure ZrO_2-500. Hence, the F^- ion is not effective in stabilizing the surface area of zirconia. In contrast, the phosphated, sulfated and NaOH-treated zirconia had much higher surface area than ZrO_2-500. The adsorbed phosphate species had been identified by Raman, DRIFT and ^{31}P-MAS-NMR as pyrophosphates and doubly bridging or chelate-bonded orthosphosphates [21]. The sulfate ion also binds via surface hydroxyl groups on the hydrous zirconia [22]. By interaction with the hydroxyl groups, sintering and loss of surface area were reduced during calcination.

Silica gel has a wide pore diameter of 64 Å (Fig. 1b). After grafting, the mean pore dimension in the grafted sample was 57 Å. The total pore volume decreased from 0.77 $cm^3 g^{-1}$ to 0.62 $cm^3 g^{-1}$. The pore size distribution curve was shifted to smaller pore sizes without change in the shape of the curve (Fig. 1). This suggests that the zirconium 1-propoxide is evenly distributed on the support so that a narrowing of the mean pore size is obtained. From ICP-AES, the Zr loading was 5.5 wt.% which gives a surface coverage of 0.81 nm^2/Zr propoxide. This value is very close to that calculated using the kinetic diameter of zirconium 1-propoxide. Molecular mechanics (MM+; Hyperchem) calculation gives a kinetic diameter of 1.79 nm for trimeric zirconium 1-propoxide, corresponding to a surface coverage of 0.84 nm^2/Zr propoxide [23]. From the close fit of the experimental and calculated values, it strongly supports the suggestion that a monolayer is obtained on the silica at 5.5 wt.% Zr.

Zr-zeolite beta had a surface area of 490 $m^2 g^{-1}$ with a pore volume of 0.27 $cm^3 g^{-1}$. The powder XRD diffracto-

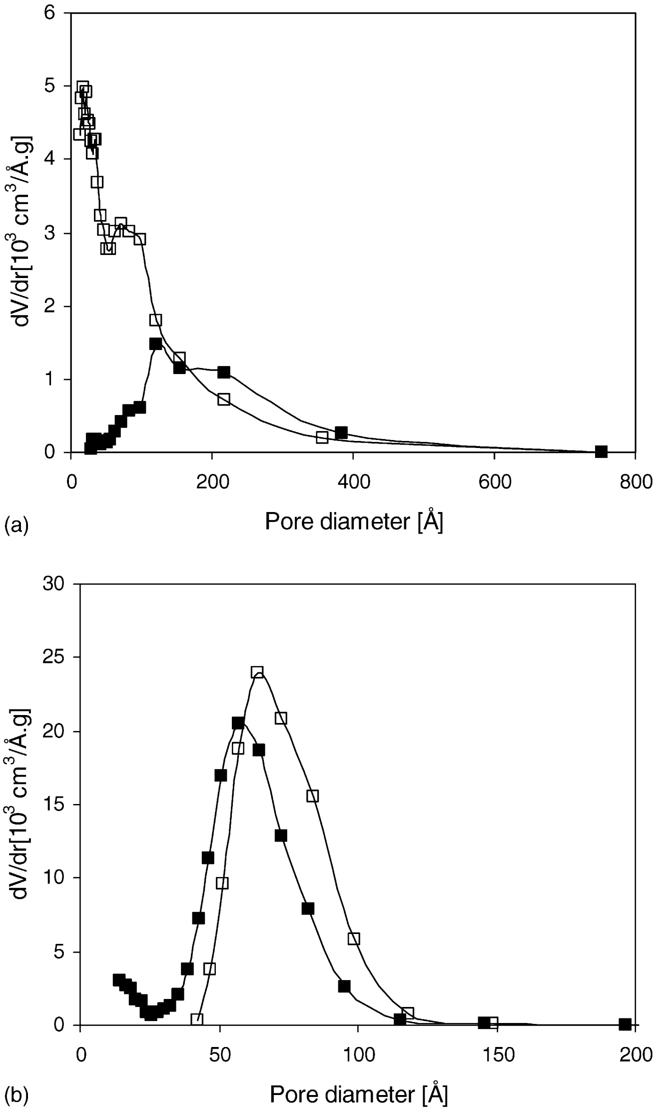


Fig. 1. Pore size distribution curve of (a) hydrous zirconia calcined at (□) 300 °C and (■) 500 °C; (b) SiO_2 and $Zr(OPr)_4/SiO_2$.

gram of the Zr-zeolite beta shows the characteristic peaks of well-crystallized zeolite beta. A pronounced asymmetry in the broad peak at $2\theta \sim 8^\circ$ indicates the presence of the two iso-structures of zeolite beta. From ICP-AES, the Si/Zr ratio was found to be 107.

3.2. Catalytic activity

The catalytic activity of the hydrous zirconia as a function of the calcination temperature is given in Fig. 2. The conversion of citral was high over pure hydrous zirconia calcined up to 300 °C. After 300 min, more than 90% conversion was reached. The selectivity towards geraniol and nerol was high, 94% initially, but decreased to 88% at longer times (Table 2). Isomerization of the formed alcohols led to by-products, 3,7-dimethyl 1,6-octadien-3-ol and 2,7-dimethyl 2,6-octadien-1-ol, lowering the selectivity of the reaction. The rate of reaction decreased when the catalyst was calcined at 400 °C and higher. Even after 24 h, the conversion was less than 30%. The initial rate of MPV reduction decreased by about six-fold over hydrous zirconia calcined at 300 °C and at 400 °C, respectively. The drop in activity can only be partly attributed to the decrease in surface area, which was halved in this temperature range. Despite the drop in activity, the selectivity to the alcohols remained high, >95%.

Modifying the hydrous zirconia with other oxides did not improve the activity or selectivity. Comparing the activity after 30 min, the basic catalyst, NaOH-ZrO_2-300, had a conversion of 7% as compared to 33.5% over pure hydrous zirconia. As the selectivity for the formation of geraniol and nerol remained high, ~90%, it would suggest that the active sites for citral conversion has been reduced, but that the presence of Na^+ ions did not influence the selectivity. Both fluorinated hydrous zirconia, NH_4F-ZrO_2-300, and phosphated zirconia, PO_4-ZrO_2-300, had lower conversion

Table 2
Conversion and selectivity of citral over zirconium catalysts at different reaction times

Catalyst	30 min		300 min	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
ZrO_2-300	33.5	94.2	90.6	88.2
NaOH-ZrO_2-300	7.0	89.7	22.5	89.5
NH_4F-ZrO_2-300	3.7	67.1	15.6	62.3
PO_4-ZrO_2-300	7.1	66.2	15.6	67.3
SO_4-ZrO_2-500	35.2	0	90.8	0
Zr-zeolite beta	39.4	87.5	90.8	73.8
$Zr(OPr)_4/SiO_2$	21.7	97.3	81.4	94.6

than the hydrous zirconia, 3.7% and 7.0%, respectively. Unlike NaOH-ZrO_2-300, the selectivity was decreased by the presence of fluoride or phosphate ions to ~67%. More dehydration products of the formed geraniol and nerol were detected over these catalysts. Over a strongly acidic catalyst like SO_4-ZrO_2-500, the conversion was high, but no unsaturated alcohol was formed. Instead, only cracking and dehydration products were observed.

Although the Zr loading in Zr-zeolite beta is very low, its activity is similar to that of the most active hydrous zirconia (Fig. 3). The reaction proceeded to almost 90% conversion after 240 min. Besides the unsaturated alcohols, geraniol and nerol, the concentration of by-products was higher than over hydrous zirconia. The initial selectivity to the unsaturated alcohols was 87.5%, but this decreased to 73.8% after 300 min. The main by-products observed by GC-MS were predominantly due to dehydration of citral/alcohols with formulae of $C_{10}H_{14}$ as well as etherification between geraniol/nerol and 2-propanol. These by-products increased with reaction time. The larger number of by-products is most probably due to the more acidic nature of the Zr-zeolite beta as compared to hydrous zirconia. Of the two unsaturated alcohols, geraniol was the main product formed (Fig. 4). The initial geraniol:nerol ratio was 97:3, but after 300 min reaction, the ratio was 87:13. Obviously, the pore size of the zeolite beta plays a role in the conversion of *cis*- and *trans*-citral with the latter having a higher rate of conversion.

The silica support was not active in the MPV reduction of citral. However, after grafting with zirconium 1-propoxide, the sample showed good activity, although the rate of reaction was smaller than that for Zr-zeolite beta or hydrous zirconia calcined at 300 °C (Fig. 3). The conversion after 60 min was 37.6% compared to 57.4% for Zr-zeolite beta and 66.4% for hydrous zirconia. The initial selectivity to geraniol and nerol was very high, 97.3%, and decreased slightly to 94.2% after 300 min. 1-Propanol was detected in the reaction mixture immediately after the start of the reaction, indicating that the 1-propoxide ligand was readily exchanged with the reductant, 2-propanol. The rate of conversion of *trans*-citral was higher than *cis*-citral, although the difference in the two rates was smaller than for Zr-zeolite beta. The filtrate obtained after refluxing the grafted catalyst in 2-propanol was inactive for the MPV reduction of citral, showing the absence of leaching into the reaction medium. However, lower activity was observed

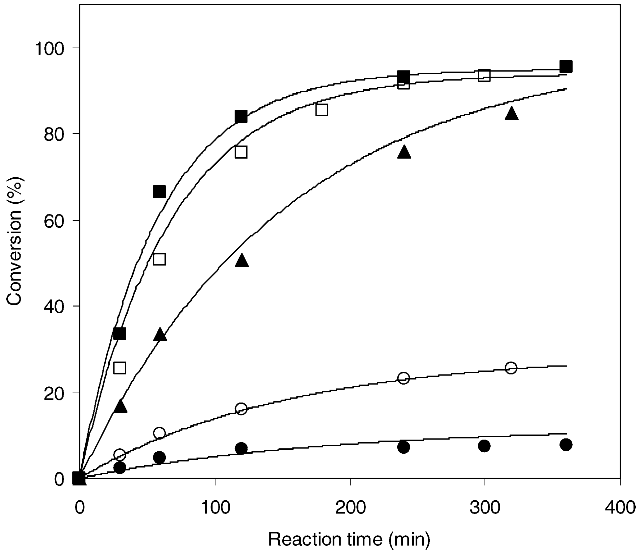


Fig. 2. Conversion of citral over pure hydrous zirconia. Calcination temperature: (■) 250 °C, (□) 300 °C, (▲) 350 °C, (○) 400 °C and (●) 500 °C.

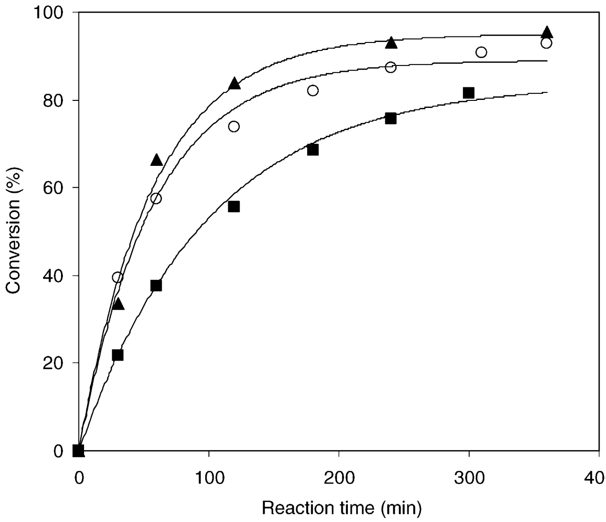
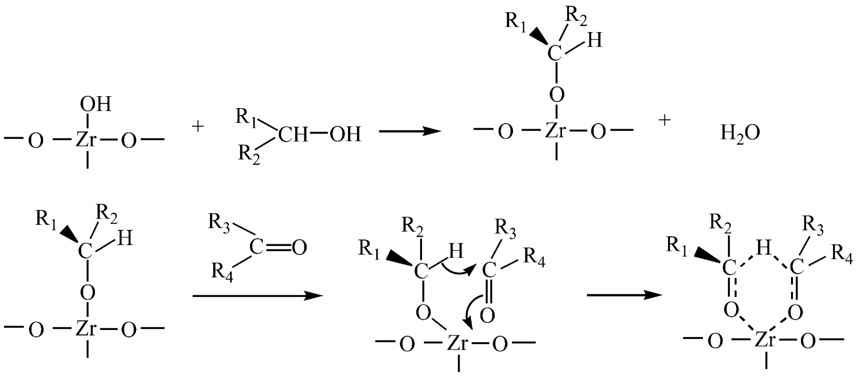


Fig. 3. Conversion of citral over (▲) hydrous zirconia dried at 300 °C, (○) Zr-zeolite beta and (■) $Zr(OPr)_4/SiO_2$.



Scheme 2. Proposed mechanism of MPV reduction over hydrous zirconia.

when the catalyst was reused, in contrast to the excellent reuse of the grafted catalyst for the MPV reduction of 4-*tert*-butylcyclohexanone [23]. This may be due to the stronger adsorption of by-products formed in this reaction.

4. Discussion

The reaction mechanism for the MPV reaction in the homogeneous phase involves a cyclic six-membered transition state in which both the ketone/aldehyde (oxidant) and the alcohol (reductant) are coordinated to the metal center of a metal alkoxide catalyst. The alcohol is coordinated as an alkoxide while the carbonyl group binds to the metal center via the oxygen. Activation of the carbonyl by coordination to metal center initiates the hydride transfer from the bound alcoholate to the carbonyl. The resulting alkoxide leaves the catalyst via an alcoholysis reaction with the bulk alcohol [9]. The activity of these metal alkoxide catalysts is related to their Lewis acidity and the ligand exchange ability. Recent studies by Creyghton et al. proposed that over heterogeneous catalysts like zeolite beta, the MPV mechanism also involves a six-membered transition state where both the alcohol and the ketone coordinate to the same Lewis acid site [10].

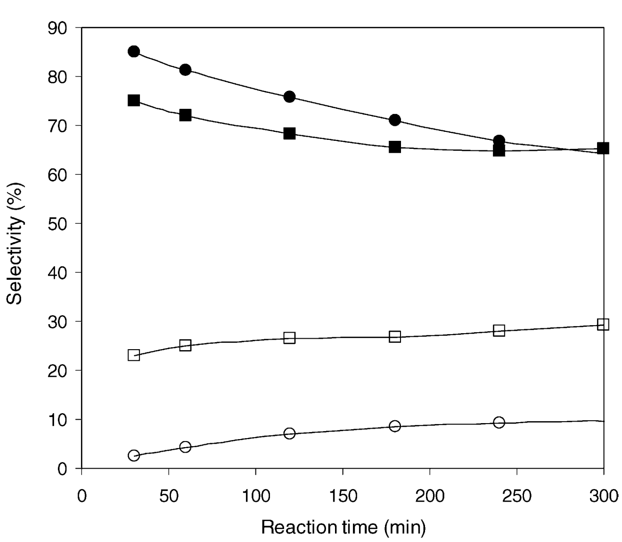


Fig. 4. Selectivity towards geraniol (filled symbols) and nerol (open symbols) over Zr-zeolite beta (●, ○) and Zr(OPr)$_4$/SiO$_2$ (■ , □).

Our studies show that hydrous zirconia progressively lost its activity when heated to higher temperatures. The loss in activity is bigger than the decrease in surface area. If Lewis acid sites were essential for the binding of the alcohol, then an increase in activity would be expected as the hydrous zirconia dehydrates to form zirconia. The decrease in activity rather points to the importance of the hydroxyl groups in the catalytic activity. We propose that the hydroxyl groups react with the alcohol to form zirconium alkoxide rather than a binding of the alcohol to the Lewis acid site (Scheme 2). The carbonyl group binds to the zirconium ion. A six-membered cyclic transition state is formed followed by hydride transfer to the carbonyl group. The concentration of the hydroxyl groups is affected by surface modification with phosphate, sulfate or NaOH, resulting in a decrease in activity. The stronger acidity induced by the presence of phosphate or sulfate groups leads to secondary reactions of dehydration of formed alcohols, lowering the selectivity of the MPV reduction.

Over the grafted zirconium 1-propoxide, exchange between the 1-propoxide ligand and the reductant, 2-propanol, occurs in the first step of the reaction before reduction of the aldehyde is possible. Due to the high concentration of the reductant and the nature of the metal center, ligand exchange is facilitated. The grafting of zirconium 1-propoxide onto the hydroxyl group of the support removes any acidic sites which may lead to secondary reactions, hence good selectivity was obtained. The immobilized zirconium 1-propoxide is resistant to leaching under reaction conditions.

The preferential formation of geraniol as compared to nerol can be explained by steric hindrance of the bulky C_8H_{17} chain when the carbonyl binds to the zirconium center. In geranial, the carbonyl group is *trans* to the C_8H_{17} chain, minimizing any steric hindrance for the binding of C=O to the Zr center. Hence, it can be expected that the rate of reaction for geranial is faster than for neral.

Moreover, the more linear shape of geranial compared to neral allows a faster diffusion when pore constraints play a role. This is clearly seen when Zr-zeolite beta was the catalyst. Due to its microporous nature with three-dimensional intersecting channels of 0.76 nm × 0.64 nm and a third channel of 0.55 nm × 0.55 nm, a high geraniol:nerol ratio was observed in the products. In comparison, grafted zirconium 1-propoxide has larger pores of around 6 nm mean diameter and the geraniol:nerol ratio was smaller than for Zr-zeolite beta. Nevertheless, the rate of geraniol formation was still faster than nerol, although the effect was smaller than for Zr-zeolite beta.

The zirconium-containing catalysts, in the form of hydrous zirconia, grafted zirconium 1-propoxide and Zr-zeolite beta are easy to handle under moisture conditions. Grafted zirconium 1-propoxide does not lose its catalytic activity following long exposure up to 48 h to ambient environment or water in the reaction medium [23]. This is in contrast to grafted aluminum 2-propoxide where stringent moisture-free conditions must be maintained for high activity. The retention of activity for grafted zirconium 1-propoxide even in the presence of moisture may be explained by the formation of hydrous zirconia. Although, hydrolysis of zirconium propoxide results in the formation of hydrous zirconia, the ease of exchange between the hydroxyl groups on hydrous zirconia and 2-propanol leads to the retention of high activity. A study by Campbell et al. reported that the MPV reaction is independent of the type of ligands [24]. The authors found that alkylaluminium such as $Al(CH_3)_3$ and $Al(CH_3)_2Cl$ converted under MPV reaction conditions to aluminum 2-propoxide. Similarly, in bis(cyclopentadienyl) zirconium dihydride, the cyclopentadienyl groups split off when reacted with 2-propanol, forming zirconium 2-propoxide [25]. We have also recently reported on the high tolerance of Zr-zeolite beta towards moisture [20]. The catalyst retained almost 50% of its activity in the presence of 9.1 wt.% water. The ease of handling of these Zr-containing catalysts together with their high activity and selectivity make them useful catalysts.

5. Conclusion

Zirconium-containing catalysts were active in the selective reduction of citral to geraniol and nerol. Hydrous zirconia calcined below 300 °C showed good activity with selectivity to the reduced alcohols of >90%. Hydrous zirconia calcined at 400 °C and higher was less active. The dependence of the activity on the calcination temperature of hydrous zirconia can be explained by decrease in the hydroxyl groups, which are required for binding of the reductant, 2-propanol. Zirconium 1-propoxide supported on silica gel also showed high activity and selectivity, >94 %. On the other hand, Zr-zeolite beta had high activity, but the selectivity to geraniol and nerol was ~84%. Dehydration of the formed alcohols led to lower selectivity. *Trans*-citral was reduced at a faster rate than *cis*-citral over all the catalysts. The effect was most pronounced in Zr-zeolite beta due to its microporous nature.

References

[1] A. Martínez-Arias, M. Fernández-García, V. Ballesteros, L.N. Salamanca, J.C. Conesa, C. Otero, J. Soria, Langmuir 15 (1999) 4796.
[2] T. Masui, K. Nakano, T. Ozaki, G. Adachi, Z. Kang, L. Eyring, Chem. Mater. 13 (2001) 1834.
[3] E. Mamotov, T. Egami, R. Brezny, M. Koranne, S. Tyagi, J. Phys. Chem. B 104 (2000) 11110.
[4] T. Yokoyama, T. Setoyama, N. Fujita, M. Nakajima, T. Maki, Appl. Catal. A 88 (1992) 149.
[5] L. Bruce, J.F. Mathews, Appl. Catal. 4 (1982) 352.
[6] B. Denise, R.P.A. Sneeden, Appl. Catal. 28 (1986) 235.
[7] D. Spielbauer, G.A.H. Mekhemer, E. Bosch, H. Knözinger, Catal. Letts. 36 (1996) 59.
[8] M. Scheithauer, R.K. Grasselli, H. Knözinger, Langmuir 14 (1998) 3019.
[9] 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.
[10] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, J. Mol. Catal. A 115 (1997) 457.
[11] P.J. Kunkeler, B.J. Zuurdeeg, J.C. van der Waal, J.A. van Bokhoven, D.C. Koningsberger, H. van Bekkum, J. Catal. 180 (1998) 234.
[12] A. Corma, M.E. Domine, S. Valencia, J. Catal. 215 (2003) 294.
[13] R. Anwander, C. Palm, Stud. Surface Sci. 117 (1999) 413.
[14] R. Anwander, C. Palm, G. Gerstberger, O. Groeger, G. Engelhardt, Chem. Commun. (1998) 1811.
[15] V.A. Ivanov, J. Bachelier, F. Audry, J.C. Lavalley, J. Mol. Catal. 91 (1994) 45.
[16] P.S. Kumbhar, J. Sanchez-Valence, J. Lopez, F. Figueras, Chem. Commun. (1998) 535.
[17] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, A. Porras, F.J. Urbano, Appl. Catal. 172 (1998) 31.
[18] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Appl. Catal. A 206 (2001) 95.
[19] M.S. Morey, G.D. Stucky, S. Schwarz, M. Fröba, J. Phys. Chem. B 103 (1999) 2037.
[20] Y.Z. Zhu, G.K. Chuah, S. Jaenicke, Chem. Commun. (2003) 2743.
[21] D. Spielbauer, G.A.H. Mekhemer, T. Riemer, M.I. Zaki, H. Knözinger, J. Phys. Chem. B 101 (1997) 4681.
[22] D. Spielbauer, G.A.H. Mekhemer, M.I. Zaki, H. Knözinger, Catal. Letts. 40 (1996) 71.
[23] Y.Z. Zhu, S. Jaenicke, G.K. Chuah, J. Catal. 218 (2003) 396.
[24] E.J. Campbell, H. Zhou, S.T. Nguyen, Org. Lett. 3 (2001) 2391.
[25] Y. Ishii, T. Nakano, A. Inada, Y. Kishigami, K. Sakurai, M. Ogawa, J. Org. Chem. 51 (1986) 240.