Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 246 (2007) 223–231
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Stereoselective cascade hydrogenation of 4-*tert*-butylphenol and *p*-cresol over Zr-zeolite beta-supported rhodium

Yuntong Nie [a], Stephan Jaenicke [a], Herman van Bekkum [b], Gaik-Khuan Chuah [a,*]

[a] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543*
[b] *Ceramic Membrane Centre "The Pore," TU Delft, Julianalaan 136, 2686 BL Delft, The Netherlands*

Received 6 October 2006; revised 9 December 2006; accepted 12 December 2006

Abstract

The hydrogenation of 4-*tert*-butylphenol and *p*-cresol was investigated over Zr-beta-supported rhodium catalysts. By designing a suitable bifunctional catalyst, the intermediate, 4-alkylcyclohexanone, formed by metal-catalyzed hydrogenation of 4-alkylphenol, could be reduced via the highly stereoselective Meerwein–Ponndorf–Verley reduction over zirconium Lewis acid sites. Thus, in the presence of 2-propanol as solvent and MPV reductant, a high stereoselectivity to *cis*-4-alkylcyclohexanol was observed. Over 0.5% Rh/Zr-beta, 4-*tert*-butylphenol, and *p*-cresol were hydrogenated to the *cis*-alcohols with 95 and 89% stereoselectivity, respectively. A higher metal loading or the use of solvents such as hexane or *tert*-butanol led to a lower stereoselectivity, as metal-catalyzed hydrogenation predominated. Similarly, the *cis*:*trans* alcohol ratio was lower for rhodium supported on zirconia or Al-beta. Compared with rhodium, palladium was less active in the hydrogenation of the 4-alkylphenols, requiring a higher hydrogen pressure and temperature. A two-step cascade reaction mechanism is proposed for the conversion of 4-alkylphenols to *cis*-4-alkylcyclohexanols.

© 2006 Elsevier Inc. All rights reserved.

Keywords: 4-*tert*-Butylphenol; *p*-Cresol; Hydrogenation; Zr-Zeolite beta; Rhodium; *cis*-Stereoselectivity; Cascade reaction; Bifunctional catalyst

1. Introduction

The selective hydrogenation of alkyl-substituted phenols to the corresponding cyclohexanones or cyclohexanols (*cis* and *trans*) is of industrial importance [1]. Some alkylated cyclohexanol products, like 2-*tert*-butylcyclohexanol and 4-*tert*-butylcyclohexanol, are useful intermediates in the fragrance and perfume industries, especially the *cis*-isomers [2,3]. Among the different monoalkylphenols, the selective hydrogenation of 4-*tert*-butylphenol and *para*-cresol (4-methylphenol) to *cis*-4-*tert*-butylcyclohexanol and *cis*-4-methylcyclohexanol, respectively, is of commercial interest.

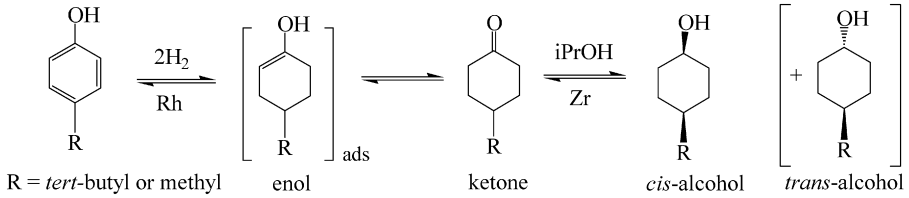
Various supported and unsupported metal catalysts, such as Pd, Ni, Ru, Pt, and Rh, have been used for the liquid-phase catalytic hydrogenation of 4-*tert*-butylphenol to either the ketone or the alcohol [4–8]. A yield of 99.1% 4-*tert*-butylcyclohexanol with 28.1% selectivity of the *cis*-isomer was obtained over a conventional Ni/Al_2O_3 catalyst in isobutyl acetate. Using Raney Ru catalysts, the reaction could be carried out at room temperature and under 5–10 bar H_2 to give a high yield (97%) of 4-*tert*-butylcyclohexanol with a *cis*:*trans* ratio of 48:52. When Ru was used alone or in combination with TiO_2, Al_2O_3, activated charcoal, MgO, or SiO_2, marked differences in the yield of *cis*- and *trans*-isomeric products were obtained, depending on the combination of catalysts and the solvent (H_2O, hexane, 2-propanol) used [8].

Rhodium is an active catalyst for this reaction and can give a high stereoselectivity to the *cis*-alcohol under certain reaction conditions. Over unsupported Rh, about twice as much *trans*-alcohol as *cis*-alcohol was formed [9]. A higher selectivity to cis-4-*tert*-butylcyclohexanol (60%) was found over a 3% Rh/C catalyst [10]. The yield of 4-*tert*-butylcyclohexanol was increased when CH_3COOH was added to Rh/Al_2O_3 in 2-propanol [11]. High stereoselectivity to *cis*-4-*tert*-butylcyclohexanol (82–91%) was obtained when a carbon-supported Rh catalyst (Rh/C) was combined with a mineral acid, such as

---

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

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.12.008



Scheme 1. Designed cascade reaction for the conversion of 4-alkylphenols to *cis*-4-alkylcyclohexanols.

HCl, H_2SO_4, $HClO_4$, or HBr as co-catalyst [12–15]. The highest stereoselectivity (100%) was claimed by Yadav and Goel [16] using Rh/C in the presence of methanesulfonic acid. They postulated that the formation of the *cis*- or *trans*-alcohol was site-specific and that the presence of the acid blocked the sites leading to the *trans*-alcohol. Compared with liquid phase, the vapor-phase hydrogenation of 4-*tert*-butylphenol over Pt/SiO_2 formed mainly 4-*tert*-butylcyclohexanol and 4-*tert*-butylcyclohexanone with deoxygenated byproducts such as *tert*-butylbenzene and *tert*-butylcyclohexane [17]. More *trans*- than *cis*-4-*tert*-butylcyclohexanol was formed under steady-state conditions with a *cis*:*trans* ratio of 0.88:1.

A number of studies also have been carried out on the hydrogenation of cresols. Palladium catalysts are highly selective for the partial hydrogenation to the corresponding cyclohexanones [18,19]. A silica-supported chitosan-palladium complex catalyzed the hydrogenation of phenol and cresols at 70 °C and 1 bar, forming high yields of the corresponding cyclohexanones [20]. A silica-supported cross-linked poly(maleic acid-co-styrene) Pt complex catalyzed the hydrogenation of *para*-cresol in water under mild conditions (30–50 °C, 1 bar) to give 4-methylcyclohexanol via 4-methylcyclohexanone as an intermediate [21]. Xia et al. [22] reported that over a zeolite-supported complex catalyst composed of Pt, polyvinyl alcohol, and amino acids, the initial rate of hydrogenation decreased from *m*-cresol to *o*-cresol to *p*-cresol, with *trans*-methylcyclohexanol preferentially formed.

The mechanism of formation of the *cis*- and *trans*-isomers has not been elucidated. Many studies have proposed a reaction scheme in which the reaction proceeds via an intermediate enol (4-*tert*-butyl-tetrahydrophenol), which can undergo tautomerization to 4-*tert*-butylcyclohexanone. Continued hydrogenation during residence on the surface could lead to the *cis*-isomer. When the ketone desorbed and subsequently readsorbed, perhaps more *trans*-isomer would be formed due to preferred adsorption with the *tert*-butyl group directed away from the surface. Another possible tetrahydro-intermediate, 4-*tert*-butyl-3-cyclohexenol, when desorbed and readsorbed, also can give rise to both *cis*- and *trans*-isomers in difficult-to-predict ratios. We previously found that Zr-zeolite beta is a highly stereoselective catalyst for the Meerwein–Ponndorf–Verley reduction of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol, with a selectivity of 99% [23]. Hence, in the present study we combined the hydrogenation activity of Rh with the high stereoselectivity of Zr-zeolita beta for *cis*-4-*tert*-alkylcyclohexanol to form a bifunctional catalyst (Scheme 1). This bifunctional catalyst should have the ability to (i) promote the hydrogenation of the phenol to the intermediate ketone, (ii) transform the ketone to the alcohol via the MPV reaction, and (iii) minimize the competing reaction of hydrogenating the ketone to alcohol. The direct formation of *cis*-4-alkylcyclohexanol (alkyl = *tert*-butyl, methyl) from corresponding alkylphenols was investigated over bifunctional Rh/Zr-beta catalysts. For comparison, zirconia, Zr-silica, γ-alumina, Al-zeolite beta, and Zr-impregnated Al-zeolite beta were used as supports. Along with Rh, Pd also was investigated for its hydrogenation activity in the reaction, because Pd is known to be a good catalyst for the phenol-to-cyclohexanone conversion.

2. Experimental

2.1. Catalyst preparation

The synthesis of aluminium-free Zr-zeolite beta (Si/Zr 100) has been described previously [23]. The Zr-beta-supported Rh catalysts (Rh/Zr-beta) were prepared by incipient-wetness impregnation at room temperature with an aqueous solution of $RhCl_3 \cdot 3H_2O$ (Pressure Chemicals). The impregnated samples were dried overnight at 100 °C. After calcination in air at 550 °C for 4 h, they were reduced in a 50/50 H_2/He mixture for 4 h at 300 °C. Samples with Rh loadings of 0.25, 0.5, 1, and 2 wt% were prepared. A commercial 5% Rh/C (Degussa) was similarly reduced and its hydrogenation activity evaluated. A 2 wt% Pd sample was prepared by impregnating Zr-beta with an aqueous solution of palladium(II) chloride dissolved in ammonia. The sample was calcined in air at 550 °C for 4 h before being reduced in H_2 for 2 h at 150 °C.

Hydrous zirconia was prepared by the hydrolysis of zirconium chloride in excess 5 M NaOH [24]. A 10 wt% $ZrCl_4$ solution was added via a peristaltic pump to the 5 M NaOH solution. After precipitation, the gel solution was digested at 100 °C for 4 days. The filtrate was washed with dilute ammonium nitrate until free of chloride, dried at 100 °C overnight, and then subjected to calcination at 500 °C for 12 h. Zr-silica (Si/Zr 100) was prepared by mixing tetraethoxysilane and $ZrCl_4$ in tetrapropylammonium hydroxide, followed by hydrothermal treatment at 160 °C for 2 days. The sample was filtered, washed, and calcined at 550 °C for 12 h. A sample of Al-zeolite beta (Zeolyst, Si/Al 12.5) was added to a solution of $ZrOCl_2$ to give a Si/Zr ratio of 100 and stirred for 4 h at room temperature, followed by evaporation of water. This sample, designated Zr-Al-beta, was dried at 100 °C and calcined at 550 °C for 4 h. The thus-obtained zirconia, Al-zeolite beta, and Zr-Al-zeolite beta were impregnated with 0.5 wt% Rh. A 3% Rh/γ-alumina sample also was prepared.

Table 1
Textural properties of catalysts

Sample	BET S.A. (m^2/g)	Langmuir S.A. (m^2/g)	Micropore S.A. (m^2/g)	Total pore vol. (cm^3/g)	Micropore vol. (cm^3/g)
Zr-beta (Si/Zr 100)	490	685	410	0.27	0.20
2% Rh/Zr-beta	443	618	358	0.26	0.17
1% Rh/Zr-beta	468	697	408	0.26	0.20
0.5% Rh/Zr-beta	473	660	403	0.26	0.20
0.25% Rh/Zr-beta	463	657	384	0.26	0.19
2% Pd/Zr-beta	372	517	318	0.22	0.17
ZrO_2	190	–	0	0.45	0
0.5% Rh/ZrO_2	147	–	1.52	0.48	0
0.5% Rh/Zr-silica	239	–	13	1.22	0.01
Al-beta (Si/Al 12.5)	560	784	335	1.05	0.17
0.5% Rh/Al-beta	497	698	299	0.99	0.15
0.5% Rh/Zr-Al-beta	489	626	308	1.03	0.16
3% Rh/Al_2O_3	132	–	0	0.24	0

2.2. Characterization

The surface area and pore volume of the catalysts were determined by nitrogen adsorption measurements using a Micromeritics Tristar 3000. The samples were first degassed under a N_2 flow at 300 °C for 4 h before measurement. The surface area was determined using the BET isotherm and for microporous samples, the Langmuir isotherm was used as well. The pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) method, and the t-plot was used to estimate the micropore surface area and micropore volume. The crystal phase of the samples was measured with a Siemens D5005 powder X-ray diffractometer equipped with a Cu anode and variable slits. A step size of 0.05° and a dwell time of 2 s/step were used.

Transmission electron microscopy (TEM) measurements were performed with a JEOL JEM3010 HR instrument operated at 300 kV. The sample was first finely ground before being suspended in ethanol. A droplet of the suspension was mounted onto the copper grid before drying.

2.3. Catalytic testing

The experiments were carried out in a Teflon-lined stainless steel autoclave (Berghof) at 80 °C. The reaction mixture typically contained 1.0 g of 4-*tert*-butylphenol (6.66 mmol) or 1.0 g p-cresol (9.25 mmol) with 100 mg of reduced catalyst in 50 ml of 2-propanol. After heating to the reaction temperature, hydrogen was introduced into the autoclave to a pressure of 5 bar. Samples were collected at regular intervals and analyzed by gas chromatography (Agilent 6890, HP 5 column or γ-dex 225 column for *cis*- and *trans*-4-methylcyclohexanol). The products were identified by GC-MS (Shimadzu GCMS-QP5000, DB5MS column) and ^{1}H NMR using a Bruker AMX500 (500 MHz) spectrometer.

3. Results and discussion

3.1. Catalyst characterization

The textural characteristics of the catalysts and supports used are summarized in Table 1. The microporous Zr-beta and Al-beta have higher surface areas than the mesoporous ZrO_2, Zr-silica, and Al_2O_3. The BET surface area of Zr-beta was slightly decreased (<10%) after impregnation with Rh up to 2 wt%, but a more drastic loss in surface area (∼25%) was observed when it was impregnated with 2 wt% Pd. The loss of surface area can be attributed to partial blockage of the micropores as the microporous pore volume decreased on impregnation. Similarly, the surface area of ZrO_2 and Al-beta was also reduced by 23 and 11%, respectively, after impregnation with 0.5 wt% Rh.

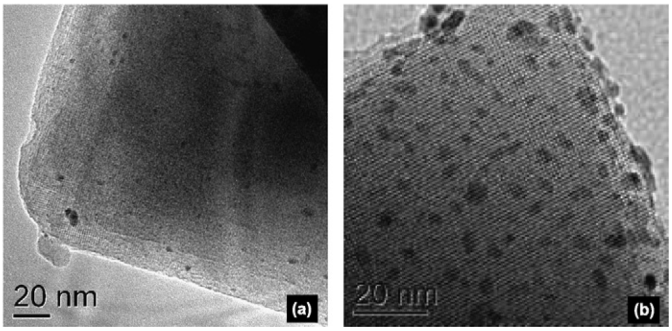


Fig. 1. Transmission electron micrographs of (a) 0.5% Rh/Zr-beta and (b) 2% Rh/Zr-beta.

The XRD patterns of the Rh- and Pd-impregnated samples showed only the diffraction peaks of the support materials. No diffraction peaks of either Rh or Pd were detected, suggesting good dispersion of the metal. Furthermore, retention of the original reflections of the supports showed that the impregnation procedure and subsequent metal reduction did not destroy the crystalline structure of the materials.

From the TEM images of 0.5% Rh/Zr-beta (Fig. 1a), the Rh particles were seen as black dots of ∼0.6–0.7 nm, well dispersed over the support along with some larger particles (mean diameter, ca. 3 nm) of rather uniform size. Although very small particles could be located at crossings within the zeolite, the larger particles could only be found on the external surface. In contrast, the particle size of the Rh clusters was less uniform for the 2% Rh/Zr-beta sample (Fig. 1b); particles of approximately 3 nm along with larger clusters of diameter up to 10.5 nm were visible.

Table 2
Hydrogenation of 4-*tert*-butylphenol over zeolite beta-supported metal catalysts

Entry	Catalyst	*T* (h)	Conversion (%)	Selectivity (%)		*cis*:*trans*
				Ketone	Alcohol	
1	0.25% Rh/Zr-beta	6	98	0.5	99.5	92:8
2	0.5% Rh/Zr-beta	4	100	0	100	95:5
3	0.5% Rh/Zr-beta[a]	5	100	0	100	94:6
4	0.5% Rh/Zr-beta[b]	5	100	38	62	46:54
		10	100	0	100	37:63
5	0.5% Rh/Zr-beta[c]	5	71	35	65	63:37
		15	100	0	100	52:48
6	0.5% Rh/Zr-beta[d]	10	100	0	100	95:5
7	0.5% Rh/Zr-beta[e]	3.5	100	0	100	92:8
8	1% Rh/Zr-beta	3.5	100	0	100	92:8
9	1% Rh/Zr-beta[f]	5	100	0	100	92:8
10	2% Rh/Zr-beta	2	100	0	100	84:16
11	2% Rh/Zr-beta[d]	3	100	0	100	85:15
12	2% Pd/Zr-beta[g]	25	54	1	99	94:6
13	0.5% Rh/Al-beta	5	99	4	96	55:45

Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

[a] Scale-up of reactant and catalyst concentration by 5 times.
[b] Hexane as the solvent.
[c] *tert*-Butanol as the solvent.
[d] 50 mg catalyst.
[e] 1 MPa H_2.
[f] 0.1 g acetic acid.
[g] 120 °C, 5 MPa H_2.

3.2. *Catalytic activity*

3.2.1. *Hydrogenation of 4-tert-butylphenol to 4-tert-butylcyclohexanol*

The results of the combined hydrogenation/MPV reduction experiments over zeolite beta-supported metal catalysts are listed in Table 2. Entries 4 (hexane as the solvent) and 13 (no Zr present and low Al-MPV activity) reflect the stereochemical result when essentially only Rh-catalyzed hydrogenation and no MPV reduction were in operation. Just slightly more *cis*- than *trans*-isomer was formed.

3.2.1.1. Effect of different Rh loading In an effort to find the catalyst that gives the highest selectivity to *cis*-4-*tert*-butylcyclohexanol, Zr-beta samples with different Rh loading were tested for the reaction (Fig. 2). Of the four catalysts tested, 0.25% Rh/Zr-beta showed the lowest activity, with an alcohol yield of 98% after 6 h. The selectivity to *cis*-4-*tert*-butylcyclohexanol was 92% (Table 2). Increasing the Rh loading led to a higher rate of reaction, so that for 2% Rh/Zr-beta, the reaction was completed within 2 h. However, the stereoselectivity to the *cis*-alcohol was only 84%. This indicates that roughly 70% of the substrate molecules followed the designed route, whereas 30% of the substrate was converted by Rh-catalyzed (stepwise) hydrogenation. This may be due to the Rh crystals at the outer surface of the zeolite, not in the direct vicinity of MPV Zr sites. Intermediate 4-*tert*-butylcyclohexanone formed on this Rh must adsorb into the zeolite, at which point it is in competition with the presumably stronger adsorbing 4-*tert*-butylphenol. 4-*tert*-Butylcyclohexanone, formed on Rh inside the zeolite, will encounter many MPV Zr sites while diffusing through the zeolite domain, trying to reach the bulk liquid. An intermediate loading of 0.5% Rh led to the highest stereoselectivity (95%), with 100% conversion reached after 4 h. This value indicates that >90% of the 4-*tert*-butylphenol followed the designed cascade route.

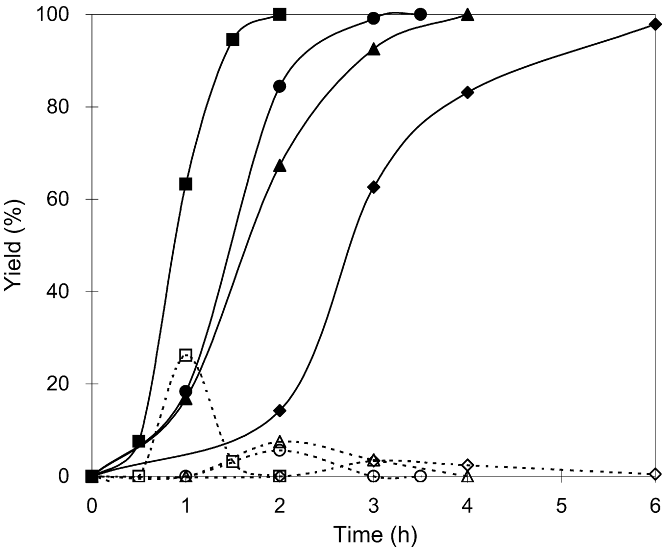


Fig. 2. Yield of 4-*tert*-butylcyclohexanone and 4-*tert*-butylcyclohexanol over Rh/Zr-beta catalyst with different Rh loadings (◆, ◇) 0.25%, (▲, △) 0.5%, (●, ○) 1% and (■, □) 2%. Open symbols: ketone; closed symbols: alcohol. Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

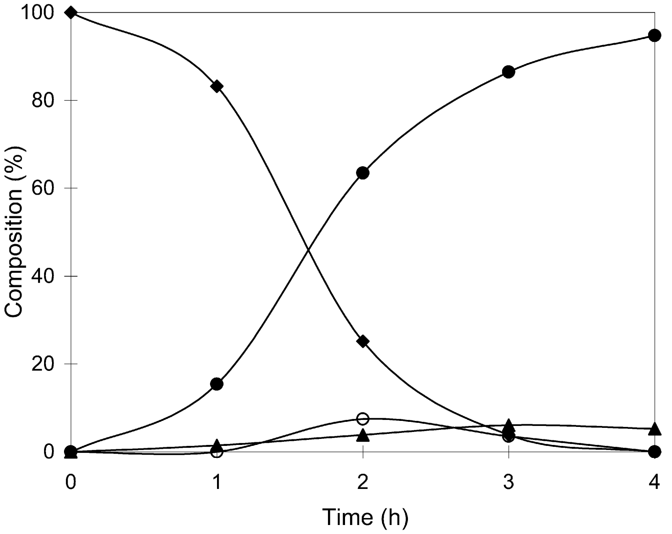


Fig. 3. Hydrogenation of 4-*tert*-butylphenol over 0.5% Rh/Zr-beta in 2-propanol. (◆) 4-*tert*-Butylphenol, (●) *cis*-4-*tert*-butylcyclohexanol, (○) 4-*tert*-butylcyclohexanone, and (▲) *trans*-4-*tert*-butylcyclohexanol. Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

3.2.1.2. Influence of solvent 4-*tert*-Butylphenol was rapidly converted over the Rh/Zr-beta catalysts under mild conditions (80 °C, 0.5 MPa H_2) in 2-propanol. Fig. 3 shows the course of reaction over 0.5% Rh/Zr-beta. A short induction time (ca. 1 h)

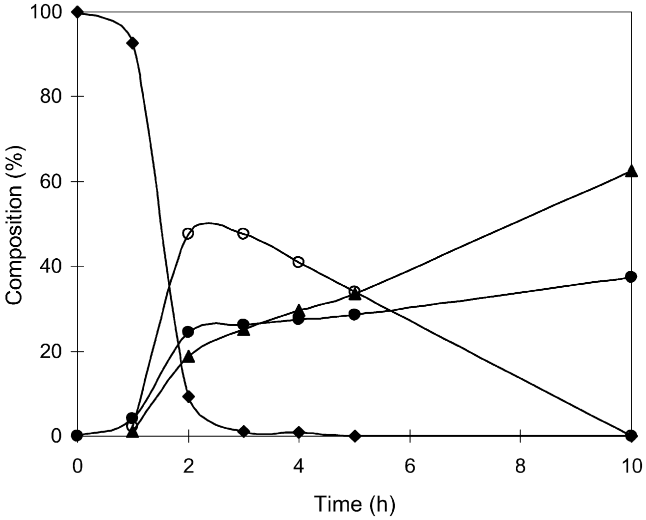


Fig. 4. Hydrogenation of 4-*tert*-butylphenol over 0.5% Rh/Zr-beta in hexane. (◆) 4-*tert*-Butylphenol, (●) *cis*-4-*tert*-butylcyclohexanol, (○) 4-*tert*-butylcyclohexanone, and (▲) *trans*-4-*tert*-butylcyclohexanol. Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml hexane, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

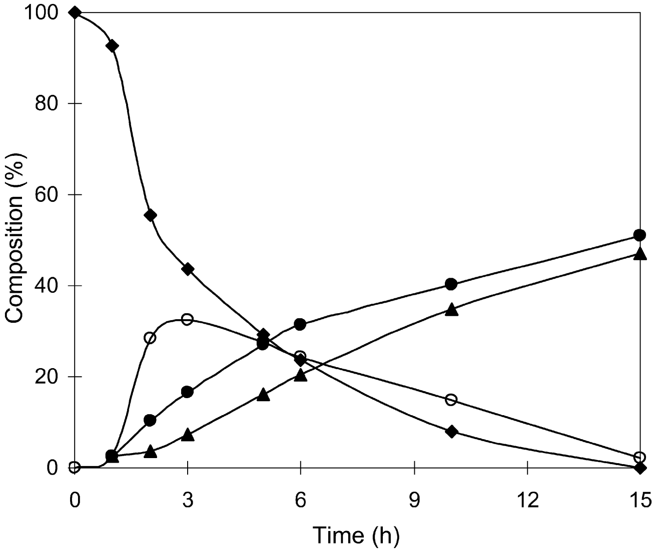


Fig. 5. Hydrogenation of 4-*tert*-butylphenol over 0.5% Rh/Zr-beta in *tert*-butanol. (◆) 4-*tert*-Butylphenol, (●) *cis*-4-*tert*-butylcyclohexanol, (○) 4-*tert*-butylcyclohexanone, and (▲) *trans*-4-*tert*-butylcyclohexanol. Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml *tert*-butanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

was observed, which might be due to the establishment of an adsorption equilibrium inside/outside the zeolite. The concentration of 4-*tert*-butylcyclohexanone as a visible intermediate reached a maximum of 7.5% at approximately 75% conversion. After 4 h, the conversion of 4-*tert*-butylphenol reached 100%. The only product formed was 4-*tert*-butylcyclohexanol. Of the two possible isomers, the thermodynamically less favored *cis*-4-*tert*-butylcyclohexanol was formed with a very high selectivity (95%). This high selectivity was maintained even when the experiment was scaled up by using 5 g of 4-*tert*-butylphenol and 0.5 g catalyst (Entry 3, Table 2).

The reaction was also carried out in hexane and *tert*-butanol using 0.5% Rh/Zr-beta as the catalyst. These solvents are unable to function as H donors in MPV reductions. The reaction profile in hexane (Fig. 4) was very different from that of 2-propanol. The rate of hydrogenation of 4-*tert*-butylphenol was higher; a phenol conversion of 91% was obtained after 2 h, compared with only 75% achieved in 2-propanol after the same time. However, the intermediate, 4-*tert*-butylcyclohexanone, was formed in significant amounts and was the main product formed after 2 h, with a yield of 48%, followed by *cis*-alcohol (24%) and *trans*-alcohol (19%). These results indicate that hydrogenation of the ketone was difficult in the presence of the more strongly adsorbing 4-*tert*-butylphenol. Moreover, the *cis*:*trans* ratio decreased with reaction time, so that a reverse selectivity of 37:63 *cis*-:*trans*-alcohol was obtained at 100% yield of alcohol (Table 2). This result is at variance with previously reported results [25], where more *cis*- than *trans*-alcohol was found over 5% Rh/C, with *cis*:*trans* ratios of 86:14 in hexane and 75:25 in 2-propanol.

When *tert*-butanol was used as the solvent, the rate of hydrogenation of 4-*tert*-butylphenol was lower than that for hexane or 2-propanol (Fig. 5); after 6 h, the conversion was only 76%. As with hexane, the observed concentration of 4-*tert*-butylcyclohexanone was high, reaching a maximum of 32.5% after 3 h. The *cis*:*trans* ratio for 4-*tert*-butylcyclohexanol decreased with reaction time, from 71:29 after 1 h to 52:48 after 10 h, and thereafter remained unchanged.

Comparing the three solvents, the concentration of the intermediate 4-*tert*-butylcyclohexanone was lower in 2-propanol than in hexane or *tert*-butanol. This is likely due to its reduction by the MPV reaction, with 2-propanol acting as the H-donor. Zr-beta has been shown to be highly active in the MPV reduction of 4-*tert*-butylcyclohexanone, giving an excellent selectivity to *cis*-4-*tert*-butylcyclohexanol (>99%) [23]. It is postulated that because of pore size restrictions of zeolite beta, *cis*-4-*tert*-butylcyclohexanol is preferentially formed over the *trans*-alcohol due to a transition state selectivity [26]. The *cis*-isomer is more or less aligned with the pore channels of zeolite beta, whereas a bulkier transition state is required for the formation of the *trans*-alcohol.

To verify that the MPV reaction is indeed operative, the hydrogenation of the intermediate, 4-*tert*-butylcyclohexanone, was investigated using different solvents with and without H_2 (Table 3). The rate of reaction was highest when 2-propanol was used in the presence of H_2, when both MPV reduction and gaseous hydrogenation of 4-*tert*-butylcyclohexanone can occur. Without H_2, the ketone can be reduced only via the MPV reaction, and the rate was reduced slightly, from 53.4 to 38.5 $\text{mmol/g}_{\text{cat}}\,\text{h}$ (18%). The reaction was slowest when hexane was the solvent, because the hydrogenation of 4-*tert*-butylcyclohexanone can occur only via gaseous H_2 without any MPV reduction. The initial rate was only 5 $\text{mmol/g}_{\text{cat}}\,\text{h}$. The stereoselectivity to *cis*-4-*tert*-butylcyclohexanol was highest for 2-propanol in He, 99:1 and decreased slightly when H_2 was present, due to the competing hydrogenation over the Rh particles. In hexane, where no MPV reaction can occur, almost equal amounts of *cis*- and *trans*-4-*tert*-butylcyclohexanol were formed.

Table 3
Reduction of 4-*tert*-butylcyclohexanone in different solvents

Solvent	Initial rate (mmol/g h)	*cis*:*trans*
2-Propanol + He	38.5	99:1
2-Propanol + H_2	53.3	97:3
Hexane + H_2	5.0	49:51

Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml solvent, 100 mg 0.5% Rh/Zr-beta, 0.5 MPa gas.

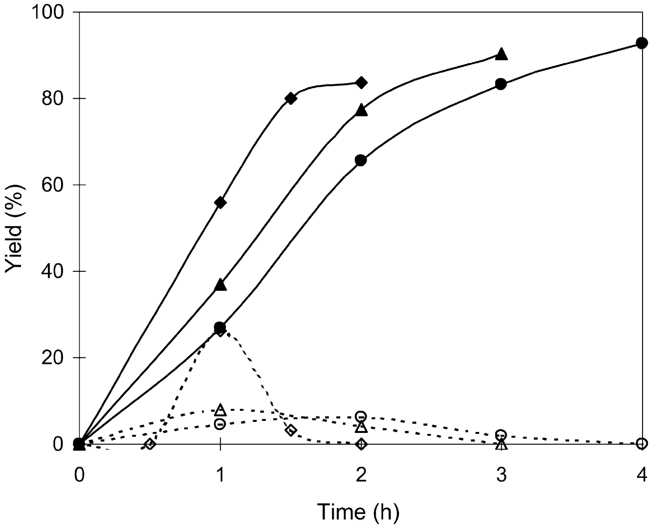


Fig. 6. Hydrogenation of 4-*tert*-butylphenol over different ratios of 2% Rh/Zr-beta to Zr-beta (◆, ◇) 1:1, (▲, △) 3:7, (●, ○) 2.5:7.5. Open symbols: 4-*tert*-butylcyclohexanone; closed symbols: *cis*- 4-*tert*-butylcyclohexanol. Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

Consequently, along with hydrogenation with gaseous H_2, the MPV reaction plays a major role in reduction, enhancing the selectivity and increasing the rate of transformation of the intermediate, 4-*tert*-butylcyclohexanone, to the desired *cis*-4-*tert*-buylcyclohexanol. The lower reaction rate to the final alcohol product and the substantial amounts of 4-*tert*-butylcyclohexanone observed in hexane or *tert*-butanol can be attributed to the relatively unreactive nature of 4-*tert*-butylcyclohexanone, the absence of MPV reduction, and low hydrogenation activity due to the small Rh loading on the catalyst.

3.2.1.3. Addition of Zr-beta to supported Rh catalysts The hydrogenation of 4-*tert*-butylphenol was also carried out with various mixtures of 2% Rh/Zr-beta and Zr-beta to boost the MPV reduction, keeping the total catalyst amount constant (Fig. 6). As expected, the rate of conversion of 4-*tert*-butylphenol decreased with decreasing amounts of 2% Rh/Zr-beta in the composite catalyst, due to a lower Rh surface area. In contrast, the stereoselectivity to *cis*-4-*tert*-butylcyclohexanol increased from 84 to 93% as the concentration of Zr-beta in the composite catalyst increased from 0 to 75% (Table 4). Furthermore, a higher concentration of the intermediate 4-*tert*-butylcyclohexanone (26.2%) was observed over the pure 2% Rh/Zr-beta, whereas for mixtures with 70 and 75% Zr-beta, the maximum 4-*tert*-butylcyclohexanone amount was only 8 and 6%, respectively.

Table 4
Effect of adding Zr-beta on *cis*:*trans* ratio of 4-*tert*-butylcyclohexanol

Catalyst	*cis*:*trans*
2% Rh/Zr-beta	84:16
2% Rh/Zr-beta & Zr-beta (30:70)	90:10
2% Rh/Zr-beta & Zr-beta (25:75)	93:7
0.5% Rh/Zr-beta	95:5
0.5% Rh/Zr-beta & Zr-beta (67:33)	98:2

Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol 100 mg catalyst, 0.5 MPa H_2. Numbers in parenthesis denote the weights (mg) of Rh/Zr-beta:Zr-beta.

These results illustrate the competitive hydrogenation of 4-*tert*-butylcyclohexanone due to the MPV reduction and gaseous H_2. Over 2% Rh/Zr-beta, the higher concentration of Rh active sites led to a relatively fast hydrogenation rate of the ketone but at the expense of lower stereoselectivity, with the reaction occurring on Rh particles at the external surface of the zeolite. The addition of Zr-beta to 0.5% Rh/Zr-beta improved the stereoselectivity to *cis*-4-*tert*-butylcyclohexanol from 95 to 98%. However, the rate of reaction was lower than for the composite system with 2% Rh loading, and complete conversion could be reached only after 22 h, compared with after around 4 h for the latter.

3.2.1.4. Effects of pressure, acid, and catalyst amount Increasing the hydrogen pressure from 0.5 to 1.0 MPa increased the conversion of 4-*tert*-butylphenol, but with decreased selectivity to the *cis*-alcohol (entry 7, Table 2). At higher H_2 pressures, more 4-*tert*-butylcyclohexanone was reduced via reaction with gaseous hydrogen, leading to a loss in stereoselectivity.

It has been reported that adding acid as a co-catalyst affects the hydrogenation activity and product distribution, with a higher selectivity toward *cis*-alcohol [11–16]. However, we found that adding acetic acid to the reaction system with 1% Rh/Zr-beta decreased the rate of hydrogenation of 4-*tert*-butylphenol but did not affect stereoselectivity; the *cis*:*trans* ratio of 4-*tert*-butylcyclohexanol remained unchanged at 92:8 (entry 9, Table 2). This may be due to the different reaction mechanism here, with the *cis*-alcohol formed mainly by the MPV reduction over Zr-beta rather than by hydrogenation over the metal catalyst.

Decreasing the catalyst amount did not change the selectivity of the alcohol formed (entries 6 and 11, Table 2). For 0.5 and 2% Rh loadings, the *cis*:*trans* ratio remained constant at 95:5 and 85:15, respectively, whereas the time needed for complete conversion of the phenol increased.

3.2.1.5. Comparison of different catalyst supports ZrO_2, Al-beta (Si/Al = 12.5), Zr-Al-beta, and γ-Al_2O_3 were tested as supports for Rh because they are active in the MPV reaction [26–28]. The conversion of 4-*tert*-butylphenol decreased in the following order: Rh/Zr-beta > Rh/Al-beta ≈ Rh/Zr-Al-beta > Rh/ZrO_2. For Al-beta- and ZrO_2-supported Rh catalysts, conversion of 99 and 96% with a ketone yield of 3.6 and 4.8%, re-

Table 5
Hydrogenation of 4-*tert*-butylphenol over Rh on other supports

Entry	Catalyst	*T* (h)	Conversion (%)	Selectivity (%)		*cis*:*trans*
				Ketone	Alcohol	
1	0.5% Rh/ZrO_2	5	96	5	95	72:28
2	0.5% Rh/Al-beta	5	99	4	96	55:45
3	0.5% Rh/Zr-Al-beta	4	98	1	99	67:33
4	0.5% Rh/Zr-silica	4	96	15	85	47:53
5	3% Rh/Al_2O_3	3	100	0	100	42:58
6	5% Rh/C	3.5	96	6	90	73:27
7	5% Rh/C & MSA[a]	2	98	4	79	88:12

Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

[a] 0.32 ml methanesulfonic acid.

spectively, was obtained after 5 h (Table 5). However, over 0.5% Rh/Zr-beta, a 100% yield of alcohol could be achieved within 4 h. The *cis*:*trans* ratio over 0.5% Rh/ZrO_2 and 0.5% Rh/Al-beta was 72:28 and 55:45, respectively. Being mesoporous (Table 1), the ZrO_2 support did not manifest any shape-selectivity effects in the formation of the alcohol, and more of the thermodynamically stable *trans*-4-*tert*-butylcyclohexanol was formed. The low stereoselectivity to *cis*-4-*tert*-butylcyclohexanol over Rh/Al-beta despite the presence of micropores indicates that here the rate of MPV reduction was much lower than the rate of Rh-catalyzed hydrogenation of the intermediate ketone. The impregnation of zirconium onto Al-beta led to a slightly higher *cis*:*trans* ratio of 67:33 for the supported Rh catalyst (entry 3, Table 5), albeit still far lower than that for Rh/Zr-beta. Therefore, incorporation of zirconium into the zeolite silicate framework is necessary for high stereoselectivity. Without the presence of well-defined pore channels in the mesoporous Zr-silica sample, the selectivity to the *cis*-alcohol was only 42% (entry 4, Table 5). The high metal loading in 3% Rh/Al_2O_3 resulted in a high rate of hydrogenation but a low *cis*-selectivity of only 42% at full conversion of 4-*tert*-butylphenol. The commercial catalyst, 5% Rh/C (Degussa), also exhibited good activity, forming 4-*tert*-butylcyclohexanol with a higher *cis*:*trans* ratio of 73:27. This agrees well with the *cis*:*trans* ratio of 75:25 reported by Griffin et al. [25]. However, the catalyst also catalyzed the hydrogenolysis of the 4-*tert*-butylphenol, giving about 4% of side products 4-*tert*-butylbenzene and 4-*tert*-butylcyclohexene. The addition of methanesulfonic acid to the reaction mixture increased the stereoselectivity to the *cis*-alcohol to 88%, but increased the concentration of side products to 17% (entry 7, Table 5). We did not observe the 100% stereoselectivity to the *cis*-alcohol reported by Yadav and Goel [16].

3.2.1.6. Comparison with another metal: Pd Because palladium is known to be the most selective catalyst for the hydrogenation of phenols to the corresponding cyclohexanones [4,18], a 2% Pd/Zr-beta sample was prepared and tested for the hydrogenation of 4-*tert*-butylphenol in 2-propanol (entry 12, Table 2). Compared with Rh/Zr-beta, the Pd/Zr-beta catalyst required a much higher pressure and temperature. The reaction could occur only at 120 °C under 5 MPa H_2, and even after 25 h, the conversion was only 54%. The concentration of 4-*tert*-butylcyclohexanone was <1% throughout the course of the reaction (Fig. 7). Because of the low activity of the Pd catalyst under these conditions, the reduction of the ketone intermediate is expected to occur via MPV reduction rather than by metal-catalyzed hydrogenation. This postulation is indeed supported by the observed high selectivity to *cis*-4-*tert*-butylcyclohexanol of 94%.

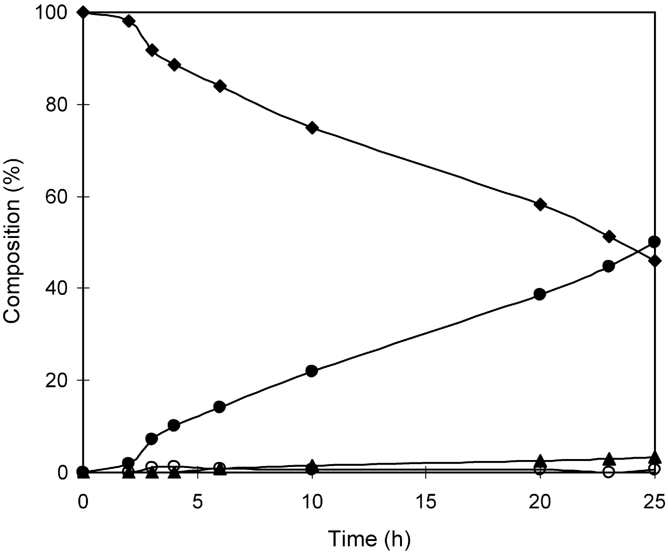


Fig. 7. Hydrogenation of 4-*tert*-butylphenol over 2% Pd/Zr-beta. (◆) 4-*tert*-Butylphenol, (●) *cis*-4-*tert*-butylcyclohexanol, (○) 4-*tert*-butylcyclohexanone, and (▲) *trans*-4-*tert*-butylcyclohexanol. Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol, 100 mg catalyst, 120 °C, 5 MPa H_2.

Table 6
Re-use of 0.5% Rh/Zr-beta catalyst

Cycle	Conversion[a] (%)	*cis*:*trans*	Treatment
1	100	95:5	Fresh catalyst
2	96	94:6	Add 6.6 mmol 4-*tert*-butylphenol
3	73	95:5	Add another 6.6 mmol 4-*tert*-butylphenol
4	100	95:5	Recalcined at 580 °C and re-reduced

Reaction conditions: 6.6 mmol 4-*tert*-butylphenol, 50 ml 2-propanol, 100 mg catalyst, 0.5 MPa H_2.

[a] After 4 h.

3.2.1.7. Regenerability of catalysts The Rh/Zr-beta catalyst was tested in several batches of reactions, where again more 4-*tert*-butylphenol was added after each batch (Table 6). The conversion decreased with each batch, but the stereoselectivity to the *cis*-alcohol remained constant. After three batches, the spent catalyst was filtered from the reaction system and recalcined at 580 °C, followed by reduction in He/H_2 for 4 h. No loss in activity or selectivity was observed with the recycled catalyst. To test for any leaching of the metal, hot filtration of the catalyst was carried out after 2 h, and the reaction was allowed to proceed without the catalyst. No further conversion was observed, thus confirming that no leaching occurred.

3.2.2. Hydrogenation of p-cresol to 4-methylcyclohexanol

3.2.2.1. Effect of different Rh loading and H_2 pressure The effect of different Rh loadings on the hydrogenation of *p*-cresol

Table 7
Hydrogenation of *p*-cresol over various supported Rh catalysts

Entry	Catalyst	*T* (h)	Conversion (%)	Selectivity (%)		*cis*:*trans*
				Ketone	Alcohol	
1	0.25% Rh/Zr-beta	8	100	0	100	88:12
2	0.5% Rh/Zr-beta	6.5	100	0	100	89:11
3	0.5% Rh/Zr-beta[a]	6	100	27	73	55:45
		10	100	0	100	43:57
4	0.5% Rh/Zr-beta[b]	5	100	0	100	86:14
5	1% Rh/Zr-beta	5	100	0	100	86:14
6	2% Rh/Zr-beta	3	100	0	100	79:21
7	0.5% Rh/Al-beta	6	95	7	93	66:34
8	0.5% Rh/ZrO_2	5	66	47	53	77:23

Reaction conditions: 9.25 mmol *p*-cresol, 50 ml 2-propanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.
[a] Hexane as the solvent.
[b] 1 MPa H_2.

was carried out with 2-propanol as solvent and MPV reductant. The rate of reaction increased with Rh loading, whereas the selectivity to the *cis*-alcohol was highest over 0.5% Rh/Zr-beta, 89% (Table 7). Only small amounts of the intermediate ketone were observed during the course of the reaction, indicating that the molecule was easily reduced to the final product, both by direct hydrogenation and by MPV reduction. The maximal *cis*:*trans* ratio, when all molecules are converted by MPV of the intermediate ketone, amounts to 96:4; therefore, our result indicates that about 85% of the *p*-cresol molecules underwent the designed cascade route, with 15% converted by hydrogenation over Rh sites.

The effect of pressure was evaluated with 0.5% Rh/Zr-beta (entry 4, Table 7). At higher pressures, the time to complete conversion of *p*-cresol decreased. The stereoselectivity to *cis*-4-methylcyclohexanol decreased slightly from 89% when the reaction was carried out at 0.5 MPa H_2 to 86% for 1 MPa H_2.

3.2.2.2. Effect of solvent The rate of conversion of *p*-cresol was similar in both 2-propanol and hexane. However, in 2-propanol, the main product formed over 0.5% Rh/Zr-beta was *cis*-4-methylcyclohexanol, with a small amount of the *trans*-alcohol (*cis*:*trans* 89:11). The concentration of the intermediate 4-methylcyclohexanone remained low during the course of reaction, constituting at most 8% of the reaction mixture. The product distribution was very different in the absence of MPV reduction when hexane was used as solvent (Fig. 8). At 93% conversion, the main products formed were 4-methylcyclohexanone (41% of the reaction mixture), followed by *cis*-4-methylcyclohexanol (32%) and the *trans*-alcohol (20%). Moreover, the *cis*:*trans* ratio gradually decreased with time, and a low selectivity to the *cis*-alcohol (43%) was achieved with complete conversion of the 4-methylcyclohexanone (Table 7). This indicates that distinctly more *trans*- than *cis*-isomer is formed on hydrogenation of the ketone.

3.2.2.3. Comparison of different catalyst supports Compared with 0.5% Rh/Zr-beta, Rh/Al-beta and Rh/ZrO_2 catalysts were less active (Table 7). The concentration of the intermediate ketone was higher than that for 0.5% Rh/Zr-beta. Over 0.5% Rh/ZrO_2, the yield of 4-methylcyclohexanone reached a maximum of 31% when the conversion of *p*-cresol was 66%. At 100% yield of the alcohol, the *cis*:*trans* ratio was only 62:38 over Rh/Al-beta and 66:34 over Rh/ZrO_2.

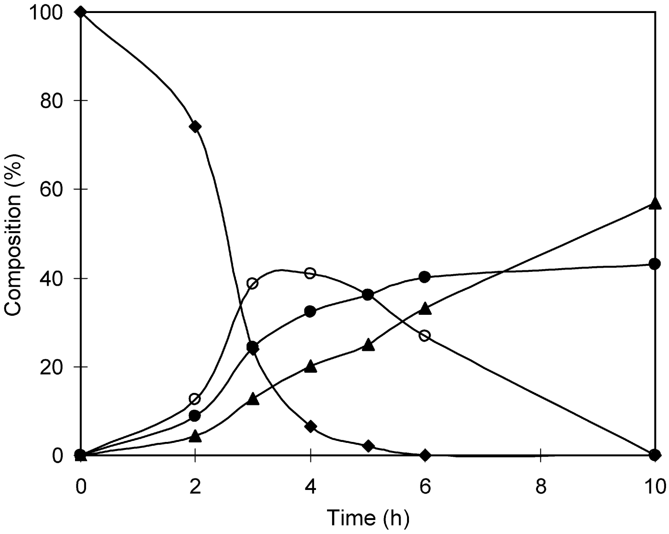


Fig. 8. Hydrogenation of *p*-cresol over 0.5% Rh/Zr-beta in hexane. (◆) *p*-Cresol, (●) *cis*-alcohol, (▲) *trans*-alcohol, and (○) ketone. Reaction conditions: 9.25 mmol *p*-cresol, 50 ml hexane, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

These findings are similar to those seen for the hydrogenation of 4-*tert*-butylphenol where the observed conversion and selectivity to the *cis*-alcohol is a result of hydrogenation over the metal catalyst and the MPV reduction of the ketone. When the hydrogenation with gaseous H_2 predominates, more *trans*-alcohol is formed. Over the mesoporous ZrO_2 support, the effect of pore constraints affecting the stereoselectivity of the MPV reaction is reduced, so that more of the thermodynamically stable *trans*-isomer is formed.

3.2.2.4. Reuse of catalysts The reuse of the 0.5% Rh/Zr-beta catalyst was tested by adding more substrate again to the system after completion of one run, without any pretreatment of the catalyst (Fig. 9). Some loss in activity occurred during the reuse; the conversion obtained after three cycles was 79%, compared with 100% for the fresh catalyst after 6 h. Despite the lower activity, the stereoselectivity to the *cis*-alcohol was still as high as 86% after 3 cycles, compared with 89% for the fresh catalyst. Moreover, the used catalyst fully regained its initial activity and selectivity after undergoing recalcination.

4. Conclusions

Bifunctional Zr-beta supported Rh catalysts exhibited high activity and stereoselectivity for the hydrogenation of 4-*tert*-butylphenol and *p*-cresol to the corresponding *cis*-4-alkylcyclohexanol under mild conditions of 80 °C and 0.5 MPa H_2. A rhodium loading of 0.5 wt% was found to be the most effective. The highest stereoselectivity to *cis*-4-*tert*-butylcyclohexanol and *cis*-4-methylcyclohexanol was 95 and 89%, respectively, at complete conversion of the phenol. Based on the pro-

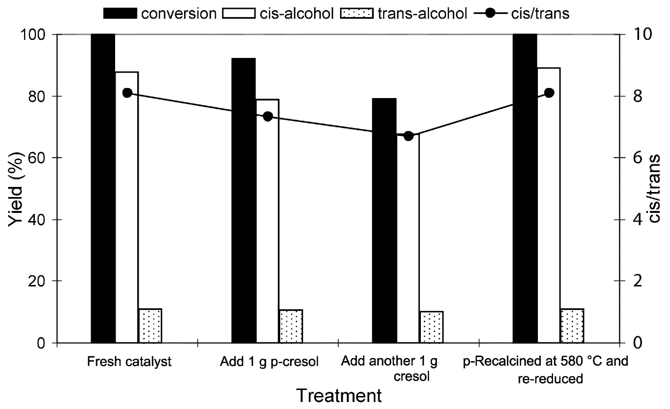


Fig. 9. Re-use of 0.5% Rh/Zr-beta catalyst in hydrogenation of *p*-cresol (measured after 6 h). Reaction conditions: 9.25 mmol *p*-cresol, 50 ml 2-propanol, 100 mg catalyst, 80 °C, 0.5 MPa H_2.

nounced effect of solvents, it is concluded that the reaction proceeds by a cascade combination of hydrogenation and MPV reduction of the intermediate ketone. The high selectivity to the thermodynamically less stable *cis*-alcohol is attributed to the MPV reduction of the ketone by 2-propanol over Zr-beta. In hexane or *tert*-butanol as solvents, no MPV reduction is possible, and the selectivity to the *cis*-alcohol dropped to $<50\%$.

Using palladium instead of rhodium required a higher temperature and pressure for the hydrogenation. The selectivity to *cis*-4-*tert*-butylcyclohexanol was 94%. A lower rate of reaction and selectivity to the *cis*-alcohol was obtained when Al-beta, Zr-impregnated Al-beta, and ZrO_2 were used as supports instead of Zr-beta. The Rh/Zr-beta catalyst is a reusable catalyst, regaining fully its fresh activity and selectivity after recalcination.

References

[1] M. Bartok, Stereochemistry of Heterogeneous Metal Catalysis, Wiley, Chichester, 1985.
[2] O.M. Kut, U.R. Dätwyler, G. Gut, Ind. Eng. Chem. Res. 27 (1988) 215.
[3] D.H. Pybus, C.H. Sell, in: The Chemistry of Fragrance, Royal Society of Chemistry, Cambridge, 1999, p. 108.
[4] W. Kiel, US patent 6 046 365 (2000), to Bayer Aktiengesellschaft.
[5] W. Vogtman, S. Lewandowski, R. Gembicki, J. Cieslar, J. Panachida, B. Wieckiewicz, PL 137526 (1986), to Inst. Chemii Przemyslowej.
[6] Kh.N. Zhanbekov, S.R. Konuspaev, Zh.A. Bizhanov, Izv. Nats. Akad. Nauk Resp. Kaz. Ser. Khim. 2 (1995) 34.
[7] K. Morikawa, T. Yoshizawa, H. Kadomae, JP 10081641 (1998), to Showa Denko KK.
[8] S.R. Konuspaev, Kh.N. Zhanbekov, Izv. Nats. Akad. Nauk Resp. Kaz. Ser. Khim. 5 (1992) 16.
[9] S.R. Konuspaev, V.K. Zhanbekov, D.Yu. Murzin, Chem. Eng. Technol. 20 (1997) 144.
[10] D.Yu. Murzin, A.I. Allachverdiev, N.V. Kul'kova, Stud. Surf. Sci. Catal. 78 (1993) 243.
[11] A.M. Pak, D.V. Sokolskii, R.C. Kuznetsova, S.R. Konuspaev, Kh.N. Zhanbekov, React. Kinet. Catal. Lett. 33 (1987) 31.
[12] M. Sekiguchi, S. Tanaka, EP 0755910 (1997), to Sumitomo Chemical Co.
[13] M. Sekiguchi, S. Tanaka, JP 10195005 (1998), to Sumitomo Chemical Co.
[14] M. Sekiguchi, S. Tanaka, JP 11021268 (1999), to Sumitomo Chemical Co.
[15] N. Hoyoshi, E. Mine, C.V. Rode, O. Sato, T. Ebina, M. Shirai, Chem. Lett. 35 (2006) 1060.
[16] G.D. Yadav, P.K. Goel, J. Mol. Catal. A 184 (2002) 281.
[17] A. Kalantar, H. Backman, J.H. Carucci, T. Salmi, D.Yu. Murzin, J. Catal. 227 (2004) 60.
[18] P.N. Rylander, Catalytic Hydrogenation in Organic Synthesis, Academic Press, New York, 1979, p. 193.
[19] M. Higashijima, S. Nishimura, Bull. Chem. Soc. Jpn. 65 (1992) 824.
[20] L.M. Tang, M.Y. Huang, Y.Y. Jiang, Chin. J. Polym. Sci. 14 (1996) 57.
[21] C. Chen, X. Wang, M.Y. Huang, Y.Y. Jiang, Chin. J. Polym. Sci. 14 (1996) 355.
[22] D. Xia, L. Liu, M.Y. Huang, Y.Y. Jiang, Polym. Adv. Technol. 10 (1999) 116.
[23] Y.Z. Zhu, G.K. Chuah, S. Jaenicke, J. Catal. 227 (2004) 1.
[24] G.K. Chuah, S. Jaenicke, Appl. Catal. A 163 (1997) 261.
[25] K.G. Griffin, S. Hawker, P. Johnston, M.-L. Palacios-Alcolado, C.L. Clayton, in: D.G. Morrell (Ed.), Chemical Industries: Catalysis of Organic Reactions, vol. 89, Dekker, New York, 2003, p. 529.
[26] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, J. Mol. Catal. A 115 (1997) 457.
[27] S.H. Liu, G.K. Chuah, S. Jaenicke, J. Catal. 206 (2002) 321.
[28] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, Chem. Commun. (1995) 1859.