

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

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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.

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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.

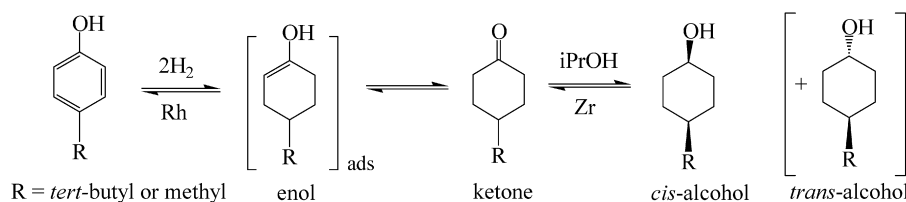
Various supported and unsupported metal catalysts, such as Pd, Ni, Ru, Pt, and Rh, have been used for the liquid-phase catalytic hydrogenation of 4-*tert*-butylphenol to either the ketone or the alcohol [4–8]. A yield of 99.1% 4-*tert*-butylcyclohexanol

with 28.1% selectivity of the *cis*-isomer was obtained over a conventional Ni/Al₂O₃ catalyst in isobutyl acetate. Using Raney Ru catalysts, the reaction could be carried out at room temperature and under 5–10 bar H₂ 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 TiO₂, Al₂O₃, activated charcoal, MgO, or SiO₂, marked differences in the yield of *cis*- and *trans*-isomeric products were obtained, depending on the combination of catalysts and the solvent (H₂O, 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 CH₃COOH was added to Rh/Al₂O₃ 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

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

HCl, H₂SO₄, HClO₄, 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/SiO₂ 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-zeolite 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 RhCl₃·3H₂O (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 H₂/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 H₂ 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% ZrCl₄ 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 ZrCl₄ 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 ZrOCl₂ 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.

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