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Journal of Catalysis 227 (2004) 60–67

JOURNAL OF CATALYSIS

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Gas-phase hydrogenation of 4-*tert*-butylphenol over Pt/SiO_2

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Received 7 April 2004; revised 23 June 2004; accepted 30 June 2004

Available online 21 July 2004

Abstract

Gas-phase hydrogenation of 4-*tert*-butylphenol (4-TBP) over 1% Pt/SiO_2 to *cis* and *trans* 4-*tert*-butylcyclohexanol (4-TBCHOL), via the intermediate 4-*tert*-butylcyclohexanone, was studied in a differential reactor at atmospheric pressure and at temperatures between 127 and 227 °C. The formation of by-products due to hydrogenolysis played an important role in the reaction at temperatures over 200 °C. The rates of 4-*t*-butylcyclohexanol and 4-*t*-butylcyclohexanone formation passed through a maximum at 187 °C. The catalyst deactivation was also considerable. Being thermodynamically more stable the *trans* form of the alcohols isomers is produced in separate experiments by epimerization in the presence of hydrogen as an astoichiometric compound. The reaction network for the reaction is proposed.

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Keywords: Hydrogenation; Gas phase; 4-*tert*-butylphenol; Pt/SiO_2

1. Introduction

Alkylated cyclohexanols, like 2- and 4-*tert*-butylcyclohexanol, are important intermediates for the fragrance and perfumery industry [1], conventionally prepared by catalytic liquid-phase hydrogenation of alkyl-substituted phenols. The problem of stereoselectivity of catalytic reactions has been encountered for many years. Alkyl-substituted phenols can be selectively hydrogenated to corresponding cyclohexanols (*cis* and *trans*) or they can be selectively directed to cyclohexanones, which are sometimes preferable products. The enol form of this intermediate (alkylcyclohexen-1-ol) is predominantly hydrogenated to the *cis* isomer [2]. It participates apparently in an increase of this isomer in the final mixture. Industrial interests, in a number of cases, are limited only to the *cis* stereoisomer form of the corresponding alkylcyclohexanols as they serve as important intermediates for the industry.

In general hydrogenation of alkylphenols is carried out in the liquid phase over palladium or nickel catalysts, depending on the product of interest. The highest selectivity to cyclohexanones is achieved by palladium whereas a mixture of *cis* and *trans* isomers is obtained from hydrogenation of alkyl-substituted phenols over nickel-based catalysts [3]. For the hydrogenation of 4-*tert*-butylphenol a stereoselectivity up to 100% has been achieved using a rhodium catalyst with an acidic cocatalyst [4]. As noted, these considerations have been studied in the liquid phase. The liquid-phase reaction places restrictions on temperature and pressure and therefore the equipment is more complicated. The catalyst must be separated from the products, creating additional complications [5]. A promising alternative could be gas-phase hydrogenation, therefore the gas-phase hydrogenation of 4-*tert*-butylphenol over Pt/SiO_2 was the focus of the present study. To the best of our knowledge no report on gas-phase hydrogenation of TBPH is given in the literature.

2. Experimental

2.1. Catalyst preparation

The Pt/SiO_2 catalysts were prepared by impregnation of a silica support (Merck, 0.063–0.2 mm), having a BET sur-

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doi:10.1016/j.jcat.2004.06.027

face area of 485 m^2/g, with a solution of $Pt(NH_3)_4Cl_2$. After the impregnation the samples were step-washed with deionized water, dried at 90 °C, and stored prior to their use. The catalyst metal content was determined by the direct current plasma (DCP) technique (Spectraspan IIIA, Spectrometrics).

A calcium-doped Pt/SiO_2 was also prepared. SiO_2 support was doped with Ca by ion exchange with nitrate salt. Pt/alumina catalysts were prepared by wet impregnation of a γ-alumina support (LaRoche, Versal GL25, BET surface area of 219 m^2/g) using a solution of H_2PtCl_6 and $Pt(NO_3)_2$. These two salts were used to study the effects of increased carrier acidity due to the presence of surface chlorine anion and its influence on the electric properties of small platinum particles.

2.2. Catalyst characterization

The dispersion and mean particle diameters of the metal were determined by hydrogen adsorption, using a Sorptomatic 1900 (Carlo Erba Instruments). The adsorption isotherms were recorded at 298 K and pressures of 0.0013–0.133 bar. Extrapolation of adsorption isotherms to zero pressure was used to determine the amount of irreversibly adsorbed hydrogen. The amount of reversibly adsorbed hydrogen was determined by the back-sorption method. Prior to the H_2 adsorption, the catalysts were reduced in situ under hydrogen flow at 400 °C for 2 h. Dissociative adsorption of hydrogen was adopted and the metal particle sizes were determined by assuming spherical particle geometry. The BET specific surface area of the fresh and used Pt/SiO_2 catalyst was measured by nitrogen adsorption using a Sorptomatic 1900 (Carlo Erba Instruments). All the samples were freed of all adsorbed materials by outgassing in vacuum at 300 °C for 3 h, before starting the N_2 adsorption.

The surface and subsurface composition of the catalysts was investigated by a scanning electron microscope (Leica Cambridge, Stereoscan 360) equipped with energy dispersive X-ray analyzer (EDXA) and X-ray photoelectron spectroscopy (Perkin-Elmer 5400). The calibration of the XP spectrometer was checked with a test sample containing Au, Ag, and Cu metal, on top of a two-sided tape. Binding energies (BE) were referenced against carbon 1s impurity peak at 284.6 eV [6]. Measurements were carried out using Mg-Kα source and 35 eV pass energy. The accuracy of the measured binding energies was ca. ± 0.15 eV. The catalyst powder was placed on top of a two-sided tape, and the reduced samples were transferred in a N_2 protective atmosphere with a Perkin-Elmer Vacuum Transfer Assembly unit. The Shirley background removal method was applied to all of the spectra. The intensity ratios and energy separations were kept fixed at their theoretical values. In the analysis, no impurities except carbon were observed. Charging of the electrically insulating samples during the measurement, due to the X-ray bombardment, was rather stable (± 0.1 eV). The sensitivity factors used for Pt 4f, Pt 4d, and Al 2p were 5.575, 3.50, and 0.234, respectively [7].

2.3. Catalytic activity measurement

The catalytic experiments were carried out mainly with 1% Pt/SiO_2 in a continuous flow tube reactor, operating at atmospheric pressure, around which a heating element was mounted. A K-type thermocouple was inserted coaxially into the catalyst bed and was used to simultaneously measure the catalyst bed temperature and control the power supply to the heating element via a programmed temperature control unit. Since 4-TBP (Acros Organics) is a solid substance, in order to avoid the crystallization problems, the reactor and the saturator were placed in an oven kept at 130 °C, which effectively prevented the crystallization of the reactant and the products. All the lines after the oven were heated. The products were analyzed by a GC (HP 5890) equipped with flame ionization detector and a DV-WAX column. The GC analyses were carried out isothermally at 170 °C. In order to determine the light products (hydrogenolysis/cracked at higher temperatures) the separation was carried out at ambient temperature after which the ramping and final dwell at 170 °C were applied. Helium was used as the carrier and the injector and detector temperatures were 250 and 240 °C, respectively. The products were further confirmed by GC-MS (HP 6890–5973 Instrument). The gas hour space velocity (GHSV) was set at 125.76 h^{-1} (124.8 mL/min) and the partial pressures of hydrogen and 4-TBP were varied from 0.058 to 0.13 bar and from 0.0088 to 0.0015 bar, respectively, using argon as a make-up gas keeping a constant GHSV. Prior to each catalytic experiment, the catalyst (60 mg, 125–150 μm) was reduced in situ in a flow of hydrogen at 400 °C for 2 h followed by cooling in hydrogen flow to the desired temperature of the reaction. All the gases were of 99.999 vol% purity. Preliminary experiments were carried out to establish the testing conditions, and to ensure that the kinetic experiments are measured in the absence of external and internal diffusion limitation problems.

Mass balance study was performed at both lowest and highest temperatures where the hydrogenolysis/cracking products were formed. The products were identified by GC-MS and special calibrations were carried out to determine the reactants/products concentration with a high degree of accuracy. The amount of light hydrogenolysis/cracking products (although in small amounts) was determined by GC and special calibration gases. The GC analysis of light and heavier products was determined both isothermally and with temperature ramping from ambient temperature. The results indicated that almost all the carbon was accounted for, and the amount that could be attributed to carbon deposition on the catalyst as well as the error was in the range of acceptable experimental error.

Isomerization and dehydrogenation of 4-TBCHOL (Acros Organics; 70% *trans*, 30% *cis*) as well as hydrogenation of 4-TBCHONE (Acros Organics) were also studied in the same experimental setup as for hydrogenation of 4-TBP. The mass and particle size of the catalyst and reduction temperature were the same as in the 4-TBP hydrogenation experiments.

3. Results and discussion

3.1. Catalyst characterization

The dispersion of the metal in 1% Pt/SiO_2 was 86.06% with a metal particle diameter of 1.2 nm. Calcination of the catalyst (calcined at 600 °C for 3 h) resulted in a particle size of almost three times of the size of the noncalcined one. For the 1% Pt/SiO_2 catalyst both EDXA and XPS analyses indicated that chlorine is practically disappearing after the reduction of the catalyst. After reduction at 673 K, the Cl/Si as well as the Cl/Pt ratio decreased below detection limit from 2.1×10^{-3} (XPS)/3.2×10^{-3} (EDXA), and 0.44 (XPS)/0.62 (EDXA), respectively. This is important to know, since the residual chlorine, an electronegative species, could affect the properties of the active metal and hence the reaction rate and product selectivity. The presence of chlorine at the surface has been shown to lower the activity of the Al_2O_3-based catalysts in aromatic hydrogenation [8,9]. The XPS analysis also indicated that the platinum particles are slightly positively charged (Pt^{2+}, BE 72.3 eV) [16]. This could be the effect of the carrier, since its acidity could result in e^- withdrawal from small Pt particles. This is comparable to the BE of Pt on alumina, 314 eV. The differences in the values reported by XPS and EDXA is probably due to the depth of the two techniques, with XPS being more surface sensitive than EDXA.

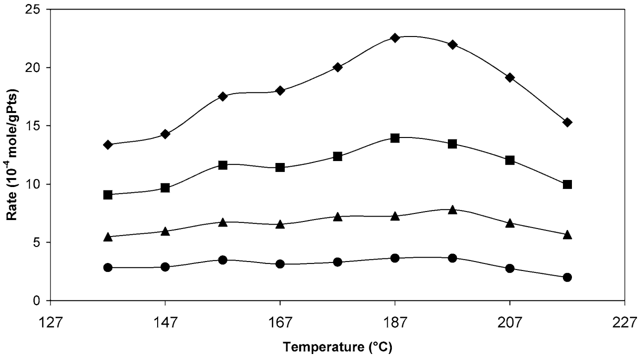


Fig. 1. Temperature dependency of the rates of 4-*tert*-butylcyclohexanol and 4-*t*-butylcyclohexanone formation over 1% Pt/SiO_2. $p_{4\text{-TBP}} = 0.0034$ bar, $p_{H_2} = 0.13$ bar (◆), 0.1084 bar (■), 0.078 bar (▲), 0.052 bar (●).

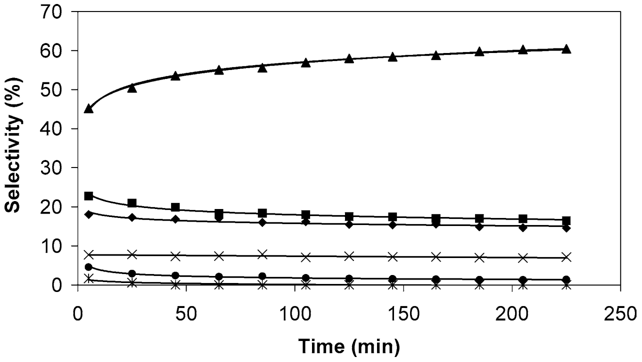
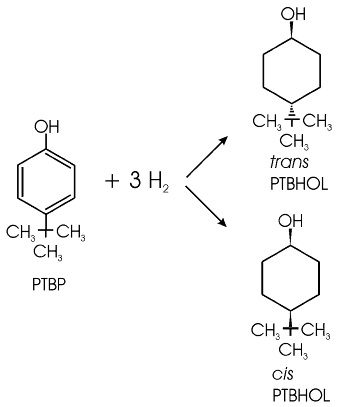


Fig. 2. Selectivities of the products vs time on stream. 4-TBP hydrogenation. 1% Pt/SiO_2, $T = 177$ °C, $p_{H_2} = 0.1048$ bar, $p_{4\text{-TBP}} = 0.0034$ bar. (∗) Toluene, (×) TBBZ, (●) TBCH, (◆) *cis*-4-TBCHOL, (■) *trans*-4-TBCHOL, (▲) 4-TBCHONE.

3.2. Hydrogenation of 4-tert-butylphenol

The main products from the hydrogenation of 4-TBP were 4-*tert*-butylcyclohexanone, *cis*- and *trans*-4-*tert*-butylcyclohexanol (4-TBCHOL); see Scheme 1. Similarly to alkylbenzene hydrogenation reactions, the rates of 4-*tert*-butylcyclohexanol and 4-*t*-butylcyclohexanone formation passed through a reversible maximum at 187 °C (Fig. 1). The hydrogenolysis of 4-TBP results in the formation of *tert*-butylbenzene (TBBZ) that can be further be hydrogenated to *tert*-butylcyclohexane (TBCH). The alcohol product (4-TBCHOL) can be dehydrated as well to form TBCH. At the beginning of the reaction formation of by-products is high but decreases rapidly after 20 min. At the end of the experiment the production of the by-products was minor compared to the production of 4-TBCHOL and 4-TBCHONE (Fig. 2). The observed pattern indicates that more ketone was formed at longer times on stream, undergoing less hydrogenation to the alcohols. The *cis* to *trans* ratio was also studied and compared at different times on stream. The ratio rises, beginning from 0.79, and closer to quasi-steady-state conditions the ratio tends to stabilize around 0.88.



Scheme 1. Hydrogenation of 4-TBP to *cis* and trans 4-TBCHOL.

The hydrogenation experiments were carried out with a prereduced catalyst. A longer run at 177 °C was made to reveal the behavior of the catalyst in a period of time (Fig. 3). As can be seen a continuous slow deactivation took place and a steady state was not reached even after 4 h. Catalyst deactivation is commonly observed for reactions involving hydrocarbons and is assumed to be a consequence of carbon deposition [10]. The BET surface area of the fresh and spent catalyst indicated that the used catalyst retained 75% of its initial surface area. The deactivation was found to be

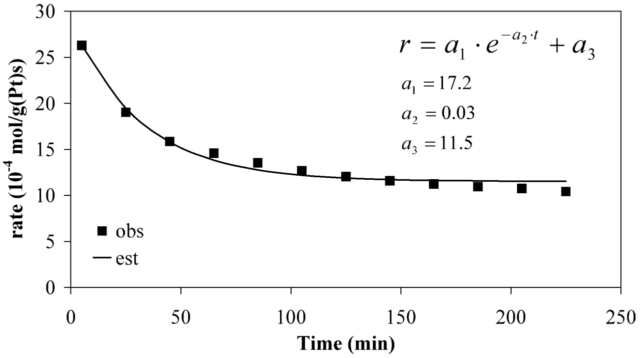


Fig. 3. Overall hydrogenation rate as a function of time on stream. 4-TBP hydrogenation, 1% Pt/SiO$_2$, $T = 177\,°\mathrm{C}$, $p_{\mathrm{H}_2} = 0.1048$ bar, $p_{\text{4-TBP}} = 0.0034$ bar. (■) Observed rate, (—) estimated rate.

reversible since the regenerated catalyst restored, and even slightly improved, the activity. The regeneration of the catalyst was carried out by heating the sample under hydrogen flow to 400 °C where it was kept for 2 h, after which the temperature was decreased to the desired temperature and the reactants were introduced. The H$_2$ treatment was done to remove the loosely deposited carbonaceous species from the surface. By approximating the reaction rate with an exponential function a mechanistic deactivation model for catalyst fouling can be applied [11],

$$r = a_1 \cdot e^{-a_2 \cdot t} + a_3,$$

where r is the reaction rate and a_i are the constants estimated in each case, as they depend on the temperature and composition of the reactants stream,

$$a_1 = \frac{k_s r_0}{k_s + k_{-s}}, \qquad a_2 = k_s + k_{-s},$$
$$a_3 = k_{-s} \cdot \frac{r_0}{k_s + k_{-s}}.$$

k_s and k_{-s} are the rate constants for deactivation and self-regeneration, and r_0 is the rate under deactivation-free conditions. a_1 plus a_3 represents the initial rate of the catalyst, when time is very close to zero, a_2 is the level of deactivation in the reaction, and a_3 is the rate at the steady state (in this case a quasi-steady state). The following values of parameters were obtained $a_1 = 17.2, a_2 = 0.03, a_3 = 11.52$ for the estimated rate in Fig. 3.

The rates at steady state were used for the determination of the kinetic data. The reaction orders in hydrogen and hydrocarbon were determined in the temperature range from 137 to 227 °C. The experiments were made with intervals of 10 °C, and the orders with respect to hydrogen and hydrocarbon were calculated at each temperature. The orders in 4-TBP increased from −0.7 to −0.35 in the temperature interval (Table 1). In this case, increase in 4-TBP pressure was proven to retard the reaction rate. Previous reports in the literature have shown orders with respect to the aromatic compound very close to zero [12] or slightly negative [20] at different temperatures. The possible reason for the temperature dependency of reaction orders could be due to a change of the mode of adsorption of the molecule of 4-TBP over the surface of the catalyst at higher temperatures or due to weaker adsorption of the alkylphenol in this range.

Table 1
Reaction orders with respect to hydrogen and 4-TBP

Temperature (°C)	H$_2$	4-TBP
127	1.47	−0.70
147	1.71	−0.64
167	1.82	−0.55
187	1.89	−0.52
207	1.72	−0.35

The reaction order with respect to hydrogen increased as the temperature increased until a maximum was reached at 187 °C (Table 1). High reaction orders with respect to H$_2$ along with an increasing tendency with temperature have been previously reported for aromatic and substituted aromatic compounds [12,13]. The hydrogenation rate passed through a maximum at approximately 187 °C. Similar temperature dependencies have been reported for hydrogenation of aromatic compounds [9,14,15]. The main reason for the observed maximum in the rate versus temperature is probably a decreased surface coverage of the aromatic molecule, analogously to *o*-xylene hydrogenation [8,20].

From a commercial point of view the *cis* isomer is the most valuable product. By increasing the partial pressure of hydrogen the selectivity toward alcohol increases and the selectivity toward ketone and by-products declines. Fig. 4 shows the selectivity of the reaction to the main products, i.e., 4-TBCHOL (*cis* and *trans* isomers) and 4-TBCHONE at 177 °C. The same tendency was observed at other temperatures as well. Regarding stereoselectivity, a higher partial pressure of hydrogen decreased the *cis*/*trans* ratio (Fig. 5) which is contrary to what has been reported for hydrogenation of xylenes [8,12]. The selectivities toward ketone and alcohols were roughly the same up to 187 °C, thereafter starting to decrease. Formation of TBBZ and TBCH can be seen at higher temperatures (> 187 °C), with hydrogenolysis playing an important role (Fig. 6). In particular formation of TBBZ increased dramatically above 200 °C, reaching selectivities of 30% (Fig. 7). The activation energy, calculated

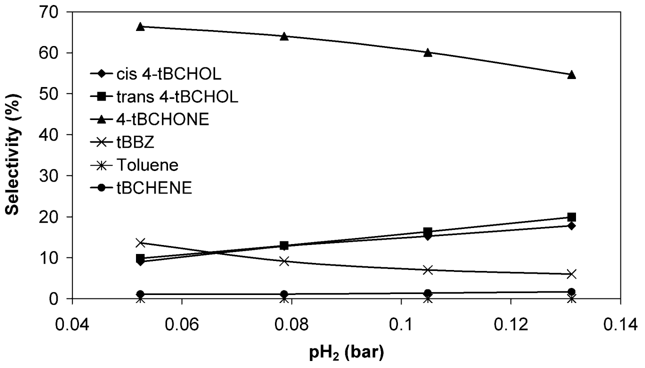


Fig. 4. Selectivity of products as a function of hydrogen partial pressure. 4-TBP hydrogenation, $T = 177\,°\mathrm{C}$, $p_{\text{4-TBP}} = 0.0034$ bar.

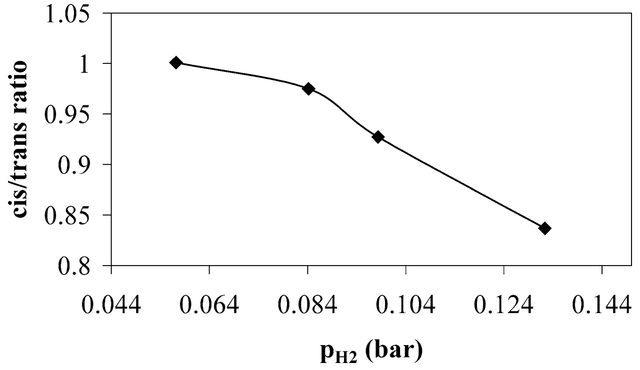


Fig. 5. *Cis*-to-*trans* ratio as a function of hydrogen partial pressure. 4-TBP hydrogenation, $T = 177\,°\mathrm{C}$, $p_{4\text{-TBP}} = 0.0034$ bar.

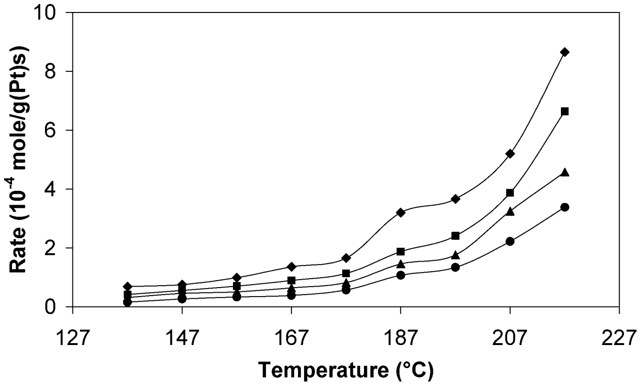


Fig. 6. Rate of by-product (tBBZ + toluene + TBCHENE) formation as a function of temperature. 4-TBP hydrogenation. $p_{H_2} = 0.13$ bar (◆), 0.1084 bar (■), 0.078 bar (▲), 0.052 (●). $p_{4\text{-TBP}} = 0.0034$ bar.

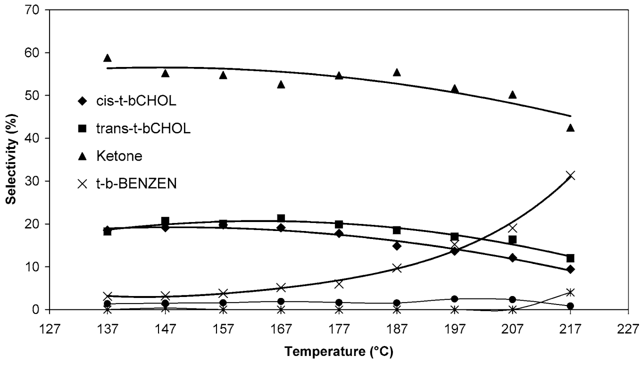


Fig. 7. Product distribution, hydrogenation of 4TBP $p_{H_2} = 0.13$ bar, $p_{4\text{-TBP}} = 0.0088$ bar.

from Arrhenius plots, in the hydrogenation of 4-tBP was 66 and 53 kJ/mol in the temperature range 127–187 and 187–217 °C, respectively.

3.3. Effect of carrier, precursor, and platinum content

To study the effect of the carrier and the precursor, two different Pt/Al_2O_3 catalysts with a metal content of 1 wt% were prepared from H_2PtCl_6 and $Pt(NO_3)_2$. Much lower initial rates (2.1×10^{-4} and 4.6×10^{-4} mol/g(Pt)s for Pt/Al_2O_3–Cl and Pt/Al_2O_3–nitrate, respectively) compared to the Pt/SiO_2 catalysts (21.6×10^{-4} mol/g(Pt)s) were observed at 177 °C ($p_{H_2} = 0.13$ bar, $p_{4\text{-TBP}} = 0.0034$ bar). Moreover, the hydrogenation of 4-TBP over Pt/Al_2O_3 catalysts mainly resulted in the formation of hydrogenolysis products and no 4-TBCHOL was observed over the Pt/Al_2O_3 catalyst prepared from Cl-containing precursor. The catalyst prepared from Pt–nitrate salt at higher hydrogen partial pressures yielded small amount of alcohols. It appears, that alumina, being a more acidic carrier than silica enhances hydrogenolysis. The XPS and EDXA analyses of the Pt/Al_2O_3 catalyst prepared from H_2PtCl_6 have clearly indicated the presence of residual surface chlorine even after the reduction at 400 °C [16], which results in an enhanced surface acidity. According to [17], one might anticipate that such surface acidity could stir the stereoselectivity of the reaction toward *cis*-4-TBCHOL (although one should differentiate between the “surface acidity” and that of the “media”). Unfortunately, the yield of alcohols was very low (to enable us a reasonable determination of *cis*- and *trans*-isomer stereoselectivity), preventing a reasonable determination of *cis* to *trans* ratio.

Calcium-doped Pt/SiO_2 catalysts were tested in order to investigate the effect of catalyst acidity on the hydrogenation activity and product distribution. Liquid-phase hydrogenation in acid solutions leads to the formation of the *cis*-alcohol, whereas the formation of *trans*-alcohol is favored in basic media [18]. The acidity of the catalyst carrier is reported to have a strong effect on the selectivity toward the formation of *cis*- and *trans*-4-TBCHOL, with the selectivity toward the formation of the *cis* isomer being enhanced by the carrier acidity, which is in accordance with the theoretical predictions [17,18]. Since the higher acidity of the carrier also results in hydrogenolysis reactions, the use of additives can direct the formation of a given stereoisomer, while suppressing the hydrogenolysis [17,21]. Addition of Ca (1 wt%) to Pt/SiO_2 catalysts resulted in a decreased hydrogenation rate (Fig. 8); however, further increases in the Ca content did not result in an additional rate decrease.

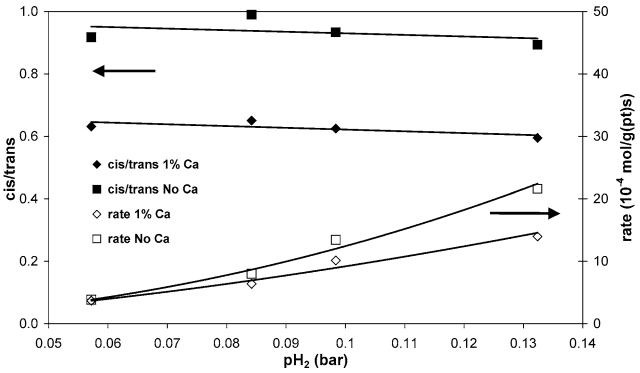


Fig. 8. Effect of acidity on hydrogenation rate and *cis*/*trans* ratio as a function of partial pressure of hydrogen. $p_{4\text{-TBP}} = 0.0034$ bar, $T = 177\,°\mathrm{C}$. *Cis*/*trans* with no addition of Ca (■) and with addition of 1 wt% Ca (◆) as well as hydrogenation rate with no Ca (☐) and with addition of 1 wt% Ca (◇).

Table 2
Composition of the stream of products, initial reaction rate, and *cis*-to-*trans* ratio after 140 min of reaction for the calcined and noncalcined catalysts ($T = 177\,^{\circ}\mathrm{C}$, $p_{\mathrm{H_2}} = 0.13$ bar, $p_{\text{4-TBP}} = 0.0034$ bar)

Catalyst	Particle size (nm)	Metal dispersion (%)	Rate ($10^{-4}\mathrm{mol}/(\mathrm{g_{Pt}\,s})$)	*CIS* (%)	*TRANS* (%)	*cis*/*trans*	ONE (%)	PTBP (%)	TBBZ (%)	TOL (%)	TBCH (%)
1% Pt/SiQ	1.2	86	21.6	1.8	2.1	0.89	6	89	1	0	0
3.03% Pt/SiQ	1.3	77	64.0	13.1	16.1	0.81	19	18	16	1	17
5.57% Pt/SiQ	1.5	65	34.8	4.6	7.3	0.63	18	0	21	4	43
5.57% Pt/SiQ (calc.)	4.0	25	26.9	10.7	19.8	0.54	14	23	27	1	5

CIS, *cis*-4-TBCHOL; *TRANS*, *trans*-4-TBCHOL; ONE, 4-TBCHONE; 4-TBP, 4-TBP; TBBZ, TBBZ; TOL, toluene; TBCH, TBCH.

Different Pt/SiO_2 catalysts (3.03 wt% Pt and 5.57 wt% Pt) were prepared from $Pt(NH_3)_4Cl_2$ and investigated for their performance in the hydrogenation of 4-TBP at 177 °C. The results indicate an activity increase with a higher Pt content (Table 2). The catalyst containing 3 wt% platinum exhibited the highest activity as well as the highest amount of generated *cis*- and *trans*-4-TBCHOL. At the same time a considerable amount of by-products was formed. A complete conversion of 4-TBP was achieved over the 5.5 wt% Pt/SiO_2 catalyst.

The results indicated that for the 5.5 wt% Pt/SiO_2 catalyst subjected to heat treatment in air at 600 °C an increased particle size due to sintering resulted in a lower hydrogenation rate.

As shown in Table 2, an increase in the catalyst Pt content, caused by increased metal uptake, resulted in a slight increase in the mean platinum particle size, and the consequent decreased metallic dispersion (it should be noted that the catalysts are prepared by ionic adsorption on high surface area silica). The overall reaction rate is found to pass through a maximum at ca. 3 wt% Pt content, whereas the *cis*-to-*trans* isomers ratio is decreased with incremental Pt content. The decreased *cis*-to-*trans* ratio, hence, cannot be attributed to the overall reaction rate (conversion dependency of the selectivity) as they do not follow the same pattern. The observed *cis–trans* stereoselectivities is believed to be governed instead by the platinum particle sizes. Larger Pt particles are needed for the *trans*-isomer formation/transformation. TBP can adsorb on the Pt surface (or Pt-carrier interface) either parallel (π-binding) or through the phenolic group (σ-binding). The possibility of simultaneous π- and σ-binding could not be excluded. The relative contribution of these adsorption modes will stir the stereoselectivity. The effect of Pt particle size on the rate of *trans*-isomer formation/transformation (see reaction mechanism section) is further manifested as the presintered 5 wt% Pt/SiO_2 catalyst (6 h at 600 °C in air), while exhibiting a similar overall reaction rate as the 1 wt% Pt/SiO_2 catalyst, gave rise to the faster formation/transformation rate of the *trans* isomer (Table 2).

3.4. 4-TBCHONE hydrogenation

Hydrogenation of ketone produced both *cis*- and *trans*-4-TBCHOL. At temperatures below 200 °C both *cis*- and *trans*-4-TBCHOL were present, which could imply that either the ketone produces both isomers or the ketone produces only one of the alcohol stereoisomers (*cis* isomer) [17] while the *trans* isomer is produced by the epimerization or from the ketone via an *enol*. The reaction order with respect to hydrogen was decreasing, from 0.71 to 0, by increasing the temperature. Fig. 9 shows the behavior of the rates of hydrogenation of 4-TBCHONE in the range of temperatures studied, at different partial pressures. At higher H_2 partial pressures, the hydrogenation rate is also higher, indicating a positive reaction order similar to hydrogenation of 4-TBP. The apparent activation energy was 32.5 kJ/mol.

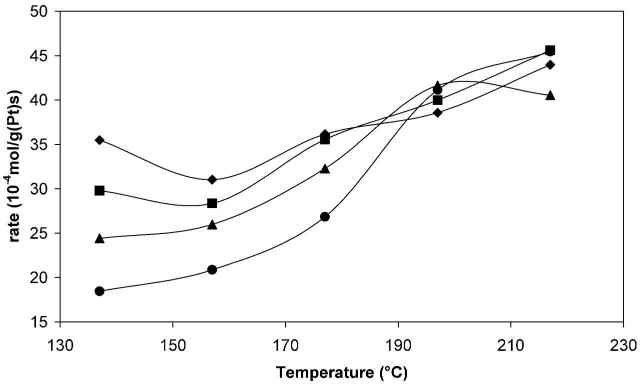


Fig. 9. Hydrogenation rates of 4-TBCHONE vs temperature at different hydrogen partial pressures, $p_{\text{4-TBCHONE}} = 0.041$ bar, (◆) $p_{\mathrm{H_2}} = 0.13$ bar, (■) $p_{\mathrm{H_2}} = 0.1$ bar, (▲) $p_{\mathrm{H_2}} = 0.078$ bar, (●) $p_{\mathrm{H_2}} = 0.051$ bar.

3.5. 4-TBCHOL dehydrogenation and isomerization

In order to better understand the reaction mechanism, the dehydrogenation and isomerization of commercial 4-TBCHOL were carried out. 4-TBCHOL dehydrogenation was studied in the temperature interval 137–217 °C with different partial pressures of hydrogen (0.05–0.13 bar). Both hydrogenation and dehydrogenation were found to take place over the Pt/SiO_2 catalyst. The temperature is the main factor that affects the rate and product distribution. At lower temperatures (up to 187 °C) the *cis*-to-*trans* isomerization is dominant. Thereafter also the *trans* isomer starts to be consumed, to form by-products (see Fig. 6). In Fig. 10 one can observe that the isomerization rate is in the same order as the 4-TBP hydrogenation rates. The ketone hydrogenation rates showed in Fig. 9 can also be compared to

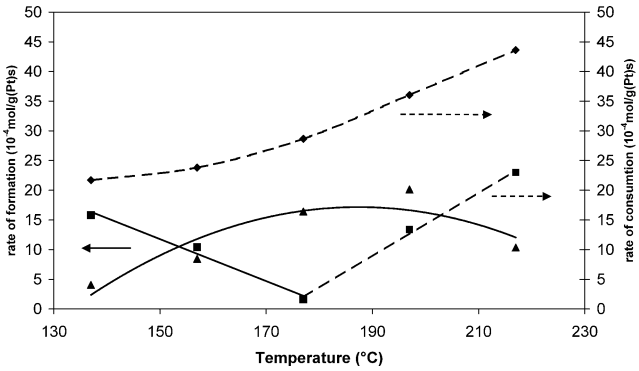


Fig. 10. Rates of formation (—)/consumption (- - -) of main products vs temperature. $p_{4\text{-TBCHOL}} = 0.06$ bar, $p_{H_2} = 0.051$ bar, (♦) rate *cis*-4-TBCHOL (consumption), (■) rate of *trans*-4-TBCHOL (formation), (▲) rate of 4-TBCHONE (formation).

the isomerization rates. Comparison at the same hydrogen partial pressure (0.051 bar) indicates that the *cis*-to-*trans* isomerization is faster than the ketone hydrogenation. It is reasonable to assume that the ketone is hydrogenated to the *cis* alcohol as previous studies of 4-TBP hydrogenation have suggested [21], and then *cis*-4-TBCHOL undergoes epimerization to form *trans*-4-TBCHOL. At temperatures above 200 °C, the consumption rate of both stereoisomers is high, leading to the formation of the by-products. At temperatures below 180 °C the *cis*-to-*trans* ratio was constant (about 0.55), although lower than in the hydrogenation of 4-TBP. At temperatures above 197 °C, this ratio increases, due to transformation of *trans*-4-TBCHOL into TBBZ. The presence of hydrogen was essential for both dehydrogenation and isomerization reactions. The reaction rates decreased considerably when hydrogen flow was halted for 30 min and balanced with argon. After reintroducing hydrogen, the activity of the reaction is partially restored (Fig. 11). The effect of hydrogen on the reaction rate shows that hydrogen plays an important role, not only in the removal of carbon deposits but also for participation in the epimerization mechanism (Scheme 2). According to this mechanism *cis*-4-TBCHOL is adsorbed parallel to the surface with hydrogen atoms forming H bonding. Here the presence of hydrogen is essential. A similar effect has been reported by Bragin et al. [19] and Kalantar et al. [8,20].

3.6. Mechanism

The detailed kinetic study of 4-TBP hydrogenation performed in this work has enabled the proposal of the following reaction mechanism. 4-TBP is transformed into with 4-TBCHONE as an intermediate. In the first hydrogenation step 4-TBCHENOL is formed as an adsorbed surface intermediate. This enol undergoes tautomeric equilibrium transformation to adsorbed 4-TBCHONE or can be hydrogenated to *trans* TBCHOL. 4-*tert*-butyl-cyclohexanone is hydrogenated into *cis*-4-TBCHOL [21], which further undergoes epimerization to form *trans*-4-TBCHOL. At higher reaction temperatures hydrogenolysis of 4-TBP results in the formation of *tert*-butylbenzene that can be further be hydrogenated to *tert*-butylcyclohexane. Dehydrogenation of the alcohol can as well form TBCH. The reaction network is depicted in Scheme 3. The epimerization of the products was observed to take place and hydrogen was proven to be an astoichiometric compound in *cis*-to-*trans* isomerization. The conversion of *cis*-4-TBCHOL takes place to form the thermodynamically more stable compound, *trans*-4-TBCHOL. Reliable thermodynamic data for these compounds cannot be found in the literature; therefore estimations were made using the Yoneda method [22]. The results suggest that the *trans* isomer is slightly more stable, since it has more negative Gibbs energy (Fig. 12), which is logical considering that the isomerization follows this path and is in accordance with relative stabilities of *cis* and *trans* dialkylcyclohexanes.

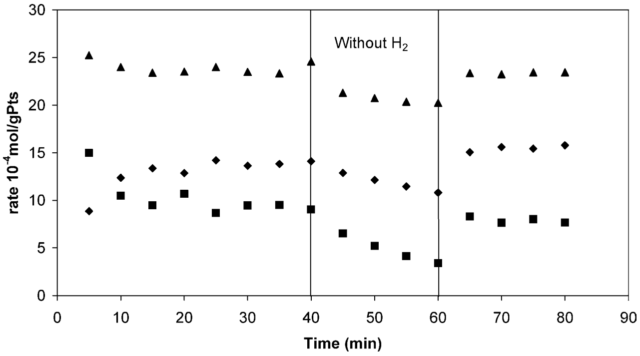
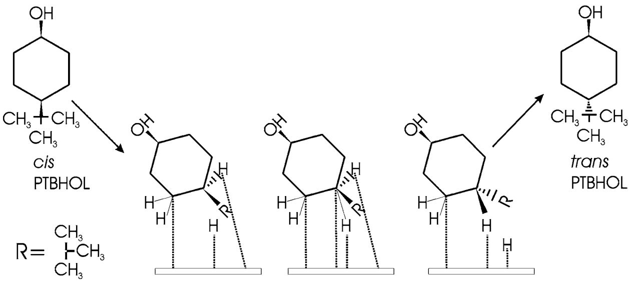


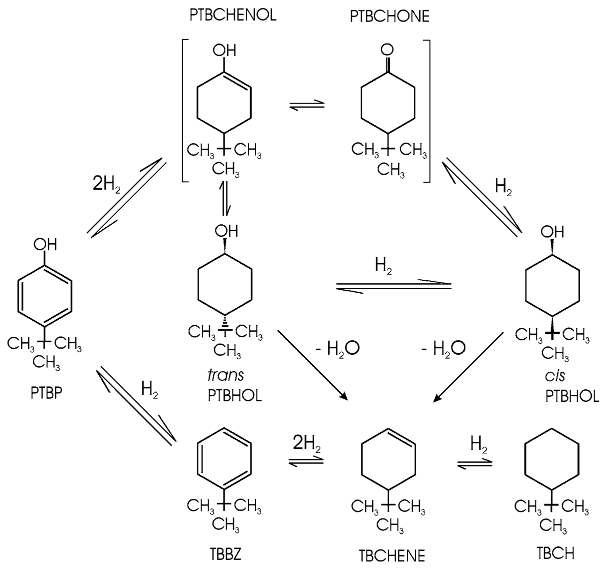
Fig. 11. Effect of hydrogen in the alcohol isomerization and dehydrogenation. (▲) Rate *cis*-4-TBCHOL (consumption), (♦) rate of *trans*-4-TBCHOL (formation), (■) rate of 4-TBCHONE (formation). $T = 177$ °C, $p_{4\text{-TBCHOL}} = 0.06$ bar, $p_{H_2} = 0.051$ bar.



Scheme 2. *Cis*-to-*trans* isomerization.

4. Conclusions

Gas-phase hydrogenation of 4-*tert*-butylphenol was studied over a silica-supported platinum catalyst in the temperature range 127–227 °C and hydrogen and 4-*tert*-butylphenol partial pressures of 0.052–0.013 and 0.009–0.0153 bar, respectively. The main reaction products from gas-phase hydrogenation of 4-*tert*-butylphenol were 4-*tert*-butylcyclohexanol (*cis* and *trans*) and 4-*tert*-butylcyclohexanone. At temperatures exceeding 200 °C *tert*-butylbenzene and *tert*-butylhexanone were also generated. A maximum in the hydrogenation rate of 4-*tert*-butylphenol was observed



Scheme 3. Reaction network for the hydrogenation of 4-TBP.

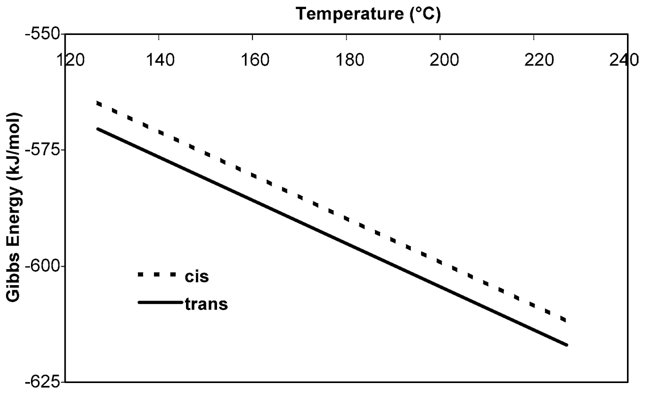


Fig. 12. Gibbs energy vs temperature for 4-TBCHOL.

at 187 °C and the overall hydrogenation rate was found to increase with hydrogen partial pressures. The reaction orders with respect to hydrogen and 4-*tert*-butylphenol varied from 1.4 to 1.9 and -0.7 to -0.35, respectively, within the studied temperature range. The 1% Pt/SiO_2 catalyst favors the formation of the intermediate product, 4-*tert*-butylcyclohexanone, with a selectivity of 55%. The *cis*-to-*trans* ratios of the alcohols were close to one at the temperatures studied. In order to establish the reaction mechanism, hydrogenation of the intermediate product, 4-*tert*-butylcyclohexanone, and its stereoselectivity orientation were studied. Additionally the dehydrogenation and epimerization of the products were observed to take place and hydrogen was found to be necessary for the *cis*-to-*trans* isomerization. Besides being an astoichiometric agent hydrogen contributes to the removal of carbon deposition. The isomerization rate can be compared to the hydrogenation rate of 4-*tert*-butylphenol and to the hydrogenation rate of 4-*tert*-butylcyclohexanone as well, entailing that ketone is hydrogenated to *cis* 4-*tert*-butylcyclohexanol and the formed *cis* 4-*tert*-butylcyclohexanol undergoes epimerization to form the *trans*-4-*tert*-butylcyclohexanol. The stereoselectivity toward the formation of *cis*- and *trans*-4-*tert*-butylcyclohexanol is strongly affected by the support acidity/basicity.

Acknowledgments

The authors are grateful to Dr. Hannu Karhu at the Department of Physics, University of Turku, for his contribution to the XPS and EDXA analyses. This work is part of the activities at the Åbo Akademi Process Chemistry Centre within the Finnish Centre of Excellence Programme (2000–2005) by the Academy of Finland.

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