Hydrogenation of phenol over supported platinum and palladium catalysts

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Abstract

The vapour-phase hydrogenation of phenol over platinum and palladium supported on alumina and zeolite LTL was studied in a vertical fixed-bed high-pressure reactor. The major products of the hydrogenation reaction were cyclohexanone and cyclohexanol with cyclohexane, cyclohexene and benzene as the minor products. The selectivity for the major products was upto 99%, the conversion being influenced by temperature, feed rate and the partial pressure of hydrogen. Platinum catalysts were found to be better for the production of cyclohexanol while palladium catalysts favoured cyclohexanone production. The platinum catalysts also showed twice as much overall conversion as the palladium catalysts.

Keywords: alumina; hydrogenation; palladium; phenol; platinum; zeolite LTL

INTRODUCTION

Supported metal catalysts have been widely used for hydrogenation and dehydrogenation reactions. Supports ensure better dispersion and stability of the metals in addition to influencing their catalytic properties through electronic interactions [1]. The hydrogenation of phenol and substituted phenols have been carried out over group VIII metals either as "blacks" or as supported catalysts [2–8]. Hydrogenation of phenol produces two important compounds, viz., cyclohexanone and cyclohexanol, both of which are utilized in the manufacture of a large number of industrial products. Cyclohexanone is a key material in the production of nylons for the synthetic fibre and tyre industries [2].

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The products of phenol hydrogenation depend on the type of catalyst and the reaction conditions [3,7]. The yield of cyclohexanone generally increases with increasing temperature [4,7]. It has been shown that phenol can be directly converted to cyclohexanol without going through the intermediate production of cyclohexanone, but phenol reacts very slowly with cyclohexanol converting it to cyclohexanone. Smith and Stump [5] gave the following mechanism for the hydrogenation of phenol over an Adams platinum catalyst and a 5% rhodium–alumina catalyst:

Phenol   ——— Cyclohexenols ———

Cyclohexanol   Cyclohexenol   Benzene

Cyclohexenol   Cyclohexanone
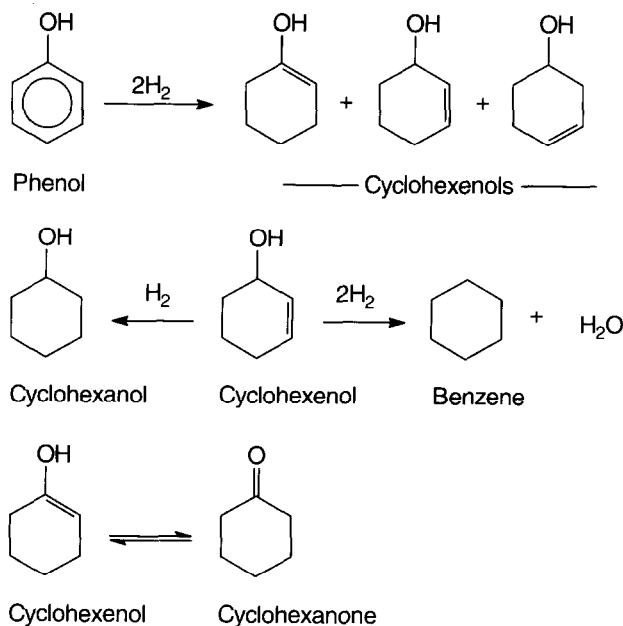
The tautomerisation of cyclohexene-1-ol to cyclohexanone takes place readily owing to the greater stability of cyclohexanone. Similar mechanisms have been suggested by Takagi et al. [6,9] for the hydrogenation of cresols over rhodium hydroxide based catalysts.

Hydrogenation of phenols and cresols have been extensively studied in the liquid phase, mostly at high pressures over Raney nickel and Adams platinum catalysts. Metals like iridium, palladium, rhodium and ruthenium have also been used in the liquid-phase catalysis of the reaction. Hydrogenation in the vapour phase has not been widely reported although a few results for nickel supported on cerium oxide [7,10] and platinum on alumina [11] are known. The present investigation deals with the hydrogenation of phenol in the vapour phase over platinum and palladium catalysts supported on nonacidic alumina and a basic zeolite LTL.

EXPERIMENTAL

Catalysts

The platinum–alumina catalysts were prepared by adding the required amounts of a standard solution of chloroplatinic acid to γ-alumina extrudates obtained from alumina hydrate (Catapal B, Sarabhai Merck) by extrusion with 2% acetic acid, followed by drying and calcining at 753 K for 3 h. The catalysts were again dried and calcined at 753 K for a further 3 h. The chloride ions were next removed by extraction with a hot ammonia (1 *M*) solution thrice. The catalysts were then impregnated with a solution of sodium carbonate and further calcined at 753 K for 6 h. The same procedure was followed for the preparation of palladium–alumina catalysts using standard palladium chloride solution.

Zeolite LTL was synthesized by following published procedures [12]. 35.84 g KOH, 6.20 g Al(OH)$_3$ and 140.00 g water were mixed and boiled to dissolve the Al(OH)$_3$. The original volume of the solution was restored by adding water and then cooled. 49.76 g of SiO$_2$ (fumed) was added slowly with constant stirring. The gel so produced was kept in an oven at 413 K for 40 h. It was filtered, washed and dried. The zeolite LTL was identified by its X-ray diffraction (XRD) pattern, sorption capacity (for benzene) and chemical analysis.

Platinum and palladium metals were loaded on the zeolite by ion-exchange methods using tetrammine platinum and palladium nitrate salt solutions, respectively. The loaded catalysts were calcined at 753 K for 6 h and made into pellets and crushed into 12–14 mesh particles.

The catalysts used are designated as: PtA, 0.6% platinum–alumina with 3% sodium; PtZ, 1% platinum–zeolite LTL; PdA, 1% palladium–alumina with 3% sodium; and PdZ, 1% palladium–zeolite LTL. The catalysts were reduced in flowing hydrogen at 753 K (PtA and PtZ) and 573 K (PdA and PdZ) for 3 h prior to a run. After each run, the catalysts were regenerated by oxidizing the coke deposits in a current of air at 753 K and later were flushed by a flow of nitrogen for at least half an hour.

Reagents

Analar grade phenol (BDH India, distilled at atmospheric pressure, b.p. 455 K) mixed with analar methanol in 90:10 (wt./wt.) ratio was used instead of pure phenol in all the hydrogenation experiments. This made the feeding of the reactants simple. The hydrogen used (Industrial Oxygen Limited, Pune) was passed to the reactor through a filter, keeping the ratio of feed-to-hydrogen at 1:3 (mole ratio).

Apparatus

The hydrogenation reaction was carried out in a fixed-bed, vertical flow, high-pressure reactor. The pressure in the system was controlled by a digital controller (Geomechanique, France).

The products were analysed by gas chromatography (HP 5880A and Shimadzu GC R1A) using 50 m×0.5 mm phenyl silicone gum and 2-m carbowax columns.

RESULTS AND DISCUSSION

The major products obtained when phenol and hydrogen were passed over platinum and palladium catalysts supported on alumina and zeolite LTL were cyclohexanol and cyclohexanone. Benzene, cyclohexane and cyclohexene were also formed in small amounts in the reaction. The catalysts supported on zeolite LTL yielded a number of other products in very small amounts; these were not identified. Products of methanol (diluent, 10 wt.-% in the feed) conversion, if any, were not detected.

The distribution pattern of products for a typical run of the reaction at 523 K at a total pressure of 1 MPa is given in Table 1. The different behaviour of platinum and palladium catalysts with respect to yield of various products can be clearly seen in this table. Cyclohexanol is the main product with an appre-

TABLE 1

Distribution of products in the hydrogenation of phenol

Conditions: temperature = 523 K; pressure = 1 MPa; hydrogen/phenol (mole ratio) = 3. selectivity = (amount of cyclohexanone and cyclohexanol produced/total amount of products) · 100

Catalysts	PtA	PtZ	PdA	PdZ	PdZ	PdZ	PdZ
Feed flow-rate ($mol\,g^{-1}\,h^{-1}$)	0.05	0.05	0.05	0.02	0.03	0.05	0.06
Total conversion (%)	97	88.7	45	44.3	42.9	41.8	40.8
Product distribution (%)							
Cyclohexanol	87.2	78.4	5.1	8.9	8.4	8	7.8
Cyclohexanone	7.7	6	39.5	32.7	32.2	32	31.6
Benzene	1.9	0.81	0.2	0.4	0.31	0.2	0.1
Cyclohexene	0.7	0.31	0.13	0.15	0.11	0.08	0.05
Cyclohexane	0.57	0.07	0.07	0.04	0.03	0.02	0.02
Others	–	3.1	–	2.11	1.8	1.54	1.24
Cyclohexanone/cyclohexanol	0.09	0.08	7.74	3.67	3.8	4	4.07
Selectivity	97.8	95.2	99.1	93.9	94.7	95.6	96.5

ciable amount of cyclohexanone in the cases of PtA and PtZ, while the pattern is reversed in the case of PdA and PdZ.

The effect of temperature was investigated by studying the reaction at four different temperatures: 473, 498, 523 and 548 K with a constant pressure of 0.3 MPa (PtA and PtZ) and 1 MPa (PdA and PdZ) and a constant feed flow-rate of 0.05 mol g^{-1} h^{-1}. The results are shown in Figs. 1 and 2, respectively for the platinum and palladium catalysts. It can be seen that the total conversion as well as the yields of the main products, cyclohexanol and cyclohexanone, decreased with increasing temperature. For the platinum catalysts, the yield of cyclohexanol decreased more rapidly than that of cyclohexanone which is reflected by the slow increase in the cyclohexanone/cyclohexanol ratio (Fig. 1). In the case of the palladium catalysts, cyclohexanone was the major product and the cyclohexanone/cyclohexanol ratio showed a much more pronounced increase between 473 and 498 K for PdA (Fig. 2). For all the catalysts, the yield of minor products did not change much with increasing temperature. The results, however, indicate a relative enrichment of cyclohexanone over cyclohexanol with increasing temperature.

The yield of major products is also influenced by changes in the pressure (Figs. 3 and 4). For the platinum catalysts (temperature 523 K, feed rate 0.5 mol g^{-1} h^{-1}, hydrogen/phenol mole ratio 3:1), an increase in hydrogen pressure yielded more cyclohexanol, which is to be expected due to the presence of a large excess of hydrogen. Cyclohexanone showed a corresponding decrease (Fig. 3). This is further reflected in the nearly exponential decrease of cyclohexanone/cyclohexanol ratio with a pressure in the range 0.1 to 1.0 MPa. The palladium catalysts, however, showed significantly different results (Fig. 4) under a similar set of conditions. Total conversion showed an almost linear increase in the pressure range 0.5 to 2.0 MPa. Initially, the yield of cyclohexanone was much greater than that of cyclohexanol which almost stagnated. With an increase in pressure, the production of cyclohexanol increased tremendously while that of cyclohexanone fell after going through a peak. For the palladium catalysts, 1.0 MPa pressure of hydrogen seemed to be ideal for the production of cyclohexanone.

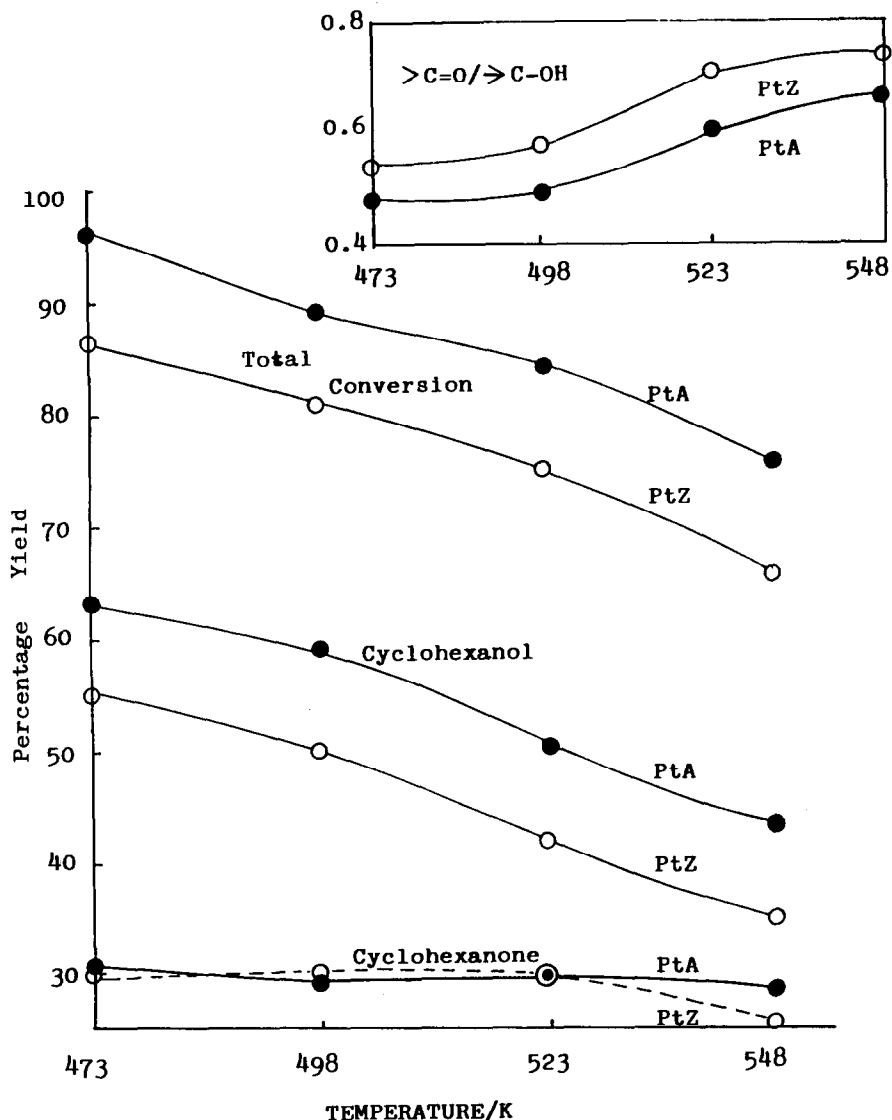The following sequence of reactions are suggested for the vapour-phase hydrogenation of phenol:
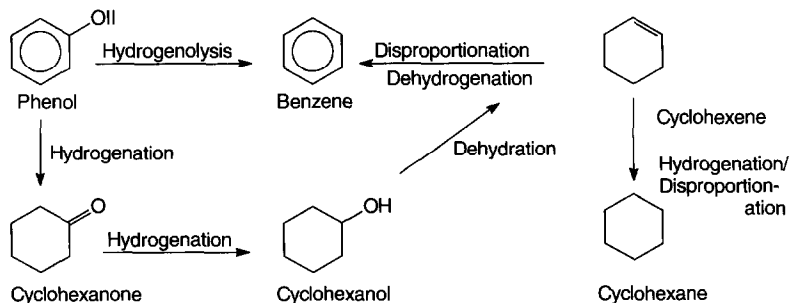
Fig. 1. The effects of temperature on the yield of principal products for the platinum catalysts. (Feed rate: 0.05 mol g^{-1} h^{-1}, pressure: 0.3 MPa, hydrogen/phenol mole ratio: 3/1.)

which, in essence, is similar to those proposed for the liquid-phase hydrogenation [5,6,9]. The increase in the cyclohexanone/cyclohexanol ratio, with temperature indicates that the dehydrogenation reaction is favoured by a high temperature, resulting in the production of more cyclohexanone. Partial hy-
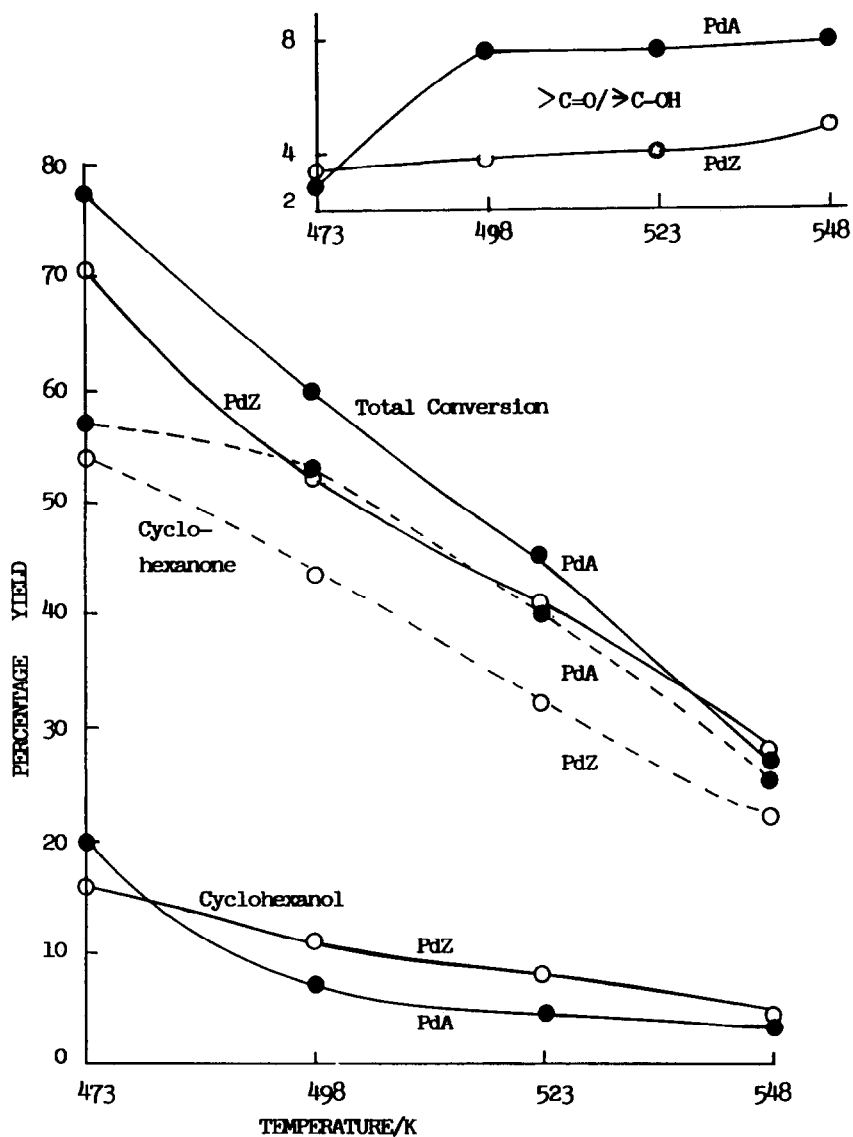
Fig. 2. The effects of temperature on the yield of principal products for the palladium catalysts. (Feed rate: 0.05 mol g^{-1} h^{-1}, pressure: 1.0 MPa, hydrogen/phenol mole ratio: 3/1.)

drogenolysis is also responsible for the production of benzene as a byproduct, whose yield was found to increase with increasing temperature.

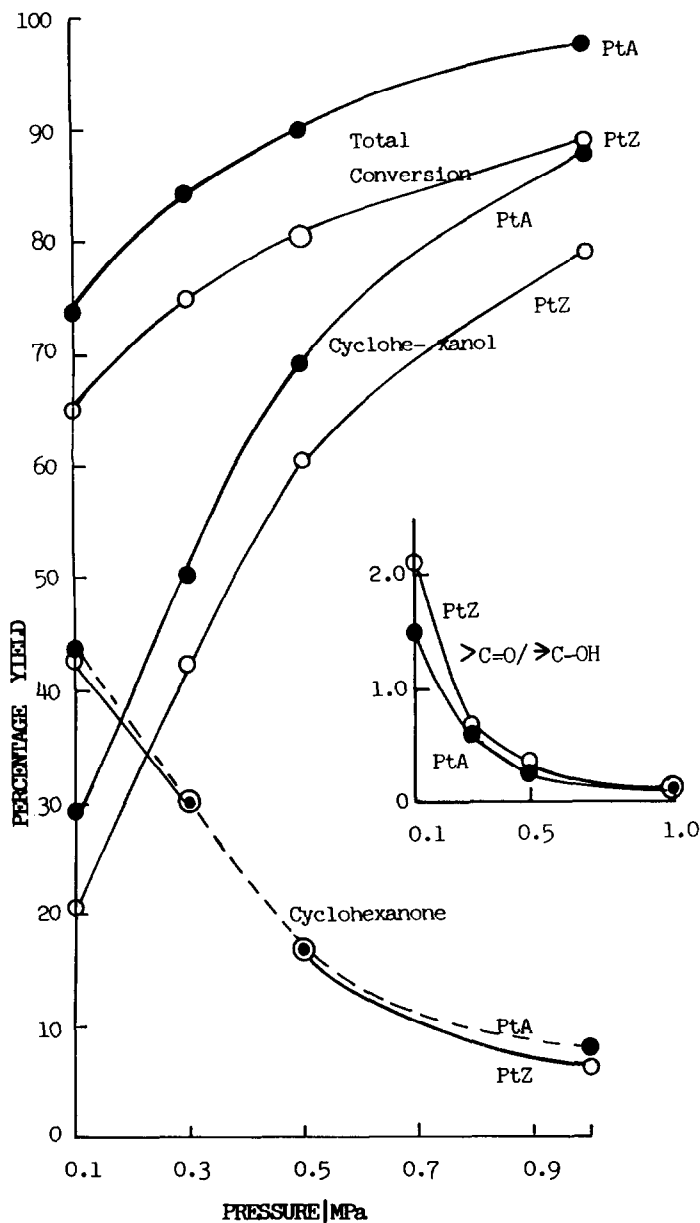The increase in the cyclohexanol yield and the corresponding decrease in

Fig. 3. The effects of pressure on the yield of principal products for the platinum catalysts. (Temperature: 523 K, feed rate: 0.05 mol g^{-1} h^{-1}, hydrogen/phenol mole ratio: 3/1.)

the cyclohexanone/cyclohexanol ratio with an increase in hydrogen pressure is obviously due to the greater availability of hydrogen. The increased yield of benzene with increasing hydrogen pressure is a clear pointer to its production through the hydrogenolysis of phenol.

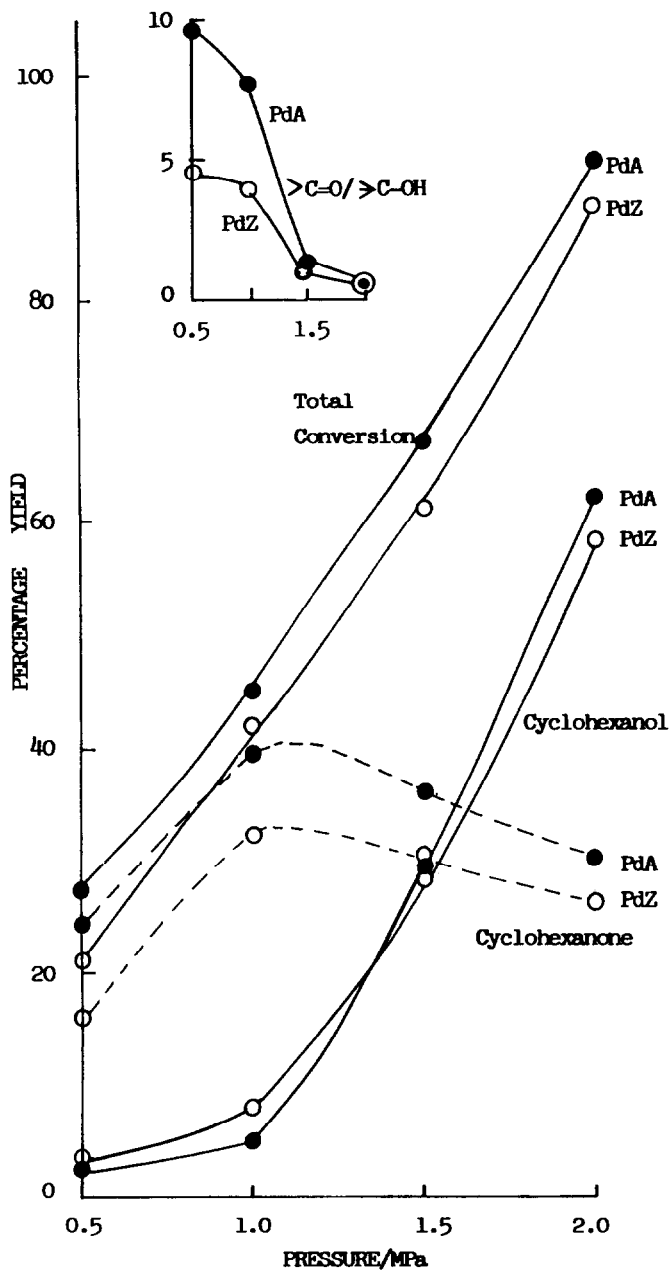An increase in the flow-rate of the feed (keeping the phenol/hydrogen ratio

Fig. 4. The effects of pressure on the yield of principal products for the palladium catalysts. (Temperature: 523 K, feed rate: 0.05 mol g^{-1} h^{-1}, hydrogen/phenol ratio: 3/1.)

constant) decreased the conversion of phenol (Table 1). The yields of all products declined with decreasing contact time, but the cyclohexanone/cyclohexanol ratio increased slightly. This indicates that cyclohexanone is the intermediate in the hydrogenation of phenol to cyclohexanol.

The conversion of phenol and the selectivities towards cyclohexanone and cyclohexanol are found to be greater in the case of alumina-supported catalysts than in the case of zeolite-supported catalysts, perhaps due to the smaller number of side reactions in the case of alumina (Table 1).

CONCLUSIONS

The vapour-phase hydrogenation of phenol seems to be very much dependent on the metal used. The conversion of phenol over platinum supported on alumina and zeolite LTL is more than twice (about 89% and 97%, respectively) that compared to the respective palladium catalysts (about 42% and 45% for alumina and zeolite LTL supports, respectively) under the same conditions of pressure and temperature for fresh catalysts (Table 1). The cyclohexanone/cyclohexanol ratio is also always lower in the case of the platinum catalysts than in the case of palladium catalysts under the same set of conditions. Rylander [13,14] has shown that when palladium is used as the catalyst, a high yield of cyclohexanone is obtained which agrees with the findings of our present study. According to Rylander, palladium has a high double bond isomerization activity and can readily isomerize cyclohexanol to cyclohexanone. Takagi et al. [15], however, do not subscribe to this view. The present work conclusively proves that platinum is a much better catalyst than palladium for the hydrogenation of phenol in the vapour phase.

This work illustrates how differently two very similar metals, palladium and platinum, behave towards the hydrogenation of phenol. On the basis of percentage d-character of the metallic bond (Pd: 46, Pt: 44), palladium in a crystalline state or in a compound is expected to show the greater catalytic activity [16]. However, this activity depends on a number of factors including temperature and pressure, and the rates of adsorption and desorption of the reactants and the products on the catalyst surface. In hydrogenation reactions, the activity of palladium is likely to be limited by its ability to dissolve hydrogen atoms, thus maintaining a low concentration of them on the surface [17]. Platinum, on the other hand, dissociates molecular hydrogen easily and has a much larger concentration of hydrogen atoms on the surface.

Sintering may also be responsible for the differing pattern of behaviour of palladium and platinum. It is known [18] that dispersed particles of palladium are more sensitive to the hydrogen reduction temperature than those of platinum. Calcining temperatures may also have some effect. Sintering reduces the surface area of the catalysts more in the case of palladium than platinum and the catalytic activity is likely to be modified correspondingly.

Strong metal support interactions (SMSI) may also play some sort of role. Levin et al. [19] have shown the order of charge transfer among the group VIII metals to be Pt > Pd > Rh > Ru, the magnitude determining the extent of activation of the molecules on the surface. Much more work needs to be done in order to draw some conclusion as to the possible cause of the differences in behaviour of palladium and platinum. Similarly, the role of the support has to be evaluated to see if the catalysts behave bifunctionally.

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