

Gas Phase Phenol hydrogenation to Cyclohexanone over Supported Metal Catalysts

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Abstract: A series of catalysts containing 1 wt.% Pd, Pt and Rh supported on magnesia (MgO) of commercial origin have been tested for gas phase hydrogenation of phenol at 473 to 563 K with H₂/phenol ratio of 5.4 at normal atmospheric pressure. The phenol hydrogenation activity showed a dependence on the irreversible uptake of hydrogen. Pd (1wt%)/Al₂O₃ was used as a reference to compare the hydrogenation of activity of Pd/MgO catalyst. Among the catalysts studied, Pd/MgO passed through a maximum at 503 K with increasing temperature. On the contrary, Pd/Al₂O₃ catalyst showed a decrease in activity. The Pd/MgO catalysts exhibited a higher dispersion of smaller Pd crystallites leading to higher activity and total selectivity for cyclohexanone. The higher resistance towards deactivation and better stability of the Pd/MgO catalysts suggest that the acidic sites of alumina may be responsible for deactivation, thereby accounting for the lowering of activity with Pd/Al₂O₃ catalysts.

Keywords: Adsorption, Catalysts, Hydrogenation, Cyclohexanone, Deactivation.

1. Introduction

Catalytic hydrogenation of phenol is industrially important to produce cyclohexanone since it is the basic intermediate raw material to produce caprolactam and adipic acid. **Figure 1** shows the world consumption of cyclohexanone consumed worldwide in the year 2010. It is evident from Figure 1 that major countries like Western Europe, China, Taiwan, and Japan are consuming around 65% of the world capacity. By 2021, this is expected to touch around 85%, reflecting the significant demand for caprolactam.

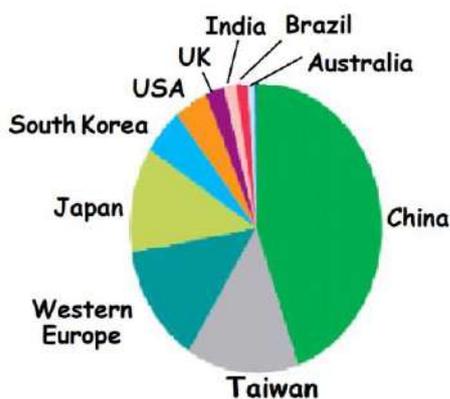
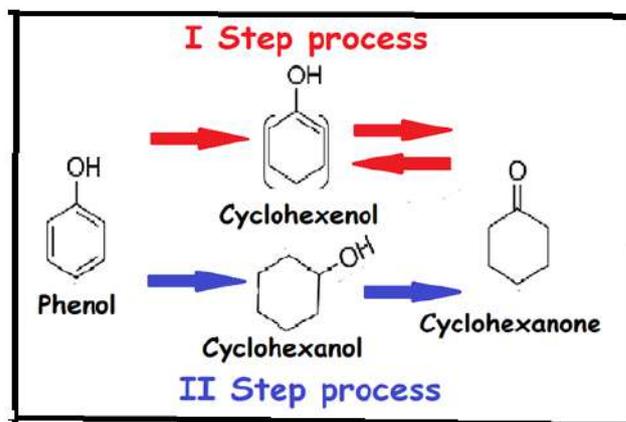


Figure 1. World consumption of cyclohexanone in 2010.

Industrially, cyclohexanone is produced by two reaction routes, namely by the cyclohexane oxidation [1] or by the catalytic hydrogenation of phenol [2]. Although the oxidation route is generally performed in industry due to its relatively low cost, but it operates at severe reaction conditions such as high temperature and high pressure. In addition, it generates a significant quantity of undesirable products which lower the selectivity of cyclohexanone or the product yield [3]. On the other hand, through catalytic hydrogenation of phenol, cyclohexanone can be produced either in "one-step" or in a "two-step" process (**Scheme 1**). The "two-step" process involves hydrogenation of phenol to cyclohexanol over a Ni catalyst as a first step and then followed by dehydrogenation of cyclohexanol to cyclohexanone on Cu/Zn catalyst as a second step [4-6]. Dehydrogenation is an endothermic reaction and normally operates at a higher



Scheme 1. The industrial production of cyclohexanone.

temperature, which is energy intensive. However, the "one-step" hydrogenation shows its superiority in numerous aspects. However, in the single-step process, there is a direct conversion of phenol to cyclohexanone through a formation of an intermediate, cyclohexenol. The intermediate cyclohexenol, being unstable, readily isomerises to cyclohexanone. This direct step of conversion saves the absence of the endothermic dehydrogenation step [7-8]. The single-step process is advantageous in terms of capital investment and energy savings since it avoids the dehydrogenation of cyclohexanol to cyclohexanone, which is significantly energy intensive. The estimation of cyclohexanol

purification and endothermic dehydrogenation step would yield an energy saving of 500 kcal/kg production of cyclohexanone.

Supported metal catalysts are used commonly for the hydrogenation reactions. Supports ensure better dispersion and stability for the active metals to hydrogenate the reactant molecule. The selectivity for cyclohexanone depends on the reaction conditions as well as on the type metal present in the catalysts system being employed. The catalytic vapour phase hydrogenation of phenol has been studied on different supported metal catalysts [9-11]. Different preparatory methods like co-precipitation, homogeneous precipitation-deposition and mixing of hydroxides are often used to prepare the supported metal catalysts [12]. These preparatory routes have shown to avoid sintering / agglomeration of metal atoms and thereby increasing the metal dispersion and longevity of the catalysts. The higher hydrogenation activity of phenol over different supports is an indication of more availability of surface metal atoms and not on the nature of the support type.

Precious noble metals like palladium (Pd), platinum (Pt), ruthenium (Ru), rhodium (Rh), iridium (Ir), rhenium (Rh) and osmium (Os) are traditionally used in industrial hydrogenation processes. Palladium, platinum, or a combination thereof are preferred. Despite their high cost, they are the preferred metals because they are used at low concentration, higher activity, and specificity. As compared to supported platinum catalyst, palladium-based catalyst is less expensive. The yield of the product is also dependent on the acid-basic strength of the support material. Higher acidity support gives lower conversion but a higher selectivity for cyclohexanone. Suitable supports have been used to study the title reaction under various conditions in the past, such as alumina, activated carbon, magnesia, titanium oxide, calcium carbonate and carbon black. It has also been reported that nanotubular titanium dioxide showing interesting results for phenol hydrogenation [13]. Palladium catalysts, either supported on alumina (Pd/Al₂O₃) or magnesia (Pd/MgO), are used for phenol hydrogenation [14-15]. The addition of alkali or alkaline earth metal to Pd/Al₂O₃ catalysts increases the hydrogenation activity and hence the selectivity for cyclohexanone without modifying the kinetics of the reaction [16]. Studies on the vapour phase hydrogenation of phenol over supported metal catalysts are rather limited. In the present investigation, the influence of three noble metals (Pd, Pt, and Rh) supported over magnesia support were

studied for the title reaction. The best amongst the three catalysts was compared with alumina support.

2. Experimental methods

Palladium catalysts were prepared by wet impregnation of magnesia (MgO, MG-061, SA=48 m²/g, PV=1.03 ccg⁻¹) with acidified solution of PdCl₂ to give a known concentration of Pd (1wt%). The samples were dried overnight at 393K and calcined in air at 673K for 4 hours. Phenol hydrogenation was studied in the vapour phase employing a flow system using a fixed bed tubular reactor at atmospheric pressure. Approximately 0.5 g of the catalyst was reduced in a hydrogen flow for 3 h at 723 K before the start of the reaction. Phenol feed was made easier by adding cyclohexane in a 1:2 w/w ratio. Under the reaction conditions used, there was no dehydrogenation or decomposition of the cyclohexane. The mixture (phenol + cyclohexane) was fed over the catalyst at a fixed rate by means of a motorised syringe. The liquid products were collected and analysed by GC using a column packed with Carbowax 20 M on Chromosorb W.

3. Results and Discussion

Studies of the vapour-phase hydrogenation of phenol over monometallic/bimetallic catalysts have shown that a change in product selectivity occurs between cyclohexanol and cyclohexanone [17]. In addition, it has also been reported that the rate of the reaction changed significantly [18]. To verify these observations, a comparison has been made between three catalysts Pd/MgO, Pt/MgO and Rh/MgO, each incorporating 1wt.% Pd with respect to their relative conversion (Figure-2) and selectivity (Figure-3) towards cyclohexanone and cyclohexanol during hydrogenation of phenol reaction at various temperatures between 473 and 563 K. The conversion activity of all three catalysts passes through a maximum (at ca. 503 K) with increasing temperature and follows the order Pt/MgO > Pd/MgO > Rh/MgO under identical reaction conditions. However, at 473 K, the selectivity for cyclohexanone (S_{c>=o}) follows the order Pd/MgO > Rh/MgO > Pt/MgO, but on increasing the temperature further the product selectivity for cyclohexanone with Pd- and Rh-impregnated catalysts is reversed (Pt/MgO > Rh/MgO) without affecting the behaviour of Pd/MgO. This provides further confirmation that phenol activity and product

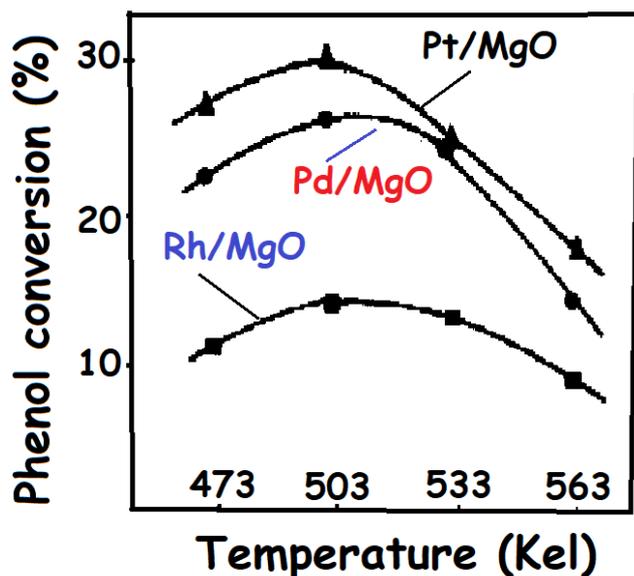


Figure 2. Effect of temperature on phenol conversion. Reaction conditions: Wt. cat.=0.5g, H/Phenol=5.4, and WHSV=0.027 mol/h.

selectivity depends upon the type of metal employed. The total selectivity for cyclohexanone with the Pd/MgO catalyst indicates that, since Pd has a high double-bond isomerisation activity [19], it can readily isomerise cyclohexenol to cyclohexanone. Based on the percentage d-character of the metallic bond, Pd is expected to exhibit enhanced catalytic activity in the crystalline state or in a compound [20]. However, such Pd activity depends on a number of factors like extent of hydride formation and sensitive towards sintering during reduction in hydrogen atmosphere as compared to platinum.

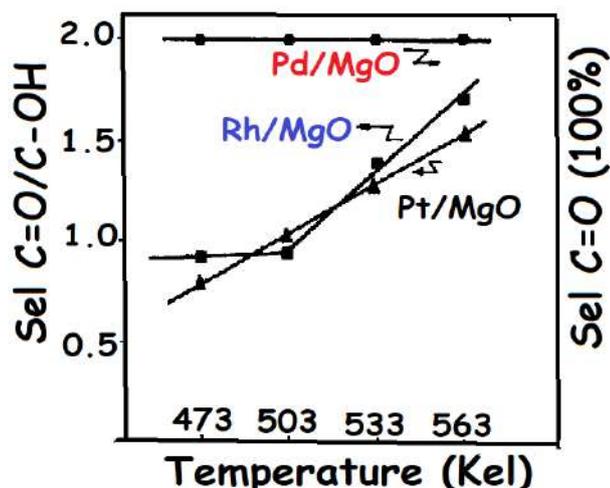


Figure 3. Effect of temperature on ratio of selectivity of cyclohexanone over cyclohexanol. Reaction conditions: Wt. cat.=0.5g, H/Phenol=5.4, and WHSV=0.027 mol/h.

The stability of the catalyst determines its usefulness for reactions requiring a longer duration.

The relationship between phenol conversion and time on stream (TOS) for Pd/Al₂O₃ and Pd/MgO

catalysts (Figure 4). The Pd/Al₂O₃ catalyst shows a faster rate of deactivation with time. In a time interval of 300 min, the conversion decreased from 17% to 3% (Pd/Al₂O₃) as

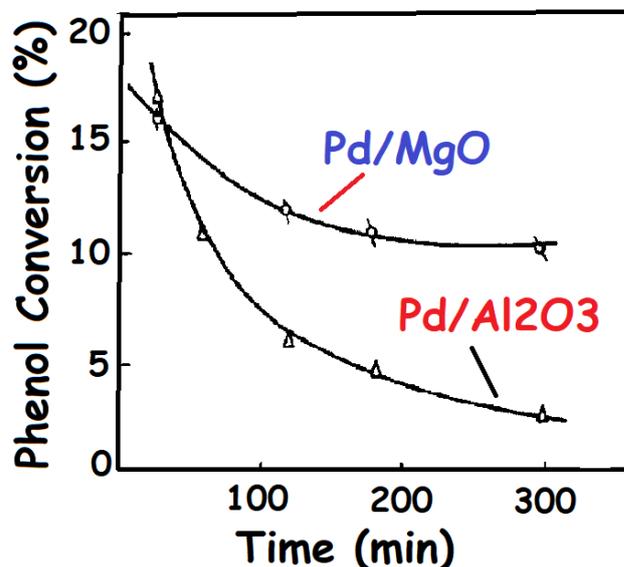
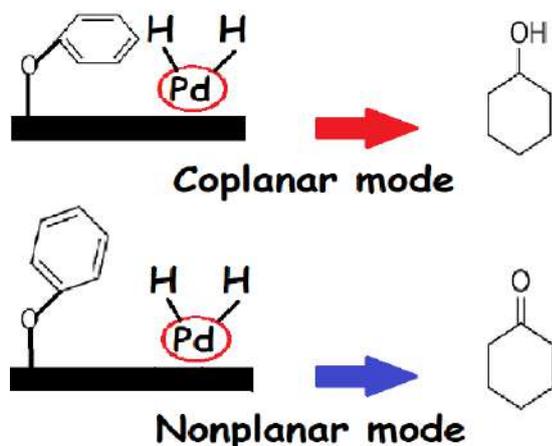


Figure 4. Influence of time on the overall conversion of phenol. Reaction conditions: Wt. cat = 0.5g, T=473K, H/Phenol=5.4, and WHSV=0.027 mol/h.

compared to 16% to 11% over the Pd/MgO catalyst. The faster deactivation over Pd/Al₂O₃ suggests the formation of coke on the acidic sites of the alumina. This is supported by the observation that treatment of a fresh Pd/Al₂O₃ catalyst with NH₄OH solution prior to reaction leads to a considerable improvement in the stability of the reaction. This agrees with the results obtained with a system where 10% CaO had been added to a Pd/Al₂O₃ system and where an improvement in the stability of the catalyst was also observed [21]. With the Pd/MgO catalyst, even though acidic sites are absent, a difference of 6% conversion over a time interval of 300 min suggests that a different type of mechanism is taking place on the basic sites of MgO which leads to deactivation.

As far as the reaction mechanism goes, it is well known that the hydrogenation of phenol occurs between the dissociation of hydrogen molecule on the surface of palladium metals and the chemisorbed phenol molecules in the phenolate form. Due to the spill over phenomenon, hydrogen is available in the aromatic ring [22]. The difference in the selectivity pattern between cyclohexanol and cyclohexanone suggests that the mode of phenol adsorption on the surface varies significantly. As shown in Scheme-2, if phenol is adsorbed on the acidic sites of the support in a planar mode, cyclohexanol is formed. While if it is adsorbed on the basic sites of the support in a nonplanar mode, cyclohexanone is formed [23]. These modes of

adsorption of phenol on the surface of the support are governed by the nature of the support, mainly the



Scheme 2. Adsorption of phenol with two different modes on the surface of magnesia support.

acid-base properties of the support [24]. In general, a high phenol adsorption uptake on magnesia (MgO) support promotes high catalytic activity and selectivity to cyclohexanone.

4. Conclusion

A comparative investigation of 3 different types of catalysts containing 1 wt.% Pd, Rh and Pt on MgO support was investigated for the gas phase hydrogenation of phenol. The phenol hydrogenation activity depends on the dispersion and metal surface area. With Pd/MgO catalysts, a higher dispersion of smaller Pd crystallites contributes to the higher activity observed. The product selectivity for cyclohexanol or cyclohexanone is dependent on the mode of absorption of phenol on the surface of the support. A higher activity with total selectivity for cyclohexanone and a higher resistance and stability towards deactivation suggest that Pd/MgO catalysts could be beneficial for the selective hydrogenation of phenol to cyclohexanone.

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