Kinetics of phenol hydrogenation over supported palladium catalyst [1]

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Abstract

Kinetics of vapor phase hydrogenation of phenol to cyclohexanone over Pd/MgO system has been studied in a flow microreactor under normal atmospheric pressure. The reaction rate is found to be negative order with respect to the partial pressure of phenol and has increased from -0.5 to 0.5 with increasing temperature (473 to 563 K). The apparent activation energy (E_a) of the process is found to be close to 65 kJ per mol. On the basis of kinetic results a surface mechanism is proposed.

Keywords: Kinetics; Hydrogenation; Phenol; Order; Rate constant; Activation energy

1. Introduction

Hydrogenation of phenol to cyclohexanone is an important industrial reaction for the production of Nylon-6 [1,2]. There are reports available wherein a single-step process being used either in a liquid or vapor phase using palladium based catalysts for the production of cyclohexanone [2–4]. The nature of oxide supports and metals used in catalysts formulation have a direct bearing on total selectivity for cyclohexanone [5,6]. The deactivation of industrial catalysts, alumina based in particular and loss in selectivity for cyclohexanone are some of the major concerns to be resolved.

Few papers concerning the reaction mechanism and kinetic models have been reported

[3,4,7–10] to explain the complex situation that arises between the adsorbed phenol and hydrogen on the surface of the catalyst. Due to severe variation reported amongst catalysts used and experimental conditions, a direct comparison of results is not possible. In view of this, the present communication is a further attempt to understand the influence of operative conditions on the rate of phenol hydrogenation along with probable surface events occurring over Pd/MgO systems.

2. Experimental

Palladium catalysts were prepared by impregnation of magnesia (Harshaw, MG-0601, SA = 48 m^2 g^{-1}, PV = 1.03 ccg^{-1}) particles (1600–1800 μm) with acidified solution of $PdCl_2$ to give a known concentration of Pd (1 wt%). The

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samples were dried overnight at 393 K and calcined in air at 673 K for 4 h.

Reaction studies were carried out in a fixed bed tubular reactor under atmospheric pressure. Ca. 0.5 g of the catalyst was reduced in hydrogen flow at 723 K for 4 h and then brought to the reaction temperature. The reaction was carried out at four different temperatures within the range of 473 to 563 K. The reaction details for carrying out hydrogenation of phenol have been reported elsewhere [5].

Reaction rates were measured under differential conditions. The partial pressure of phenol and hydrogen were adjusted using nitrogen stream. Under the experimental conditions used, cyclohexanone was the only product. It was analyzed by a gas chromatograph using a carbowax column.

3. Results and discussion

The reaction rates (R in mol s^{-1} g^{-1}) were calculated from the equation

$$R = X/(W/F) \tag{1}$$

where X = fractional conversion, W = weight of the catalyst (g), F = feed rate of phenol (mol s^{-1}). A plot of X versus (W/F) showed a linear portion up to a conversion of 20% at all temperatures. In order to treat the rate data under differential conditions, the conversion was maintained below this level.

The influence of partial pressure of phenol (P_p) and hydrogen P_H on the reaction rate is shown in Fig. 1(A and B). A smooth correlation is seen over a wide range of partial pressure (0.05 to 0.80 atm) for all four temperatures. This implies a direct dependency between rate and partial pressure of the reactants. In the form of a rate expression, it is written as

$$R = kP_p^x P_H^y \tag{2}$$

where x and y are the reaction orders with respect to phenol and hydrogen. At 473 K, the order of the reaction is negative with respect to
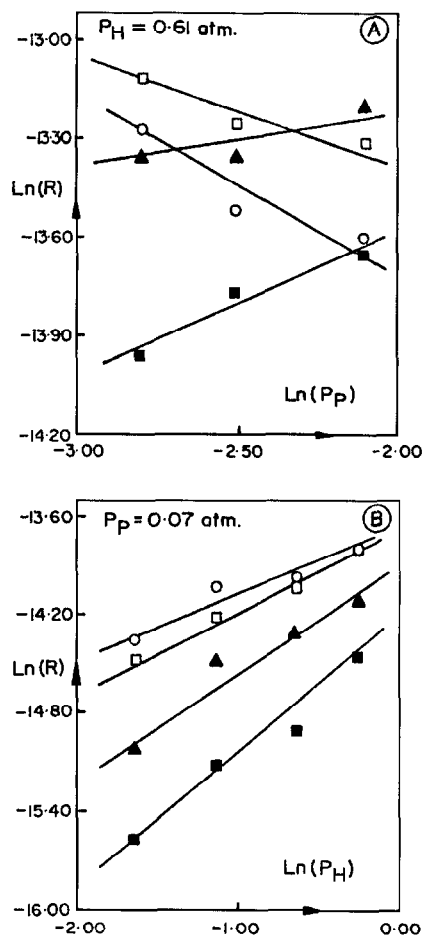

Fig. 1. Effect of partial pressure of phenol (A) and hydrogen (B) on the rate of reaction over Pd(1 wt%)/MgO catalyst at different temperatures (T (K) = 473 (O); 503 (□); 533 (▲); and 563 (■)).

phenol and positive with respect to hydrogen. This is in agreement with Neri et al. [9] who have reported that in the case of Pd/MgO, $x = -1$ and $y = 1$ and for Pd/Al$_2$O$_3$, $x = 1$ and $y = 2$, measured at 433 K. The variation in x and y with temperature is shown in Table 1. The increase in the order of phenol with raise in temperature suggests a weak mode of adsorption on the surface at higher temperature. This confirms with the results of Xu et al. [11] wherein the temperature desorption of phenol is shown to be much higher on magnesia as compared to the acidic support.
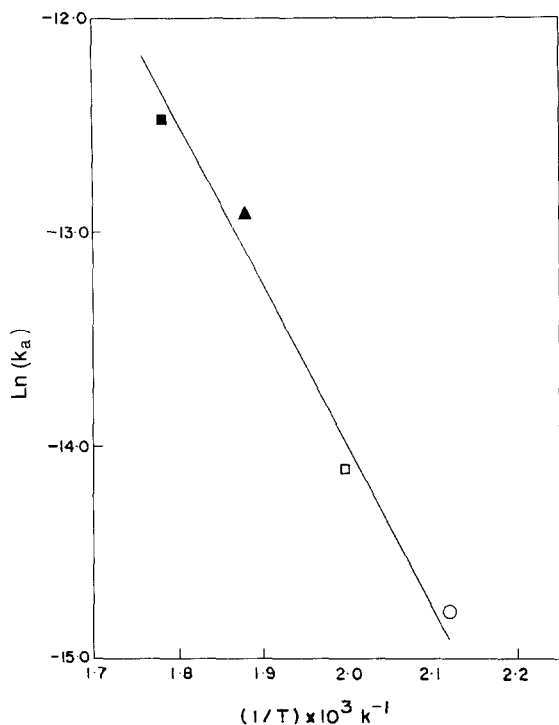
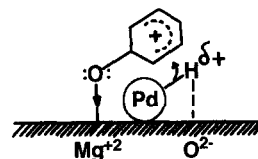From the values of x and y at different

Fig. 2. Arrhenius plot of Pd(1 wt%)/MgO. See Fig. 1 for symbols.

Scheme 1.

fast reaction between gas phase phenol and surface hydrogen atom forms cyclohexanol which subsequently give cyclohexanone.

The foregoing results are tempting us to believe that under steady state approximation if one assumes that adsorption isotherms of the reactants follow a similar behavior as that of Langmuir isotherms, the rate expression may be written as

$$R = kb_p P_p b_H P_H / \left(1 + b_p P_p + b_H P_H\right)^2 \qquad (3)$$

where b_p and b_H are the adsorption coefficients of phenol and hydrogen, respectively. Since phenol is strongly adsorbed over magnesia one may consider $b_p P_p \ggg 1 + b_H P_H$. Hence the Eq. (3) reduces to that of Eq. (2) which is experimentally observed.

The strength of adsorption of phenol depends upon the acid–base properties of the support. On magnesia, phenol in the form of phenolate is oriented with its aromatic ring non-planar with the surface [12]. Based on information and with our results, a reaction mechanism is proposed wherein the strongly adsorbed phenol (as indicated by the negative order) in a non-planar form reacts with the dissociatively adsorbed hydrogen atom in a step-wise fashion to give cyclohexanone (Scheme 1).

temperature (Table 1), the average rate constants K_a were determined (Appendix A). From the values of K_a at various temperatures, the apparent activation energy of the process (E_a) was found to be 63 kJ per mol (Fig. 2).

Few papers concerning the kinetic expressions are found in literature [3,4,7–10] for the title reaction. Studies on Pt/SiO$_2$ [4], Pd/CaO–Al$_2$O$_3$ [7] and Pd/Al$_2$O$_3$ [9] have indicated that the rate controlling step is the desorption of cyclohexanone from an individual active site. On the other hand Pd/molecular sieve [3] shows a complex situation wherein a

4. Conclusion

On the basis of kinetic results available on the hydrogenation of phenol over Pd/MgO, the rate-controlling step is a surface reaction between the strongly bound phenol molecule and the weakly adsorbed hydrogen atom. The higher value of E_a further suggests the absence of a

Table 1
Kinetic data on phenol hydrogenation

Catalyst	Temperature (K)	Reaction order	
		phenol (x)	hydrogen (y)
Pd(1 wt%)/MgO	473	−0.53	0.42
	503	−0.33	0.50
	533	0.17	0.69
	563	0.46	0.85

facile migration or a spillover of hydrogen atom on the surface of magnesia.

Acknowledgements

Appendix A

Determination of the average rate constant (k_a) (see Eq. (2)):

$$\text{Rate} = (R) = kP_p^x P_H^y \tag{A.1}$$

Taking logarithm on both sides, Eq. (A.1) becomes

$$\ln(R) = \ln(k) + x\ln(P_p) + y\ln(P_H) \tag{A.2}$$

(1) At constant P_p, Eq. (A.2) becomes

$$\ln(R) = C + y\ln(P_H) \tag{A.3}$$

where

$$C = \ln(k) + x\ln(P_p) \tag{A.4}$$

From Eq. (A.3), C and y are determined (plot of $\ln(R)$ versus $\ln(P_H)$).

On a similar approach:

(2) At constant p_H, Eq. (A.2) becomes

$$\ln(R) = C' + x\ln(P_p) \tag{A.5}$$

where

$$C' = \ln(k) + y\ln(P_H) \tag{A.6}$$

From Eq. (A.5), C' and x are determined (plot of $\ln(R)$ versus $\ln(P_p)$).

(3) Knowing the values of C, x and $\ln(P_p)$ and C', y and $\ln(P_H)$ for a given temperature, the rate constant of the reaction with respect to phenol (k_p) and hydrogen (k_H) are determined.

(4) Finally,

$$k_a = (k_p + k_H)/2 \tag{A.7}$$

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