VAPOR PHASE HYDROGENATION OF *o*-CHLORONITROBENZENE (*o*-CNB) OVER ALUMINA SUPPORTED PALLADIUM CATALYST – A KINETIC STUDY

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Abstract

Kinetics of the vapor phase hydrogenation of *o*-chloronitrobenzene (*o*-CNB) over Pd/Al$_2$O$_3$ catalyst has been studied in a downflow microreactor under atmospheric pressure. Reaction rates have been measured at three different temperatures with respect to the partial pressures of *o*-CNB and hydrogen. The order of the reaction with respect to *o*-CNB was 0.53 at 280°C and increased with increasing temperature. However, with respect to hydrogen, a negative order was observed at 280°C, which decreased further with increasing in temperature. The apparent activation energy (Ea), from the Arrhenius plot was found to be 41 kJ/mol. On the basis of kinetic results a surface mechanism is suggested.

Keywords: Kinetics, hydrogenation, *o*-chloronitrobenzene, rate constant, activation energy

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INTRODUCTION

Aryl-chloroamines are important chemical intermediates in the production of drugs, dyes, herbicides and pesticides. The conventional synthesis method involves the reduction of the corresponding chloronitro compounds, either with a metal-acid system, or with hydrogen at a supported noble metal catalyst. It is known that the catalytic hydrogenation of chloronitrobenzene (CNB) involves hydrodehalogenation during the course of the reaction, which decreases the selectivity for chloroaniline (CAN). Therefore, to achieve the desirable selectivity for chloroaniline, it is absolutely necessary to minimize the side reaction, *viz*., hydrodehalogenation. Reviews on this subject have been published by Kosak [1], Bond [2] and Greenfield *et al*. [3].

Supported noble metal catalysts such as Pd/C [4], Pt/Al$_2$O$_3$ [5], Pt-M/Al$_2$O$_3$ [6], Ru/SnO$_2$ [7], Pt/γ-Fe$_2$O$_3$ [8] and Pt/PVP-Ni [9] have been used for this reaction. Most of the authors agreed that the nature of the oxide supports and metals used in the catalyst formulation have a direct influence on the total selectivity for the desired product. The deactivation of the catalysts, particularly that of Al$_2$O$_3$-based ones and the loss in selectivity for chloroaniline are some of the major concerns to be resolved in CNB hydrogenation.

Few papers concerning the reaction mechanism and kinetic models have been reported [4-6,10,11] to explain the complex interactions arising between the adsorbed CNB and hydrogen on the surface of the catalyst. Coq and co-workers [5] have reported that at lower CNB concentrations, competitive adsorption exists between CNB and hydrogen. The reaction direction is also shown to be determined by the lower adsorption strength of chloroaniline with respect to chloronitrobenzene on the support surface of the catalyst and not necessarily due to the decrease in the reactivity of the C-Cl bond in chloroaniline [7]. Liu *et al*. [11] have shown that the *o*-CNB-hydrogenation reaction is independent of the concentration of *o*-CNB, while it depends on the partial pressure of hydrogen. It is also indicated that kinetic data may have some dependency on the type of the catalyst [4]. In view of the severe differences between catalysts reported, a direct comparison of the results is not yet possible to understand the reaction mechanism of *o*-CNB hydrogenation. The present communication is an attempt to understand further the influence of operative conditions on the rate of *o*-CNB hydrogenation over the Pd/Al$_2$O$_3$ system.

EXPERIMENTAL

Palladium (1 wt.%) catalysts were prepared by impregnation of commercial γ-Al$_2$O$_3$ (Harshaw, Al-III-61, SA = 234 m^2/g and PV = 0.65 cm^3/g) with palladium acetate salt dissolved in an acetonitrile solvent. The samples were dried overnight and calcined in air at 400°C for 4 h.

Reaction studies were carried out in a fixed-bed microreactor under atmospheric pressure. *Ca*. 0.5 g of the catalyst was reduced in a hydrogen flow at 300°C for 3 h and then brought to the desired reaction temperature. The reaction was performed at three different temperatures within the range of 250° to 310°C. The reaction rates were measured under differential conditions. The partial pressures of *o*-chloronitrobenzene (*o*-CNB) and hydrogen were adjusted by using a N_2 stream. Under these experimental conditions the only product was *o*-chloroaniline (*o*-CAN). The reaction product was analysed by means of a gas chromatograph equipped with a flame ionization detector (FID) and a packed capillary column of Zebron (ZB-5).

RESULTS AND DISCUSSION

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

$$R = X / (W / F) \qquad (1)$$

where X, W and F are the fractional conversion, weight of the catalyst and the feed rate of *o*-CNB (mol s^{-1}), respectively. A plot of X *vs*. (W / F) showed a linear portion up to a conversion of 20 % at all temperatures. In order to treat the experimental results under differential conditions, the conversion was maintained well below this level.
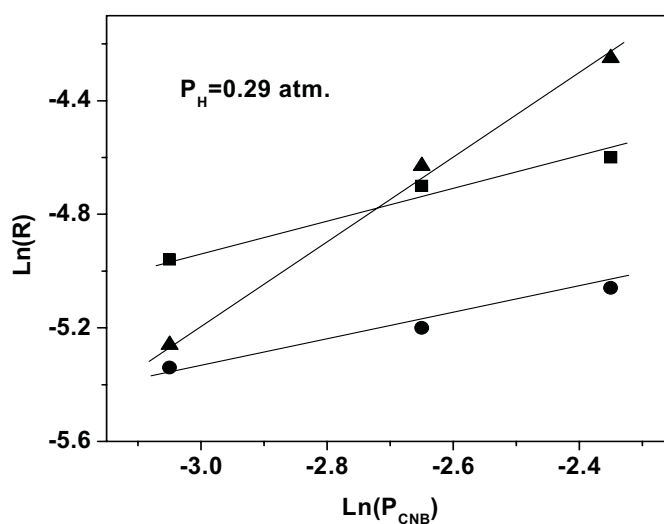

Fig. 1. Effect of the partial pressure of *ortho*-chloronitrobenzene (*o*-CNB) on the rate of reaction over the Pd (1 wt.%)/Al_2O_3 catalyst at different temperatures. [T/°C = 250°(●); 280°(■) and 310°(▲)]
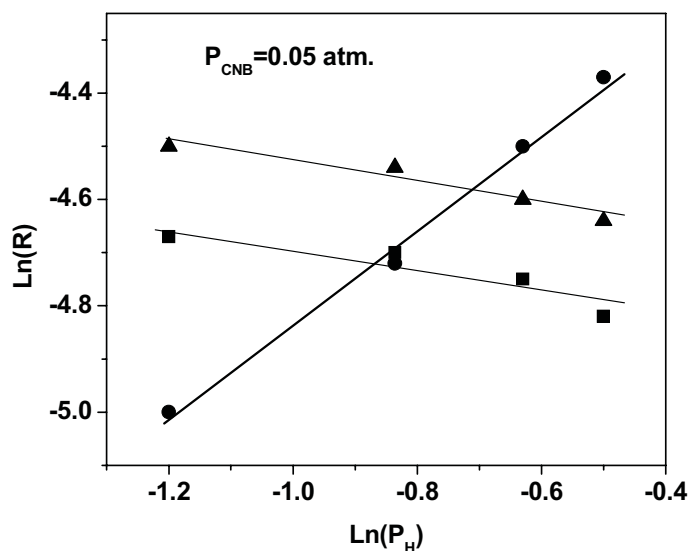
Fig. 2. Effect of the partial pressure of hydrogen on the rate of reaction over Pd
(1 wt.%) / Al$_2$O$_3$ catalyst at different temperatures.
[T/°C = 250°(●); 280°(■) and 310°(▲)]

The influence of the partial pressure of *o*-chloronitrobenzene (P$_{CNB}$) and hydrogen (P$_H$) on the reaction rate is shown in Figs 1 and 2. A linear correlation is seen over a wide range of partial pressures (0.05 to 0.60 atm) for all three temperatures. This implies that a direct dependency exists between the rate and the partial pressure of the reactant. In the form of a rate expression, it is written as

$$R = k\ P_{CNB}^{\ x}\ P_H^{\ y} \tag{2}$$

where 'x' and 'y' are the reaction orders with respect to *o*-CNB and hydrogen, respectively. The variation in 'x' and 'y' with temperature is shown in Table 1. At 250°C, the order of the reaction with respect to *o*-CNB is 0.39 and increases with increasing temperature to 1.45 at 310°C. The increase in the order of the reaction of *o*-CNB with rising temperature suggests a weak adsorption on the surface at higher temperature. This is in conformity with the results of Xu *et al.* [12], wherein they have reported that the desorption temperature of the reactant on a basic support, such as magnesia is higher than that observed on the acidic support. On the other hand, with respect to the hydrogen partial pressure, the order of the reaction is 0.91 at 250°C and decreases with increasing in reaction

at 310°C. The negative order of the reaction with respect to hydrogen as compared to *o*-CNB at higher reaction temperatures is attributed to the strength of adsorption of hydrogen on the metal surface. In other words, the order negativity implies that the adsorption of hydrogen on the Pd surface is stronger.

Table 1

Kinetic data on *ortho*-chloronitrobenzene (*o*-CNB)

Catalyst	Temperature (°C)	Reaction order	
		o-CNB (x)	Hydrogen (y)
Pd (1 wt.%)/Al$_2$O$_3$	250	0.39	0.91
	280	0.53	-0.19
	310	1.45	-0.23

From the values of 'x' and 'y' at three different temperatures, the rate constants (k$_a$) were determined (Appendix-A). From the Arrhenius plot, the activation energy (E$_a$) of the reaction was found to be 41 kJ/mol. This agrees well with some of the E$_a$ values indicated in the literature. In the case of hydrogenation of 2,4-dimethylnitrobenzene over Pd/C catalyst a value close to 40 kJ/mol has been reported [13]. Similarly, a value between 29 to 40 kJ/mol has been found for nitrobenzene hydrogenation over supported Pd catalysts [14]. In few cases even lower values of E$_a$ (20 to 27 kJ/mol) have been found for the CNB-hydrogenation [5,11]. The lower value of the apparent activation energy (E$_a$ = 41 kJ/mol) suggests that the hydrogenation of *o*-CNB is less activated over the Pd/Al$_2$O$_3$ catalyst.

The kinetic model and reaction mechanism suggest a complex situation arising between the adsorbed CNB and hydrogen on the surface of the catalyst. Coq and co-workers [5] have reported that at lower concentration of *p*-chloronitrobenzene a competitive adsorption takes place between CNB and hydrogen, while at higher CNB concentration the adsorption competition may not occur. On the Ru/SnO$_2$ system, higher activity of *o*-CNB hydrogenation was reported due to a weaker adsorption of *o*-CAN as compared to *o*-CNB and not because of the decrease in the reactivity of the C-Cl bond [7]. A study on a polymer-stabilized Ru colloidal system studied shows that the reaction is independent of the concentration of *o*-CNB and depends on the hydrogen pressure [11].

The reaction scheme which can account for our experimental results is one that considers the surface reaction between the adsorbed *o*-CNB through the aromatic ring and the strongly adsorbed hydrogen atoms as a rate-controlling

step. Under steady state approximation, if one assumes that the adsorption isotherms of the reactants are of the Langmuir type, the rate expression may be written as

$$R = kK_{CNB}K_H^{0.5}P_{CNB}P_H^{0.5}/(1+K_{CNB}P_{CNB}+\{K_HP_H\}^{0.5})^{0.5} \qquad (3)$$

where K_{CNB} and K_H are the adsorption coefficients of *o*-CNB and hydrogen, respectively. If $K_{CNB}K_H \ll 1$ and $(K_HP_H)^{0.5} \ll 1$, then eq. (3) reduces to eq. (2), which was experimentally observed. This is in agreement with the kinetic model derived by Coq *et al.* [5].
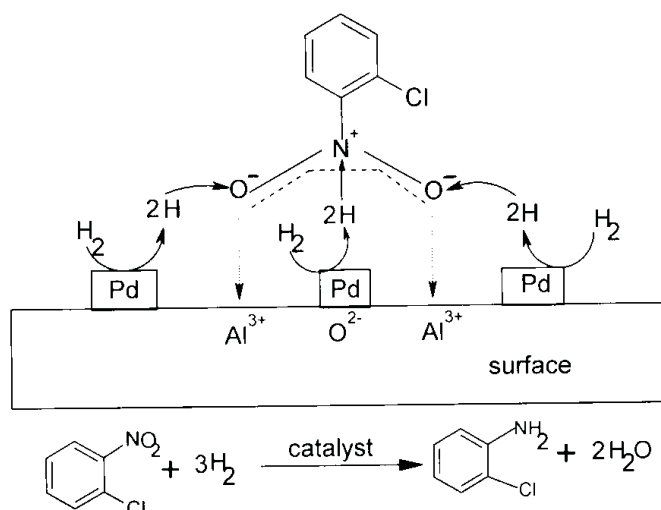
Scheme 1. Adsorption of *ortho*-chloronitrobenzene (*o*-CNB) giving rise to *ortho*-chloroaniline (*o*-CAN)

Based on our kinetic results it is envisaged that the adsorption of *o*-CNB may occur on two types of sites on the surface of the catalyst. One of the adsorption modes will involve the π-electron cloud of *o*-CNB with metallic sites, while the second mode of adsorption could take place *via* the nitro group of *o*-CNB interacting with the active sites of the support, as shown in Scheme 1. The extent of interaction depends on the activation of the nitro($-NO_2$) group and the dissociation of the adsorbed hydrogen on the surface of the catalyst.

However, the extent of adsorption of *o*-CNB in this reactive mode depends on the total amount of *o*-CNB adsorbed as well as on the extent of adsorption of *o*-CNB through nitro group on the support of the catalyst. The ratio of these two adsorption modes will be a function of temperature. This accounts for the variation of the order of the reaction with respect to the substrate as a function of temperature. This could also mean that though the reaction mechanism may be the same at different temperatures, the extent of reaction of these molecules adsorbed on the surfaces could be different thus accounting for the variation of the frequency factor with temperature. The cumulative effect is what one observes in the reaction.

Appendix (A)

Determination of the average rate constant (k_a)(refer eq. (2)):

$$\text{Rate} = (R) = kP_{CNB}^{x}P_{H}^{y} \tag{A.1}$$

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

$$\ln(R) = \ln(k) + x\ln(P_{CNB}) + y\text{Ln}(P_H) \tag{A.2}$$

    (1)   At constant P_{CNB}, Eq. (A.2) becomes

$$\ln(R) = C + y\ln(P_H) \tag{A.3}$$
$$\text{where } C = \text{Ln}(k) + x\text{Ln}(P_{CNB}) \tag{A.4}$$

From eq. (A.3), by plotting $\ln(R)$ *vs*. $\ln P_H$, values of C and y are determined.
    (2)   At constant P_H, Eq. (A.2) becomes

$$\ln(R) = C' + x\ln(P_{CNB}) \tag{A.5}$$
$$\text{where } C' = \ln(k) + y\ln(P_H) \tag{A.6}$$

From eq. (A.5), by plotting $\ln(R)$ *vs* $\text{Ln}P_{CNB}$, values of C' and y are determined.
    (3)   Knowing the values of C, x and $\ln(P_{CNB})$ and C', y and $\ln(P_H)$ for a given temperature, the rate constant of the reaction with respect to CNB (k_{CNB}) and hydrogen (k_H) are determined.
    (4)   Finally, $k_a = (k_{CNB} + k_H)/2$.

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