

SELECTIVE HYDROGENATION OF BENZOYL CHLORIDE OVER SUPPORTED PALLADIUM CATALYSTS

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Liquid-phase hydrogenation of benzoyl chloride has been studied using palladium supported over inorganic (Al_2O_3 , C, $CaCO_3$) and polymeric (nylon, styrene-vinylbenzene) materials. The reaction is zero order with respect to benzoyl chloride. The rate of reaction has been found to be dependent on the support used. It is suggested that the lower reaction rate found on the polymeric support is related to the presence of palladium not completely reduced.

Жидкофазное гидрирование бензоилхлорида было исследовано на палладии, нанесенном на неорганические (Al_2O_3 , C, $CaCO_3$) и полимерные (наилон, полистирол) материалы. Реакция имеет нулевой порядок по хлористому бензоилу. Скорость реакции зависит от используемого носителя. Полагается, что наблюдаемое уменьшение скорости на полимерном носителе связано с присутствием неполностью восстановленного палладия.

INTRODUCTION

Group VIII metals supported on nylon show unique catalytic behavior in the hydrogenation of benzene /1-3/. Selectivities towards cyclohexene higher than 50% have been reported on Pt/nylon in contrast to Pt/ Al_2O_3 on which cyclohexane is the only reaction product /2/. In order to find alternative industrial applications of this peculiar catalytic system, it was decided to extend our investigation to other selective hydrogenation reactions.

In this paper we report results obtained in the hydrogenation of benzoyl chloride (Rosenmund reduction) over supported Pd either on inorganic or polymeric supports.

Although the partial hydrogenation of benzoyl chloride to benzaldehyde over Pd has been known /4/, few papers have been recently published /5, 6/, moreover, a detailed kinetic investigation has never been reported.

EXPERIMENTAL

Pd/CaCO₃, Pd/C and Pd/Al₂O₃ were commercial samples supplied by Engelhard. Pd/nylon was obtained by impregnation of nylon-66 powder (270–400 mesh, surface area < 1 m²/g) with an aqueous solution of PdCl₂. Pd/resin was obtained by impregnation of a styrene-vinylbenzene resin, exchanged with (CH₃)₃N groups (surface area 30 m²/g), with a solution of dichlorobis(benzonitrile) palladium(II).

Chemical analysis of Pd samples is reported in Table 1.

Table 1
Chemical analysis and rate constant, K,
obtained over Pd supported samples.
T_R = 110 °C, P = 1 atm

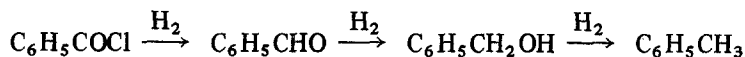
Support	Pd (wt.%)	K × 10 ⁴ (mol/g Pd s)
CaCO ₃	5	3.1
Al ₂ O ₃	10	4.3
Al ₂ O ₃	5	4.6
C	10	3.8
nylon 66	1	0.9
styrene-vinylbenzene	6.5	0.8

Benzoyl chloride (C. Erba > 99%) was used after repeated distillation. Meta-xylene (Aldrich > 99%) was purified by bidistillation from aluminum chloride. Ultra high purity hydrogen was used after passage through a Pt/Al₂O₃ catalyst at 400 °C, followed by a molecular sieve trap.

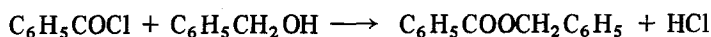
Hydrogenations were carried out in a 50 ml reaction vessel equipped with a magnetic stirrer under hydrogen flow at 110 °C. The reaction volume was about 26 ml (1 ml benzoyl chloride + 25 ml m-xylene). The amount of catalyst used was 15 mg of Pd. Reactions were followed gas-chromatographically by withdrawing samples of 0.1 ml at different times of reaction. Before catalytic activity measurements, catalyst samples slurried in the solvent, were activated for 0.5 h at the reaction temperature under H₂ flow. The absence of diffusional limitations was ascertained by preliminary runs performed under different stirring conditions (100–500 rpm).

RESULTS AND DISCUSSION

Under the experimental conditions used the hydrogenation of benzoyl chloride produced benzaldehyde, benzyl alcohol and toluene according to the following overall scheme:



Other possible secondary reactions such as:



were not observed. Decarbonylation of benzoyl chloride to benzene was found to proceed at a very low rate (Fig. 1-2).

Figure 1 shows the variation in the composition of the reaction mixture as a function of time over Pd supported on inorganic materials, namely C, CaCO₃, Al₂O₃. In Fig. 2 are reported the data obtained over Pd supported on polymeric supports. On all catalysts used the decrease in concentration of benzoyl chloride caused a corresponding increase in benzaldehyde which reaches a maximum and then decreases with a simultaneous appearance of benzyl alcohol. It can be noted that the sequence of formation of the products is characteristic of consecutive reactions with toluene being the end-product of the reaction. Furthermore, it should be pointed out that the reduction of benzoyl chloride to alcohol and toluene did not start until almost all benzoyl chloride disappeared from the reaction vessel. These results indicate that benzoyl chloride is strongly chemisorbed on the catalytic surface blocking those sites which are responsible for the further reduction of the aldehyde. This was confirmed by adding benzoyl chloride dropwise to the reaction mixture. It was observed that by maintaining a concentration of the reactant higher than 5%, the reduction could be stopped at the first stage with production of only benzaldehyde.

Similar results have been reported by Peter et al. /5/ in the reduction of acid chlorides in the presence of ethyldiisopropylamine.

At variance of the results reported by Affrossman et al. /6/, it was not necessary to add a sulfur regulator in order to avoid further reduction of the benzoyl chloride. Although the presence of very small amount of sulfur cannot be ruled out, it should be mentioned that a further purification by contacting the reaction mix-

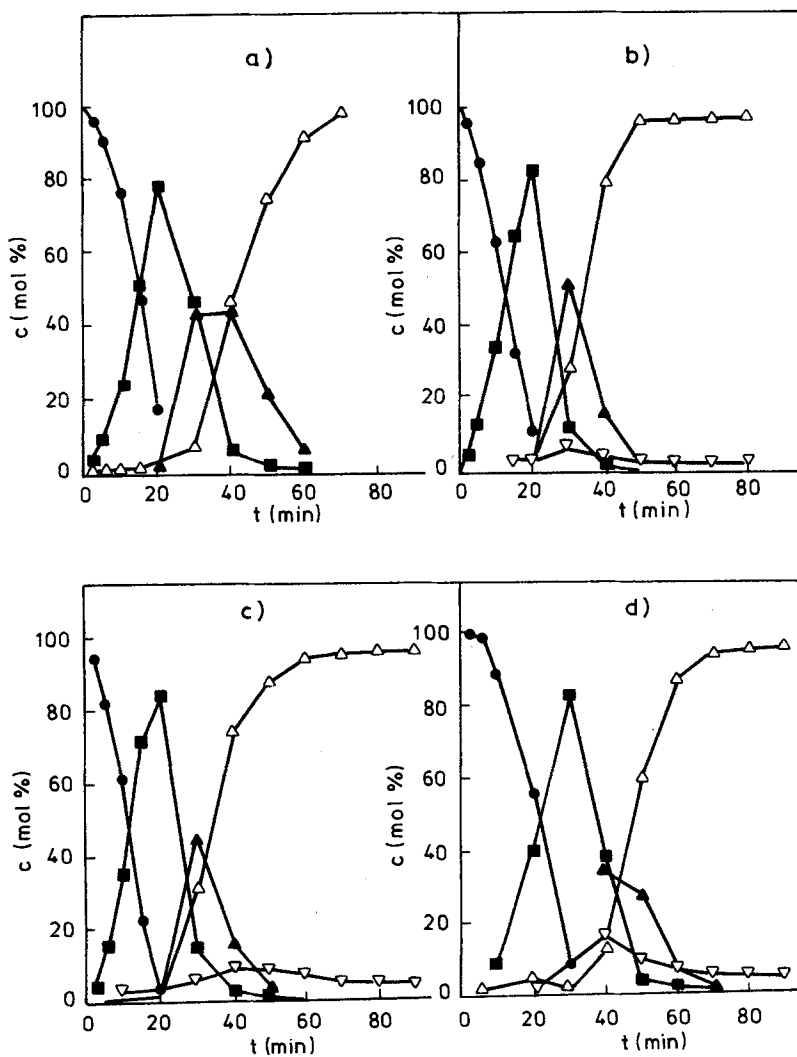


Fig. 1. Product distribution as a function of time in the hydrogenation of benzoyl chloride over: (a) 5% Pd/CaCO₃; (b) 10% Pd/Al₂O₃; (c) 5% Pd/Al₂O₃; (d) 10% Pd/C. $T_R = 110^\circ C$; ● - C_6H_5COCl ; ■ - C_6H_5CHO ; ▲ - $C_6H_5CH_2OH$; △ - $C_6H_5CH_3$; ▽ - C_6H_6

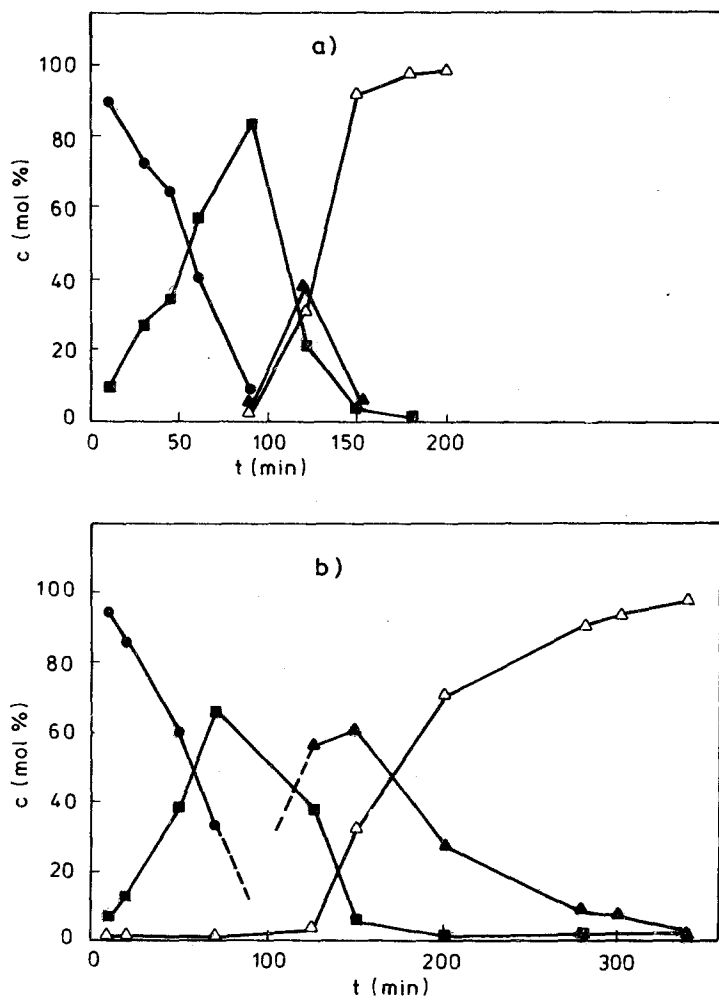


Fig. 2. Product distribution as a function of time in the hydrogenation of benzoyl chloride over: (a) 1% Pd/nylon; (b) 6.5% Pd/styrene-vinylbenzene. $T_R = 110^\circ\text{C}$; (symbols as in Fig. 1.)

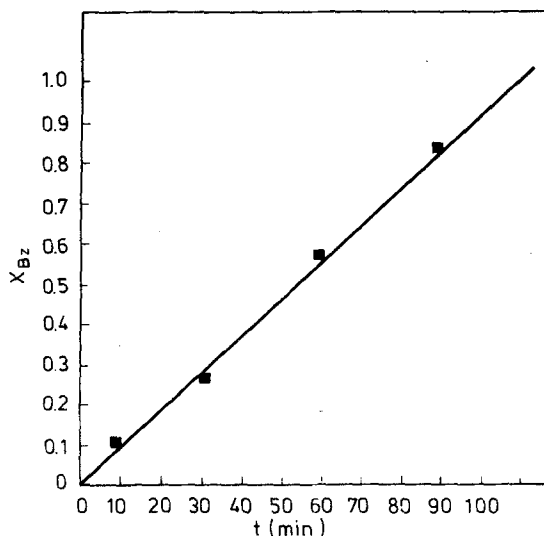


Fig. 3. Conversion of benzoyl chloride, X_{Bz} , as a function of time over Pd/nylon. $T_R = 110^\circ C$

ture (in the absence of hydrogen) with 3 g of Pd/C did not produce any change in the reaction pathway.

Fig. 3 shows the conversion values X_{Bz} as a function of reaction time measured on a 1% Pd/nylon. X_{Bz} was calculated from the following expression:

$$X_{Bz} = \frac{[C_{Bz}]^i - [C_{Bz}]}{[C_{Bz}]^i}$$

where:

$[C_{Bz}]^i$ = initial concentration of benzoyl chloride,

$[C_{Bz}]$ = concentration of benzoyl chloride at time t .

From Fig. 3 it can be concluded that the rate of the disappearance of benzoyl chloride is independent of its concentration, therefore the rate equation can be expressed as:

$$V = K_{Bz}[C_{Bz}]^0$$

A reaction order equal to zero was really found on all the catalysts investigated. These results give further support to the hypothesis that benzoyl chloride chemisorbs much stronger than benzaldehyde leading to a catalytic surface completely covered by acid chloride. At variance, the simultaneous appearance of benzyl alcohol and

toluene in the reaction products (Figs 1–2) indicates that their precursors (benzaldehyde and benzyl alcohol, respectively) have comparable adsorption constants.

Rate constants calculated from the slope of the plots X_{Bz} versus t are reported in Table 1. Pd/nylon and Pd/styrene-vinylbenzene show a rate constant at least 4–6 times lower than that obtained on the other catalysts. A comparison of Figs 1 and 2 shows that the behavior of all catalyst is qualitatively similar, therefore the lower reaction rate found on Pd supported on polymeric materials has probably to be ascribed to a lower fraction of active sites. By considering that nylon 66 used as support has a practically non-porous surface, the lower reaction rate has to be ascribed either to the presence of larger metal particles and/or to palladium not completely reduced. In this regard it is interesting to note that Pd/nylon has been reported to be able to hydrogenate partially benzene to cyclohexene. The peculiar behavior of the metal/polyamide system has been ascribed to the stabilization of metal atoms over nylon in higher oxidation states /2, 7/. It is therefore likely that the Rosenmund reduction occurs over zero valent Pd and that under our experimental conditions, at least a fraction of the metal available is not completely reduced due to a strong interaction with the polymeric support.

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REFERENCES

1. A. W. Harrison, H. F. Rase: *Ind. Eng. Chem. Fund.*, **6**, 161 (1967).
2. P. Dini, D. Dones, S. Montelatici, N. Giordano: *J. Catal.*, **30**, 1 (1973).
3. C. Hoang-Van, G. Turnier, G. Michel, S. J. Teichner: *Stud. Surf. Sci. Catal.*, **7** (PtB, New Horiz. Catal.) 1508 (1981).
4. Rosenmund: *Ber.*, **51**, 585 (1918).
5. J. A. Peters, H. Ven Bekkum: *Red. Trav. Chim. pays-Bas.*, **100**, 21 (1981).
6. S. Affrossman, S. J. Thomson: *J. Chem. Soc.*, 2024 (1962).
7. S. Galvagno, P. Staiti, P. Antonucci, A. Giannetto, N. Giordano: *React. Kinet. Catal. Lett.*, **21**, 157 (1982).