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KINETICS OF SOLID STATE HYDROGENATION : A THEORETICAL STUDY

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Abstract A theoretical model based on a diffusional process is proposed for a better understanding of the migration phenomenon of mobile hydrogen species. The validity of the model is tested by theoretical simulation of the various parameters. The model is compared with kinetic experimental results of solid 4-tert-butylphenol hydrogenation.

Keywords: Solid state hydrogenation, Solid state kinetics, Theoretical model, Diffusional process, Mobile hydrogen species

INTRODUCTION

The subject of kinetics of solid state reactions in general is not well understood. Organic solid state reactions show complex rate behavior which cannot be easily fitted to a single kinetic equation.

The kinetics of organic solid state decomposition reactions have been extensively studied¹, because these data are used to make shelf-life predictions of pharmaceuticals. Whereas, for gas-organic solid reactions very few data are available².

Usually the kinetic studies of solid state reactions are restricted to the direct application of models allowing to analyze plots of fraction decomposed versus time. These models use series of kinetic equations derived from the PROUT-TOMPKINS³ (1) and AVRAMI-EROFEEV (2) equations,

$$\ln \left(\frac{1}{1 - \alpha} \right) = kt \quad (1)$$

$$[-\ln(1 - \alpha)]^n = kt \quad (2)$$

where α refers to the fraction decomposed, t refers to the time and k refers to the rate constant. But these models include a series of approximations in the order of the reactions, and do not allow us to elucidate the mechanisms of gas solid reactions with a high degree of certainty.

The aim of this paper is to propose a theoretical model in which all the physical characteristics and parameters of the gas-solid system are taken into account, and to test the validity of the model by theoretical simulations of these parameters.

In previous work we have reported that catalytic hydrogenation of solid phenols and other aromatic compounds can occur in mild conditions and with high conversion ratios^{5,6}. We have demonstrated⁷ that the mechanism is based on hydrogen spillover effects according to the four following steps :

- Molecular hydrogen adsorbs on the catalyst and dissociates to form dissociate hydrogen species (H_s : Hydrogen spillover)
- Diffusion of the H_s from the catalyst (metal + support) to the organic solid
- H_s reacts with organic solid
- Formation of the solid products.

This mechanism has been established from data obtained during reaction between hydrogen and solid 4-tert-butylphenol in presence of catalysts. We have found⁸ that the kinetics of this reaction depends on various physical parameters : solid surface, grain size, hydrogen pressure,..., and that the reaction occurs at the interface of the catalyst and solid phenol.

THEORETICAL CONSIDERATIONS : DIFFUSION MODEL

The proposed model is based on the following assumptions :

- step 2 is the rate determining step ; that means diffusion of H_s controls the rate of the reaction
- catalyst/organic solid interface is planar.

The mathematical representation of the model is based on solution of two differential equations

- Equation of material balance or mass
- Equation of rate of formation of products

Material balance

Let us consider a thin layer dz of the organic solid

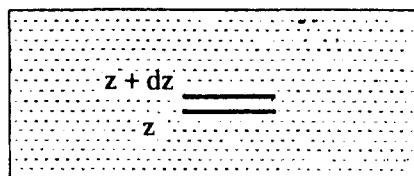


FIGURE 1 : Schematization of organic solid

We can calculate from the material balance the entering and leaving H_s quantity through dz

$$Q_{\text{diff}} = Q_{\text{acc}} + Q_{\text{dis}} \quad (3)$$

where Q_{diff} refers to the quantity of H_s entering into dz by diffusion, Q_{acc} refers to the accumulated H_s in the pores of the organic solid and Q_{dis} refers to the H_s which disappears during the reaction.

Replacement of each term of equation (3) by its value gives the following differential equation :

$$D \frac{\partial^2 C_s}{\partial z^2} = V_p \frac{\partial C_s}{\partial t} + \mu V \quad (4)$$

D : Diffusion coefficient of H_s ,

C_s : Concentration of H_s ,

V_p : Volume of the pores of the solid,

μ : Coefficient of proportionality,

V : rate of disappearance of H_s .

The rate of disappearance of H_s in the solid can be expressed by :

$$V = -k[S][C_s] \quad (5)$$

where $[S]$ refers to the organic solid concentration.

Neglecting Q_{acc} in equation (4) we obtain equation (6)

$$\frac{\partial^2 [C_s]}{\partial z^2} + \frac{\mu k}{D} [C_s][S] = 0 \quad (6)$$

The solution of equation (6) gives $[C_s]$ which represents the quantity of H_s going through the solid by diffusion

$$[C_s] = \Phi \sqrt{\frac{\mu k [S_o]}{D}} \exp \left[\frac{-z \sqrt{\mu k [S_o]}}{D} \right] \quad (7)$$

Formation of products

The rate of formation of products depends on the quantity of H_s reacting with the solid and on the concentration of the solid and/or its surface. Equation (8) gives the expression of this rate

$$V = \frac{d[C_p]}{dt} = k_p [C_s] [S] \quad (8)$$

where k_p is the rate constant of product formation and $[C_p]$ is the concentration of products formed.

After a time t the solid concentration is given by :

$$[S] = [S_0] - [C_p] \quad (9)$$

and by integration of (8) we obtain the expression of C_p for a finite layer of solid

$$[C_p] = [S_0] [1 - \exp(-k_p C_s t)] \quad (10)$$

From the expression of $[C_s]$ equation (7) and for the whole solid we obtain the final expression of $[C_p]$

$$[C_p] = \frac{k_p}{k} \Phi t \left[1 - \frac{k_p \Phi}{\sqrt{kD[S]}} t^2 + \frac{1}{18} \left(\frac{k_p \Phi}{\sqrt{kD[S]}} \right) t^3 + \dots \right] \quad (11)$$

The same development of the diffusion controlled method has been proposed by FILIKOV⁹ for similar gas-solid system by using a different expression of the rate of reaction.

RESULTS AND DISCUSSION

The kinetic expression of $[C_p]$ (11) could be considered as the kinetic model which fits better with the data of the gas solid reactions. In this expression $[C_p]$ represents either the transformation of the solid substrate or the formation of products. It takes into account the main physical characteristics of a solid state reaction between a gas and a solid. The solid is represented in equation (11) by $[S]$, which refers to the

molar concentration of the solid and/or its surface. The gas is modeled by its physical parameters, the diffusion coefficient, D and the flux density or the quantity of gas getting into the solid, Φ . In this expression k_p is the rate constant of transformation of the solid substrate or of the formation of solid products ; k is the rate constant of the gas disappearance.

Some restrictions must be done on this model to fit with our experimental data dealing with the catalytic hydrogenation of solid 4-tert-butylphenol. We have direct access not to the value of the k_p/k ratio, but to the overall rate constant k' , which is the rate constant of the interface reaction.

$$V = k' [\text{Catalyst/Organic solid}] \quad (12)$$

Φ is also not experimentally measurable, but we can modify the quantity of catalyst in order to generate more or less hydrogen spillover species near the surface of the solid phenol.

The dependence of $[C_p]$ on these different parameters k_p/k , Φ and D have been simulated by computational techniques. Figure 2 shows the variation of $[C_p]$ versus time for different values of the k_p/k ratio. The product formation increases along with the k_p/k ratio.

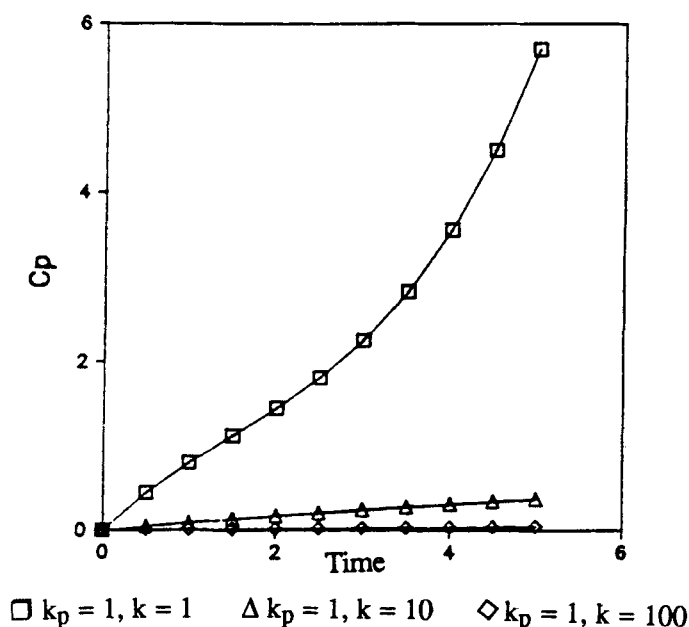


FIGURE 2 : Variation of $[C_p]$ versus time

For the k_p/k values higher than 1 the diffusional phenomenon is observed with an induction period in which the formation of products is delayed. In this case the theoretical curves are similar to the experimental ones (figure 3). The product formation increases along with the k_p/k ratio while the induction period decreases. Hence, k_p/k could represent the interface rate constant (equation 12).

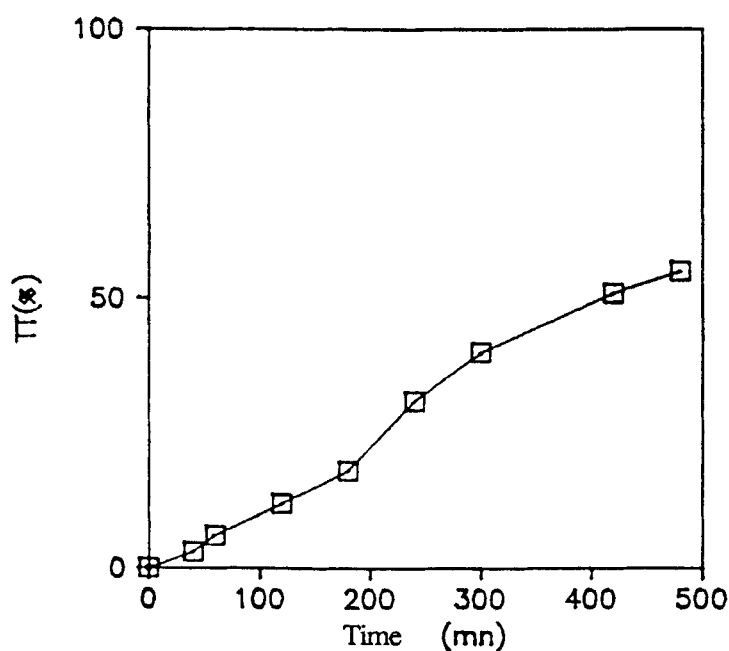


FIGURE 3 : Variation of conversion ratio versus time

Figure 4 represents the variation of $[C_p] = f(t)$ for different values of Φ , the other parameters beeing fixed.

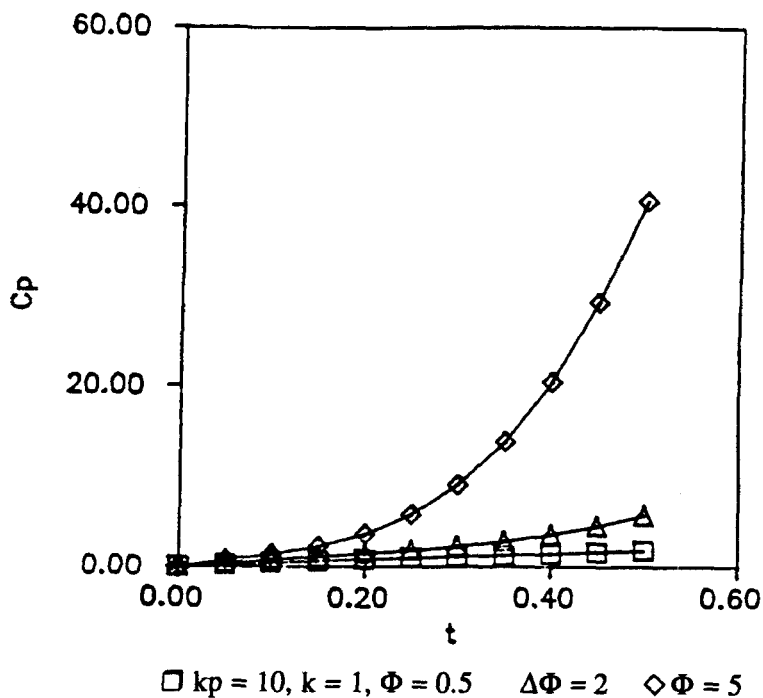


FIGURE 4 : Variation of $[C_p]$ versus Φ

The induction period is observed with the smallest values of Φ . Experimentally, Φ , the flux of spillover hydrogen species, can be modified by addition of various quantities of catalysts in order to produce more or less H_s on the surface of the catalysts. Figure 5 shows the role of the catalyst quantity on the reaction. The greater the quantity of catalyst, the more the flux of H_s is high and the more the induction period is short.

The others parameters D and $[S]$ have been studied and the curves obtained are similar to the experimental ones.

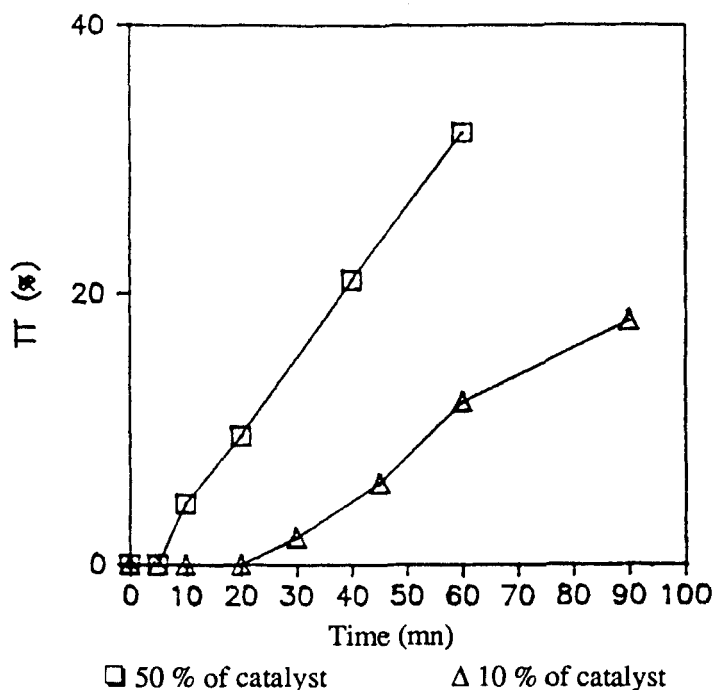


FIGURE 5 : Variation of conversion ratio versus catalyst percentage

CONCLUSIONS

The proposed model gives a good description of the kinetic and physical parameters of the gas-solids systems. The diffusion model that we describe may be regarded as a means of investigation of the mechanisms of organic solid state reactions.

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