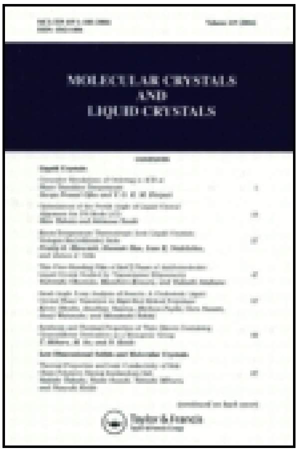

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Catalytic Organic Solid Gas Reaction: Kinetic and Mechanism

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CATALYTIC ORGANIC SOLID GAS REACTION : KINETIC AND MECHANISM

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Abstract

The alkylation of solid 4-tertiobutylphenol by gaseous isobutene in the presence of a catalyst has been studied according to different parameters such as, temperature, initial pressure of isobutene, proportion of catalyst and the granulometry of the catalyst and the solid reactant. Among the predefined kinetic models, the unreacted core model for spherical particles of unchanging size is the best adapted to the experimental results. Based on this model, a mechanism is proposed involving the intervention of a carbocation.

INTRODUCTION

The kinetics of the reactions in the solid state are of a complex nature for two reasons. The first is related to the difficulty in finding a basic mathematical model to interpret the phenomena, which is both close to reality and easy to use. The second concerns the interpretation of the reaction mechanism. This is due to the fact that the reaction kinetics in the solid state can often be described by different kinetic equations with complex reaction rates. The results obtained from these different equations are not generally transposable from one mathematical process to another. Furthermore, the reactant systems correspond to mixtures of different powders, which makes the study even more complex due to their heterogeneity.

In the case of the alkylation of 4-tertiobutylphenol by gaseous isobutene, it has been observed that diffusion phenomena limits the reaction. A kinetic model is adapted to describe the catalytic reaction gas-organic solid, and a mechanism is proposed.

I. EXPERIMENTAL

The studied alkylation reaction uses solid 4-tertiobutylphenol (m. p. 100° C) and isobutene gas (see figure 1), the catalyst, consisting of phosphoric acid is either liquid or solid. The products formed, 4-tertiobutyltertiobutylphenylether (m. p. 68.7° C) and 2,4-ditertiobutylphenol (m. p. 55.6° C) are either solid or liquid according to the experimental conditions.

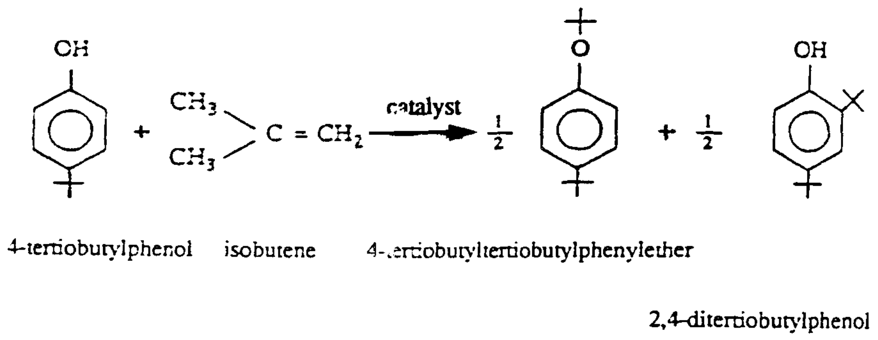

FIGURE 1 Equation of the chemical reaction between solid 4-tertiobutylphenol and isobutene gas.

The reaction is studied in a batch reactor (the isobutene is stagnant), a tubular (with and without isobutene flux) and a fixed bed reactor (with isobutene flux) under mild conditions. The gas-organic solid reaction consists of at least three phases : the solid reactant, the gaseous reactant and the catalyst. It is therefore a three phases system. According to whether the catalyst is either liquid or solid, the system will consist of the following phases :

solid/gas/solid

solid/gas/liquid

The solid reactant, 4-tertiobutylphenol can either be deposited on a solid support (silica or alumina) or directly on the solid catalyst leading to the following reactions systems :

solid-solid/gas/solid

solid-solid/gas

The influence of the five parameters was studied in most cases on all four reaction systems, in the different types of reactor [1].

The experimental results show that in the case of the solid/gas/solid system in a batch reactor or tubular reactor that the fractional conversion increases with increasing temperature, initial gas pressure, the proportion of catalyst and the surface contact between the solid reactant mixture/catalyst and the gaseous reactant. However, the fractional conversion decreases when the isobutene flux is increased in the tubular reactor. For a given catalyst granulometry, the fractional conversion varies very little with varying granulometry of the reactant. However, for a given reactant granulometry, the fractional conversion increases when the radius of the catalyst particles decreases.

II. KINETIC STUDY

The kinetic curves are treated by a polynomial function of the third order. First of all we show that the fractional conversion curves versus time are transformable by the affinity : (X,t) → (X,bt), b being a constant. This confirms that alkylation of 4-tertiobutylphenol in the different reactors takes place according to the same process at different temperatures [2]. Furthermore, calculation shows that the energy of activation varies according to the fractional conversion, which is probably due to modifications of phenomena controlling the reaction. It can be supposed that in the beginning, a purely chemical reaction is taking place between the solid reactant and the gas. Very quickly, there is accumulation of the product formed which modifies the access to and contact with the reactants. In order to react, the gas reactant must diffuse through the layer of products to come in contact with the unreacted core. As the fractional conversion increases, the layer of products becomes thicker, thereby increasing the phenomenon of diffusion.

Testing of the different kinetic models [3] confirms that the reaction is controlled by diffusion phenomena. Among the diffusional models, the unreacted core model for particles of unchanged size with diffusion in three directions of the reactant gas through the reaction products is the one which best fits the experimental results. The mathematical equation corresponding to the kinetic model retained to describe the reaction is as follows :

$$k.t. = 1-3(1-x)^{2/3}+2(1-x) \qquad \text{(Eq. 1)}$$

where : k is the rate constant and t is the necessary time to obtain a fractional conversion x of the solid reactant.

III. MECHANISM

The reaction partners

In the absence of a catalyst, whatever the conditions of contact between the two reactants, no alkylation takes place. In a similar fashion, if the reaction is carried out only in the presence of the solid catalyst support (silica or alumina) no alkylation takes place. Therefore, the catalyst is indispensable in order for the gas-organic solid reaction to take place.

The solid or liquid catalysts elaborated for this study are of an acid type. In the presence of isobutene, it can be supposed that an acid catalyst will supply a proton to form the tertiobutyl carbocation (see Figure 2).

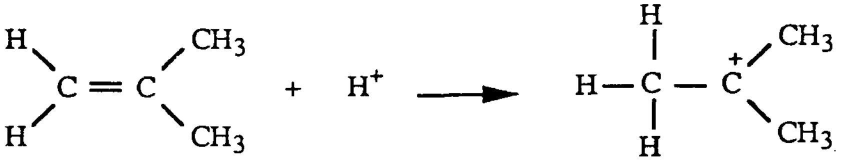

FIGURE 2 Formation of the tertiobutyl carbocation.

The carbocation could therefore constitute the alkylating entity and thereby be considered as one of the reaction partners.

The reaction mixture consists of gaseous isobutene, solid 4-tertiobutylphenol, a liquid or solid catalyst, and a phase in which the active alkylating entity can be found i.e. the carbocation. When the different partners are united, the reaction takes place and a new phase appears corresponding to the reaction products.

The diffusional model

Examination under the microscope of reaction mixtures with various fractional conversions shows that the particles of organic solid which have reacted gradually become surrounded by a fluid phase in which the reaction products can be found.

Figure 3 shows an instant t = 0 and then a time t, a model of the reaction system of 4-tertiobutylphenol on the particle level, presumed to be spherical.

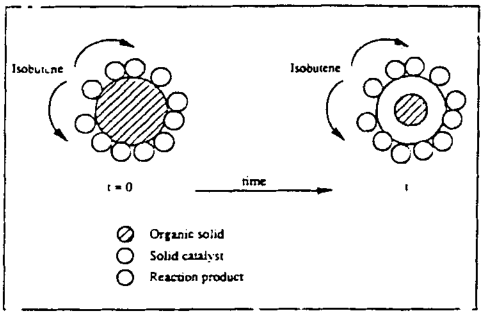

FIGURE 3 Unreacted core model for spherical particles of unchanging size for a reaction gas - organic solid - catalyst

The form of the kinetic curves (Figures 4 and 5), shows that the chemical reaction starts rapidly at the organic solid/catalyst interface. After a time t, a few minutes, the reaction rate decreases, the alkylating entity formed on contact with the catalyst has then to diffuse through the layer of products which thickens with time. The fluid layer which surrounds the organic solid core constitutes a barrier which the reactive species must cross.

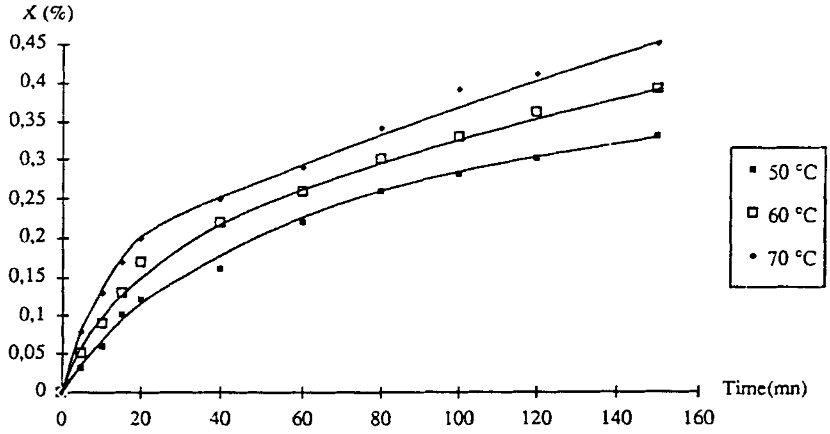

FIGURE 4 Variation of fractional conversion versus time for the solid/gas/solid system in a batch reactor.

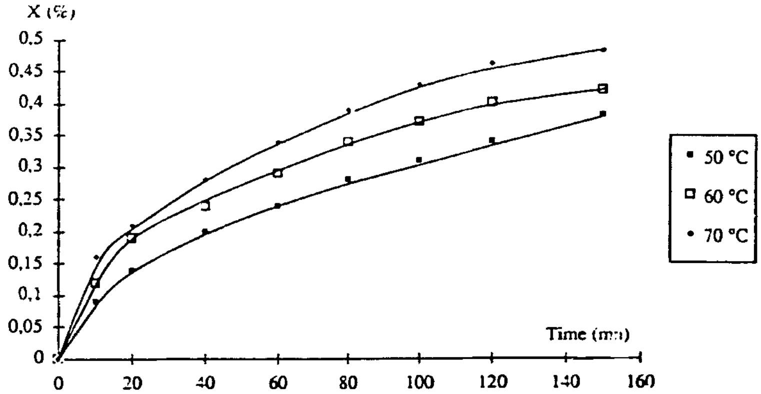

FIGURE 5 Variation of fractional conversion versus time for the solid/gas/solid system in a tubular reactor.

In the unreacted core model for spherical particles of unchanging size developed by YAGI and KUNI [4a], five steps have been described :

1. Diffusion of the gaseous reactant A towards the surface of the solid reactant B through a gaseous film surrounding the surface of the solid reactant B.
2. Penetration and diffusion of the gaseous reactant A towards the surface of the solid reactant through the layer of products.
3. Reaction of the gaseous reactant A with the solid reactant on the reaction surface.
4. Diffusion of gaseous products through the layer of product towards the outer surface of the solid reactant.
5. Diffusion of the gaseous products through a gaseous film towards the exterior, in the direction of the fluid mass.

In order to take into account the particularities of the reaction under study, we must consider the role of the catalyst and include it in their model. Furthermore, certain steps described in the model of YAGI and KUNI do not exist in our model. In this way, during the alkylation of solid 4-tertiobutylphenol no gaseous products are formed and in consequence the steps 3 and 4 cannot contribute directly to limit the reaction. Furthermore, as we have established, the diffusion phenomenon governs the reaction rate and therefore step 3 is probably not the limiting step of the reaction.

The diffusion phenomena of transfer of matter, can only occur during steps 1 and 2. The limiting step will be the step which controls the reaction rate.

Step 1 is represented by a linear mathematical equation [4b].

$$x = k.t \qquad \text{(Eq. 2)}$$

Experimentally and as shown by the form of the kinetic curves, the fractional conversion x, does not vary in a linear way with time. Under these conditions, the diffusion through the gaseous film would not seem to be the limiting factor of the reaction. However, the variation of $1\text{-}3(1\text{-}x)^{2/3}+2(1\text{-}x)$ with time is linear (Figures 6 and 7). Experimentally, diffusion through the layer of reaction products would seem to be the factor controlling the reaction rate.

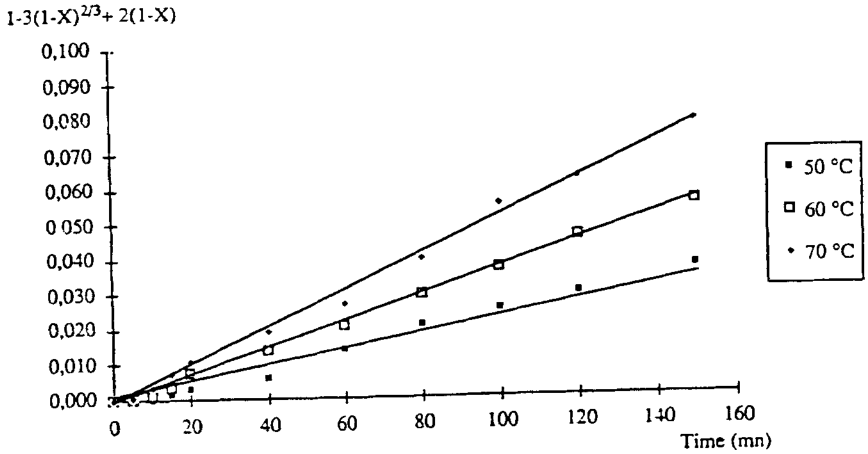

FIGURE 6 Variation of $1-3(1-x)^{2/3}+2(1-x)$ versus time for the solid/gas/solid system in a batch reactor.

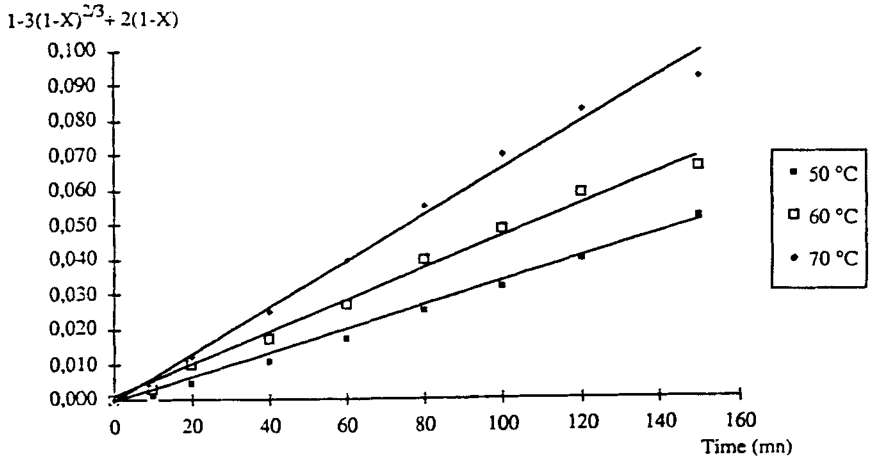

FIGURE 7 Variation of $1-3(1-x)^{2/3}+2(1-x)$ versus time for the solid/gas/solid system in a tubular reactor.

The good agreement between the experimental and theoretical results shows that the unreacted core model for spherical particles of unchanging size with the limiting factor being the diffusion of the reactant gas through the layer of reaction products, allows us to describe the catalytic alkylation process of solid aromatic compounds and to propose a complete reaction diagram of the gas - organic solid - catalyst reaction.

When in contact with the catalyst, isobutene will give tertiobutyl carbocations which will diffuse towards the unreacted core. This alkylation process appears to be quite similar to the hydrogenation process in the solid phase [5] and can be described in four steps :

1- Isobutene arrives on the catalyst forming tertiobutyl carbocations
2- Diffusion of carbocations towards the unreacted core
3- Reaction of carbocations with solid 4-tertiobutylphenol
4- Formation and rearrangement of the products

During the steps 3 and 4 which correspond to the chemical reaction we can invoke the commonly accepted mechanisms for electrophilic aromatic substitution reactions. To explain the alkylation mechanism of the phenolic group, two reaction schemes are proposed : the reaction either begins with the formation of ether which rearranges to form alkylphenol[6,7,8,9,10], Figure 8, or alkylation of the phenolic group is direct[11,12,13], Figure 9.

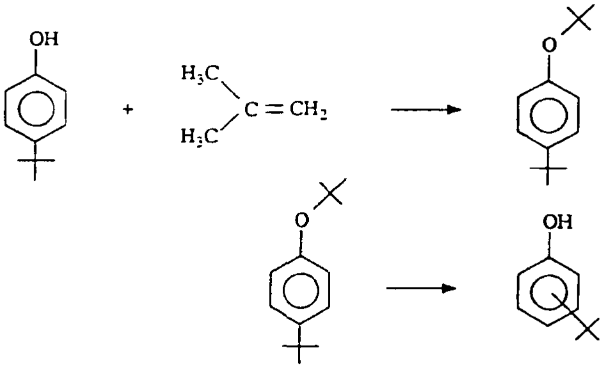

FIGURE 8 Indirect alkylation of 4-tertiobutylphenol.

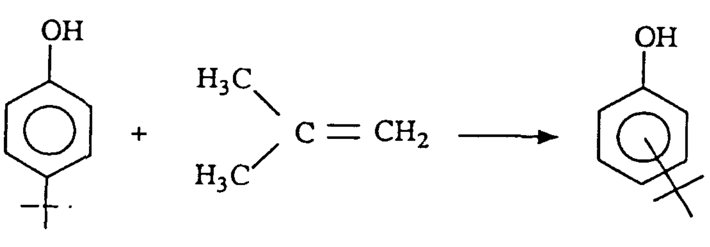

FIGURE 9 Direct alkylation of 4-tertiobutylphenol.

Taking into account the results obtained and the experimental conditions of alkylation in the solid phase, it is probable that the formation of alkylphenols takes place using both pathways : formation of ether with rearrangement to alkylphenol and direct alkylation of the aromatic group.
We could imagine in the second step in which the carbocation diffuses through the layer of products i.e. 2,4-ditertiobutylphenol and 4-tertiobutyltertiobutylphenylether, that tertiobutylation of these products occurs. This is in fact not the case, as analysis detects neither tritertiobutylated phenol nor ditertiobutylated ether. Trials of tertiobutylation of 2,4-ditertiobutylphenol under the same conditions as for 4-tertiobutylphenol in the solid state have also proved negative. As for tertiobutylation of 4-tertiobutyltertiobutylphenylether, the cumbersome steric conformation renders this reaction highly improbable.

CONCLUSION

The microscopic examination of the different reaction mixtures allows us to identify the reaction partners and to locate the reaction interface. The kinetic reaction study of alkylation of 4-tertiobutylphenol by isobutene in the presence of solid catalysts leads us to suggest that diffusion phenomena are the limiting factor. From the equations giving kt = f(x), the confrontation of the experimental and theoretical results shows that it is the phenomenon of diffusion through the reaction products which controls the reaction rate.
This alkylation reaction can be described by a four step mechanism, Figure 10.

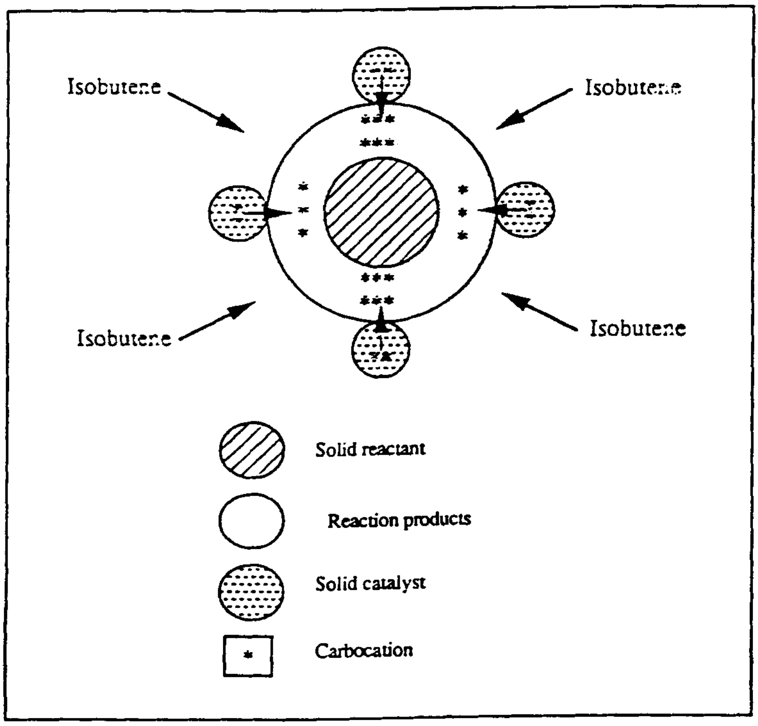

FIGURE 10 Scheme representing the reaction process.

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