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The role of acidity in the catalytic hydroxylation of phenol by hydrogen peroxide

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Abstract

The heterogeneous acid catalysis of the hydroxylation of phenol by hydrogen peroxide was investigated over protonic faujasites containing various amounts of aluminium or partially neutralized. Over strong acids, such as dealuminated protonic faujasites, dihydroxybenzenes result, mainly from an acid catalysed electrophilic aromatic substitution. Over weaker acids, an induction period is observed, the length of which is related to the strength of the acid sites. In that case, the initiation of the reaction occurs by the products of the former acid mechanism, and it is demonstrated using protonated and unprotonated electron transfer agents, that the subsequent autocatalysis involving a redox mechanism, also needs acid catalysis.

Keywords: Hydroxylation; Phenol; Hydrogen peroxide; Heterogeneous catalysis; Solid acid; Zeolite

1. Introduction

The heterogeneous catalysis of the direct hydroxylation of aromatic hydrocarbons by hydrogen peroxide has proposed serious challenges. A remarkable development was obtained with the discovery of metallosilicates [1]. The activity of such catalysts was found not to depend on their acidity [2], but on the redox properties of the isolated transition metal atoms [3]. Moreover, it was suggested that the simultaneous presence of aluminium, which generates strong acid sites, decreases the efficiency of the catalytic process [4,5]. Nevertheless, one of the industrial processes for the production of dihydroxybenzenes from phenol is based on homogeneous acid catalysis [6]. It would be desirable to determine if catalysis by solid acids constitutes an alternative route to dihydroxybenzenes.

A study of the hydroxylation of phenol by hydrogen peroxide catalysed by porous acid aluminosilicates, such as amorphous silica–alumina, acid clays and proton forms of various zeolites has been undertaken. Preliminary results [7] have shown the efficacy of solid acid catalysts, as long as their pore sizes are sufficiently large. However, the reaction appears not to be a simple electrophilic aromatic substitution by a hydroxonium cation, which would be generated from hydrogen peroxide at the surface of the acid catalyst. In fact, the mechanism of

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this catalysis would be more complex. In a batch reactor, the predominant feature of the reaction is the existence of an induction period, followed by an autocatalysis. Moreover, in addition to the dihydroxybenzenes (hydroquinone and catechol), transitory *p*-benzoquinone is also formed. In fact, we have proved, by adding it into the initial reaction mixture, that this quinone is not a by-product, but a reactive intermediate involved in the autocatalysis of the hydroxylation [8]. A redox mechanism, similar to the Fenton reaction, but involving the couple hydroquinone/*p*-benzoquinone, was suggested. Therefore, the reaction seems to proceed without intervention of the solid. Nevertheless, no reaction occurs in the absence of acid. This paper focuses on the possible role of the acidity of the solid on the development of the reaction.

2. Experimental

2.1. Catalysts

Commercial zeolites were used as catalysts. Faujasite with Si/Al = 2.5 (FAU 2.5), a Linde Y type molecular sieve SK-41, was obtained from Alfa-Products. Dealuminated faujasites with various Si/Al ratios of 10, 15 and 20 (FAU 10, FAU 15 and FAU 20) were gifts from Zeocat. Changes in catalyst acidity were carried out by cation exchange for 20 h at room temperature, in a 0.1 N solution of the selected sodium salt (1 ml per g of catalyst). The sodium contents of the catalyst FAU 15, FAU $NaNO_3$ and FAU Na_3PO_4, determined by atomic absorption analysis after dissolution of the sample (SCA-CNRS, Solaize, France), were respectively 0.22, 1.31 and 9.72 wt%. The catalysts were freshly calcined at 773 k before use.

2.2. Reactants

Phenol, a Gen-Apex chemical, and hydrogen peroxide, a 30 wt% aqueous solution stabilized by sodium stannate (5 ppm), were purchased from Prolabo. Hydroquinone, catechol, resorcinol, *p*-benzoquinone, *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine, and *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine dihydrochloride were obtained from Aldrich.

2.3. Procedure

The reactions were carried out batchwise at atmospheric pressure under air, in a thermostated glass reactor. At initial time, hydrogen peroxide was added at once to the magnetically stirred suspension of the catalyst in the solution of phenol in water. Products were analyzed by sampling periodically (50 mm^3) the solution with a microlitre syringe through a septum. Each sample was poured in a methanolic solution (2 cm^3) of fluorophenol used as external standard. After filtration, products were analysed by HPLC (Shimadzu) equipped with a C-8 column, with methanol/water (30 : 70) as eluent and a UV detection operating at a wavelength of 280 nm. The amount of oxygen emitted during the reaction was determined by volumetry at atmospheric pressure.

3. Results and discussion

3.1. Effect of the acidity on the induction period

Fig. 1 shows the formation, as a function of time, of dihydroxybenzenes over protonic fauja-

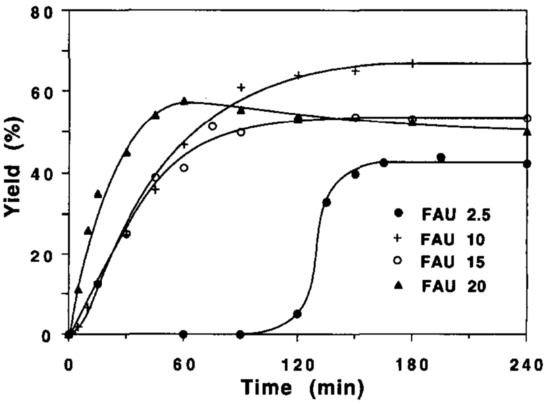

Fig. 1. Effect of the Si/Al ratio on the formation of dihydroxybenzenes over Faujasites (phenol, 21 mmol; H_2O_2 (30%), 9.4 mmol; FAU, 50 mg; H_2O, 10 cm^3; 60°C).

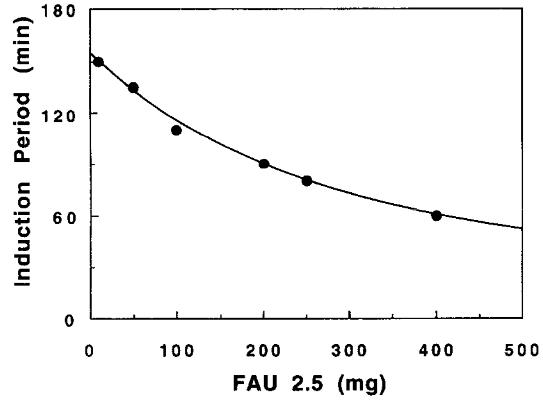

Fig. 2. Influence of the amount of FAU 2.5 on the induction period (phenol, 21 mmol; H_2O_2 (30%), 9.4 mmol; H_2O, 10 cm^3; 60°C).

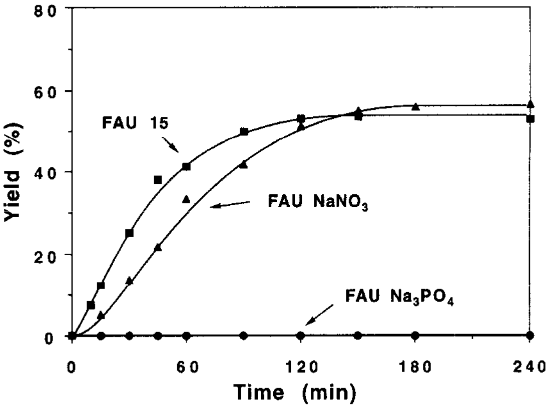

Fig. 3. Effect of partial neutralization of FAU 15 on the formation of dihydroxybenzenes (same conditions as in Fig. 1).

sites with various Si/Al ratios. Catechol and hydroquinone are the dihydroxybenzenes obtained in a ratio around 3/2. In the best case, the yield reaches 70% at complete conversion of H_2O_2.

The induction period decreases as the Si/Al ratio increases. Higher than 90 min with FAU 2.5, the induction period is lower than 5 min with FAU 10 and disappears with FAU 20. The reduction of the induction period is related to the increase of the strength of the acid sites by dealumination. This is in agreement with the concept of the aluminium topological density proposed by Barthomeuf [9], that specifies that dealumination increases the efficiency of the acid sites, until all the aluminium atoms become isolated.

As illustrated in Fig. 2 the induction period also decreases when the amount of FAU 2.5 is increased in the reaction mixture. This clearly shows that the autocatalysis is related to the products formed in an acid catalysed process.

The effect of the acidity on the induction period is confirmed by the study of the activity of FAU 15 partially neutralized (Fig. 3). When treated with a weak base, such as sodium nitrate, FAU 15 remains active, but a small induction period is observed. When treated with a strong base, such as sodium phosphate, the catalyst totally loses its activity. This demonstrates that the initiation of the reaction is the result of the acid properties of the catalyst.

From these results, we propose that the first formation of hydroquinone and *p*-benzoquinone, able to initiate the redox mechanism, is the result of an electrophilic aromatic substitution catalysed by the acid function of the solid.

3.2. *Effect of the acidity on the redox mechanism*

Table 1 shows the effect of various additives on the induction period. As we have already noted [7,8], the initial addition of hydroquinone or *p*-benzoquinone reduces the induction period observed with FAU 2,5. Moreover, the addition

Table 1
Effect of additives on the induction period of the hydroxylation of phenol in the presence or absence of FAU 2.5

Additive (1 mmol)	Induction period (min)	
	With FAU 2.5	Without catalyst
None	90	∞
Hydroquinone	3	> 1500
p-Benzoquinone	5	> 1500
TMPD [a]	0	> 1500
TMPDH [b]	0	0

Phenol, 21 mmol; H_2O_2, 9.4 mmol; FAU 2.5, 250 mg; H_2O, 10 cm^3; 60°C.

[a] TMPD, *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine.

[b] TMPDH, *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine dihydrochloride.

of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine dihydrochloride, a powerful electron transfer agent with a structure similar to hydroquinone, totally suppresses the delay. We could therefore conclude [8] that a redox mechanism, involving the couple hydroquinone/*p*-benzoquinone, is responsible of the autocatalysis. However, in the absence of an acid catalyst, neither hydroquinone nor *p*-benzoquinone can initiate the hydroxylation of phenol. The same behaviour is observed with the addition of the unprotonated *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine, while the addition of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine dihydrochloride alone initiates the reaction. These results mean that the redox agent must be protonated in order to be active. Thus, with a solid acid catalyst, the autocatalysis cannot occur in the solution because hydroquinone (or *p*-benzoquinone) must be adsorbed at the surface of the solid. Then, three species must be in the proximity to the surface: the redox agent, the hydroxylating agent and the substrate. So, the reaction requires a large space which explains why MFI zeolites are inactive while TS-1, the titanosilicate having the same structure, is active [7].

It can be pointed out [8] that an emission of oxygen takes place when the autocatalysis begins. This gas is produced by the decomposition of hydrogen peroxide which occurs, according to a redox mechanism, in competition with the hydroxylation. Like hydroxylation, this undesirable reaction takes place only in the presence of protonated redox agent. The decomposition of hydrogen peroxide is then attributed to the simultaneous presence of the hydroquinone/*p*-benzoquinone couple and of acid sites of the solid catalyst. Such a mechanism can explain why the yields of dihydroxybenzenes are reduced when aluminium is also present in titanosilicalites.

4. Conclusion

The heterogeneous acid catalysis of the hydroxylation of phenol by hydrogen peroxide occurs by two pathways, according to the strength of the acid sites. The acidity of the catalyst initiates the formation of dihydroxybenzenes and if the strength of the acid is high, the reaction occurs immediately. If the acid strength is low, the reaction exhibits an induction period. In this case, the autocatalysis is the result of a redox mechanism involving hydroquinone and *p*-benzoquinone. However, this reaction also requires acidity.

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