Origin of the deactivation of HBEA zeolites during the acylation of phenol with phenylacetate

D. Rohan [a], C. Canaff [b], P. Magnoux [b], M. Guisnet [b,*]

[a] *Department of Chemical and Life Sciences, University of Limerick, Limerick, Ireland*
[b] *URA CNRS 350, Catalyse en Chimie Organique, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

Abstract

During the transformation of a phenol–phenylacetate mixture over a HBEA zeolite (Si/Al = 10), carried out in a batch reactor at 160°C in sulfolane or in dodecane solvents, a rapid initial decrease in the formation of hydroxyacetophenones is observed. The compositions of the reaction mixture, of the organic material recovered in methylene chloride by a direct soxhlet treatment and of the compounds retained in the zeolite pores ('coke') were compared after 2 h and 24 h reaction. 'Coke' is mainly constituted of phenol and hydroxyacetophenones and of a small amount of heavy secondary reaction products: bisphenol A and acylated derivatives, hydroxy or acetoxy phenylbenzoate, hydroxy or acetoxydypnone, 2 methyl coumarine and 4 methyl chromone, and of sulfolane but not of dodecane. Only a very small quantity of phenylacetate is found. The rate of hydroxyacetophenone formation depends on the order of introduction of the reactants. It is shown that the rapid initial deactivation is not due to the heavy reaction products but to the limitations by phenols (reactant and products) of the access of phenylacetate to the inner acid sites. © 1998 Elsevier Science B.V.

Keywords: Phenol acylation; Zeolites; Deactivation

1. Introduction

Fries rearrangement and Friedel Crafts acylation of aromatic esters to aromatic hydroxy ketones is a useful synthetic route for the preparation of intermediates in the fine chemical and pharmaceutical industry, e.g. the manufacture of Ibuprofen and (*S*)-Naproxen involves an aromatic acylation step [1,2]. Due to environmental pollution replacement of the classical Friedel–Crafts catalyst $(AlCl_3)$ by a solid based catalyst is continuously being sought [2–11]. Some promising catalysts for the liquid phase synthesis of benzenic ketones include large pore tridimensional zeolites such as (HBEA and HFAU) [12,13].

However, deactivation of the acid zeolite catalysts is often rapid. This deactivation is mainly due to deposition within the pores or on the outer surface of the crystallites of heavy secondary products

---

* Corresponding author. Fax: +33-5-46453499; e-mail: guisnet@zevs.univ-poitiers.fr

[14–16]. Thus, extensive investigations on the prevention of zeolite deactivation and on their regeneration are continuously being carried out. However, as shown in this paper a decrease in catalyst activity is not necessarily due to formation of heavy secondary products. The polarity of the reactants and solvent can play an important role, as there is competition for adsorption on the zeolite between these compounds.

2. Experimental

2.1. Standard reaction conditions

All of the reactions were carried out in the liquid phase at 160°C under nitrogen in a batch reactor equipped with a condenser and a magnetic stirrer (600 rpm). A HBEA10 zeolite provided by PQ Zeolites was used (total and framework Si/Al ratios of 11 and 15.5 respectively). The conditions were as follows: 500 mg catalyst (previously activated overnight in air at 500°C), 9.1 cm^3 mixture of phenol, phenylacetate and solvent, i.e. 30 mmol of phenol and of phenylacetate (concentrations of 3.3 M) and the corresponding amount of solvent (sulfolane or dodecane). All of the liquid reagents were distilled and dried on magnesium sulphate before use. Small samples of the reaction mixture (about 0.1 ml) were taken periodically, diluted with methylene chloride and analyzed by gas chromatography on a 25 m capillary column of CP Sil 8 CB.

2.2. Recuperation and analysis of the organic material retained on the zeolite

A simple method was developed in our laboratory which consists of two extractions on the deactivated zeolite.

(i) Extraction by soxhlet – the deactivated catalyst was initially filtered on a fritted glass at ambient temperature for approximately half an hour and weighed. To recuperate the organic material on the external surface of the zeolite, the deactivated catalyst was then treated in a soxhlet for 8 h with methylene chloride. The solvent was evaporated and the remaining organic material was weighed and analyzed by GC-MS.

(ii) Extraction of coke [17] – 300 mg of the deactivated zeolite (which has previously undergone extraction by soxhlet) was dissolved in a 40% solution of hydrofluoric acid. Threefold extraction with methylene chloride was carried out followed by evaporation of the solvent. The soluble coke components were weighed and analyzed by GC-MS.

Elemental analysis of the deactivated catalyst was carried out before and after direct soxhlet treatment by methylene chloride.

3. Results and discussion

3.1. Influence of time on the transformation of a phenylacetate mixture

The transformation of an equimolar mixture of phenol and of phenylacetate (3.3 M) was carried out in dodecane (1.2 M) or in sulfolane (2.9 M) solvents over 500 mg of HBEA 10. As previously shown,
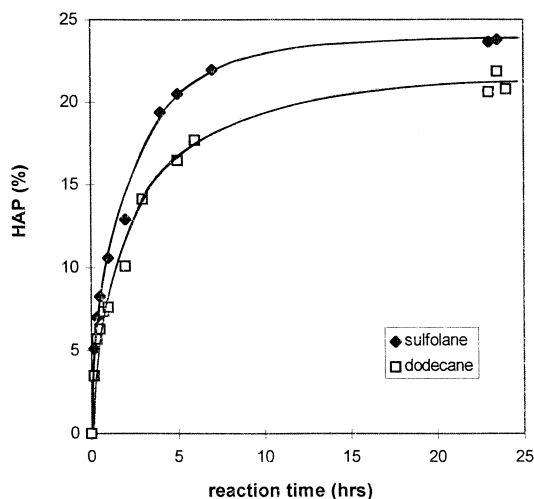
Fig. 1. HAP yield (%) as a function of time (h) in sulfolane and dodecane.

o-HAP, *p*-HAP, *p*-AXAP and excess phenol appear as primary products while bisphenol A and its mono and diacylated derivatives, hydroxy phenylbenzoate and its mono acylated derivative as well as traces of other heavy compounds appear as secondary products. The amount of these secondary products is greater in dodecane than in sulfolane [18].

The initial rates of hydroxyacetophenone (HAP) production were similar in both solvents (Fig. 1). However, the *p/o* HAP ratio is much greater in sulfolane than in dodecane. In both solvents a significant decrease in the rate of HAP formation (drawn from the slope of the tangents to the curves in Fig. 1) is observed. However, the deactivation is faster in dodecane than in sulfolane (Fig. 2).

Deactivation of zeolite catalysts is often due to the formation of heavy secondary products inside the pores or on the outer surface of the crystallites which block the access of the reactant to the acid sites [14–16]. To discuss this possibility, the zeolite catalysts were recovered after 2 h and 24 h reaction and the products retained on the catalysts were characterized. Approximately 450 mg of
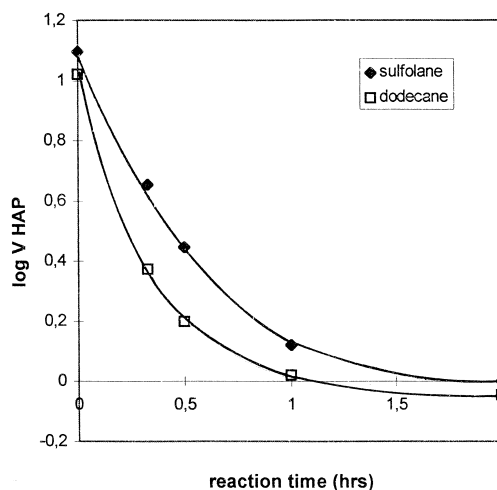

Fig. 2. Catalyst deactivation: log of the rate (mmol/h/g) as a function of time (h) in sulfolane and dodecane.

organic materials were retained on the catalysts (i.e. 90% of the zeolite weight), whatever the solvent and the reaction time. The soxhlet treatment of the recovered catalyst results in approximately 90% of the organic material solubilizing in methylene chloride. The remaining part (approximately 10% of the zeolite weight) is also soluble in methylene chloride, but only after dissolution of the zeolite in a hydrofluoric acid solution, which shows that the corresponding compounds are strongly retained inside the zeolite pores. The compositions of the organic material recovered by the direct soxhlet treatment (Ext.) and after the zeolite dissolution (coke) were estimated and compared to the composition of the reaction mixture (RM), all the weight compositions being directly obtained by simple integration of the chromatogram peaks i.e., without calibration.

Table 1 shows the results obtained after 2 h reaction. Whatever the solvent the reactants (P + PA) are the main components: in the case of sulfolane as solvent their content in Ext and coke being similar to that of RM, whereas in the case of dodecane as solvent their content in Ext and coke is greater than that in RM. Sulfolane constitutes a very significant part of Ext and coke while practically no dodecane is found. These differences can be related to the difference in the solvent polarity: the polar sulfolane solvent enters the pores of the zeolite while dodecane, much less polar than the reactant, cannot enter the pores. For the same reason, the amount of PA found in coke, hence in the zeolite pores, is very small compared to that of the more polar reactants and to sulfolane. It has been checked that the low value of the amount of PA in coke was not due to its rapid hydrolysis during the dissolution of the zeolite in the hydrofluoric acid solution. Indeed the stirring of a PA-hydrofluoric acid solution for 1 h, (as carried out for the treatment of coked zeolite), leads to a maximum hydrolysis of PA into phenol of 25%. Furthermore, the direct treatment by hydrofluoric acid of the zeolite recovered after 24 h reaction leads to practically the same proportion of phenol and PA (76%, 24%) as that calculated from the compositions of Ext and 'coke' (73%, 27%).

While the formation of the expected reaction products (o, p-HAP and p-AXAP) is faster in sulfolane than in dodecane (line 1, Table 1), the amount of these products in Ext and in coke is greater in dodecane. It can also be emphasized that the percentages of these products in the reaction mixture (RM), in Ext and in coke are again identical when sulfolane is used as a solvent, whereas in dodecane their percentage is greater in coke and especially in Ext than in RM. This could indicate limitations in the desorption of these products from the zeolite when the reaction is carried out in dodecane.

Furthermore, the percentage of the para isomers (p-HAP and p-AXAP) in the products is greater in sulfolane than in dodecane (in RM but also in Ext and coke). However, in both solvents this

Table 1

Composition of the reaction mixture (RM), of the organic material recovered by soxhlet treatment with methylene chloride (Ext) and of 'coke' obtained after 2 h reaction

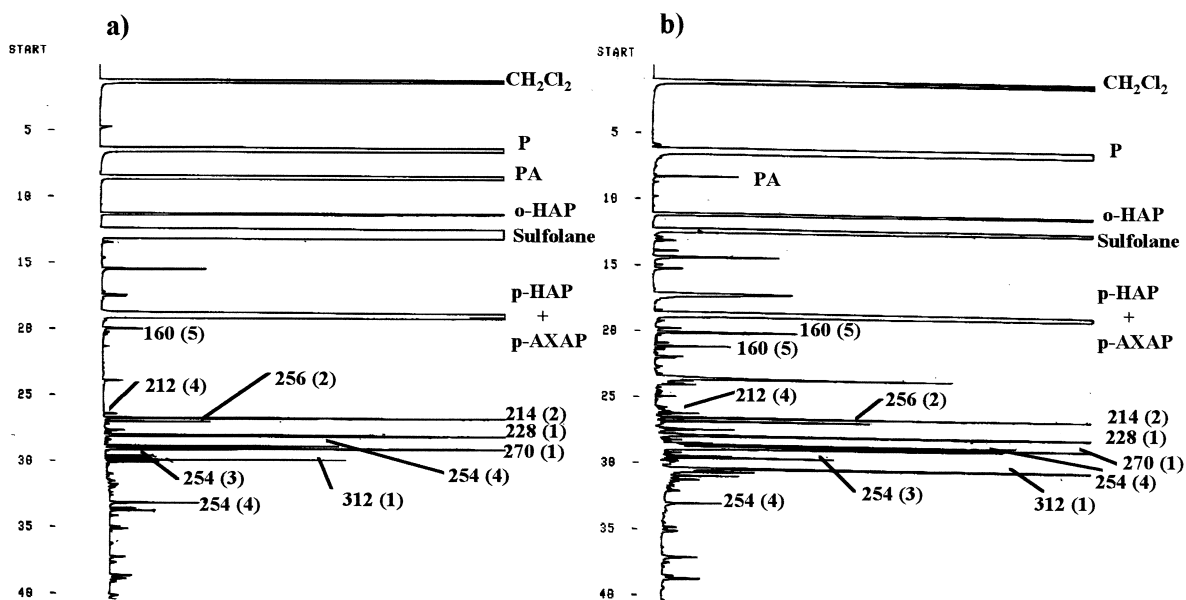|	Solvent (%)	Reactants (% phenol)	Products (% para)	Heavy products (%)
Sulfolane				
RM	20.7	58 (52)	6.2 (91)	0.07
Ext	43.7	46.6 (59.5)	9.0 (87)	0.055
Coke	16.0	47.3 (> 99.5)	4.6 (78)	1.6
Dodecane				
RM	23.3	55.2 (52)	3.2 (63)	0.075
Ext	6.1	77.6 (53)	15.2 (74)	0.48
Coke	0.45	58.4 (> 99.5)	5.3 (64)	2.1

Fig. 3. Chromatogram (a) of the reaction mixture (RM) and (b) of 'coke' after 24 h reaction in sulfolane. The molecular weight and family in brackets are indicated.

percentage is lower in coke than in Ext and RM, which confirms an effect of the pore size on the orientation of the reaction to the para isomer (product shape selectivity).

With both solvents only traces of heavy products are observed in the reaction mixture (RM). In the Ext fraction heavy products are only found in trace amounts with sulfolane as solvent, whereas with dodecane they are more abundant. With both solvents the amount of the products is greater in coke than in Ext and RM, which indicates a strong retention of these products in the zeolite pores.

The same conclusions can be drawn from the comparison of the compositions of RM, Ext and Coke after 24 h reaction (e.g. chromatograms of RM and coke in Fig. 3). However, there is an increase in the amount of heavy products particularly in the reaction mixture.

3.2. Heavy products: Nature, distribution and mechanisms of formation

The main heavy reaction products can be classified into the 5 families indicated in Table 2. Traces of other products: hydroquinone, β-methylstyrene, hydroxydiacetophenone, anthrone are also observed.

At short reaction times only compounds of families 1 and 2 appear. The two families are in equivalent amount in RM while family 2 is predominant in Ext and especially in coke. At long reaction times (e.g., 24 h) families 1 and 2 are predominant in the RM and Ext and families 2 and 5 in coke (Table 3).

All the heavy products result from well known acid catalyzed reactions. The formation of bisphenol A can be explained by reaction of phenol with acetone [19], resulting probably from phenylacetate transformation.
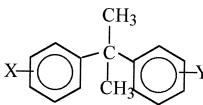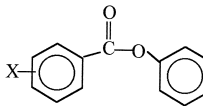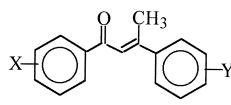
Table 2
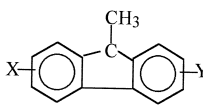Heavy reaction products – main families
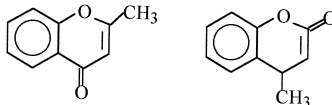
| Family	Chemical structure and molecular weight	
1. Bisphenol A and acylated derivatives		M=228 X=Y=OH M=270 X=OH Y=OAc M=312 X=Y=OAc
2. Hydroxyphenylacetate and acylated derivative		M=214 X=OH M=256 X=OAc
3. Dihydroxy dypnone and acylated derivatives		M=254 X=Y=OH M=296 X=OH Y=OAc M=338 X=Y=OAc
4. Dihydroxy, 9-methylfluorene and acylated derivatives		M=212 X=Y=OH M=254 X=OH Y=OAc M=296 X=Y=OAc
5. 2-Methylchromone and 4-Methylcoumarine		M=160

Table 3
Distribution of the heavy products (wt%) in the reaction mixture (RM) in the organic material recovered by soxhlet treatment with methylene chloride (Ext) and in 'coke', obtained after 2 h (between brackets), and after 24 h reaction
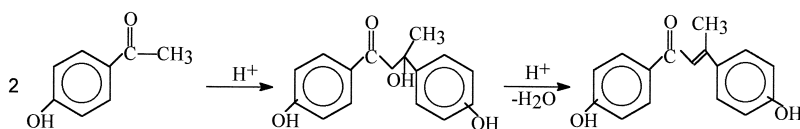
|	Family					
	1	2	3	4	5	others
Sulfolane						
RM	1.15 (0.038)	0.7 (0)	0.16 (0)	0.175 (0)	0 (0)	0.16 (0)
Ext	2.8 (0.035)	1.8 (0.0135)	0.4 (0)	0.37 (0.006)	0.03 (0)	0.09 (0)
Coke	3 (1.45)	0.46 (0.0135)	0.17 (0)	0.27 (0.20)	0.22 (0)	0.2 (0)
Dodecane						
RM	0.86 (0.04)	0.57 (0.03)	0.045 (0)	0.08 (0)	0 (0)	0.07 (0)
Ext	3.0 (0.19)	2.25 (0.19)	0.12 (0)	0.33 (0)	0.05 (0)	0.09 (0)
Coke	2.1 (2.0)	0.57 (0.06)	0 (0)	0.45 (0)	1 (0)	0.3 (0)
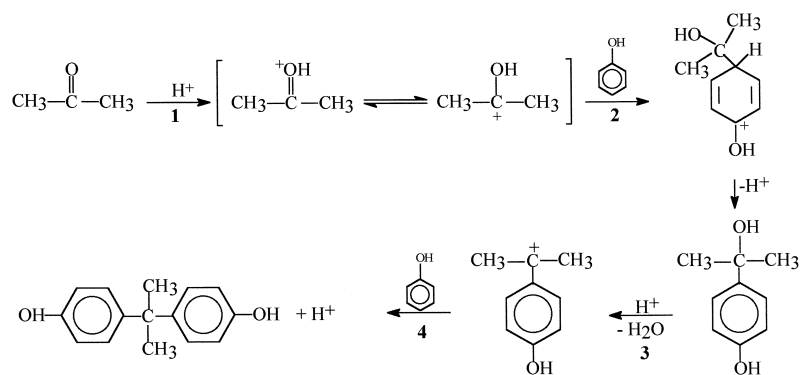
Steps similar to steps 1–3 are involved in the formation of family 4 products followed by a rearrangement of the obtained carbenium ion (step 4).
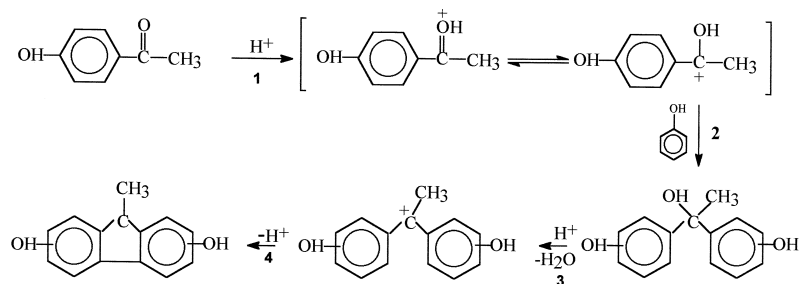
Compounds of family 3 result from the aldolization of hydroxyacetophenone followed by the alcohol dehydration [20].

Compounds of family 2 can result from the β scission of carbenium ions formed from the alcohol (or from the alkene formed above), followed by attack of the resulting acylium ion by phenol [20].
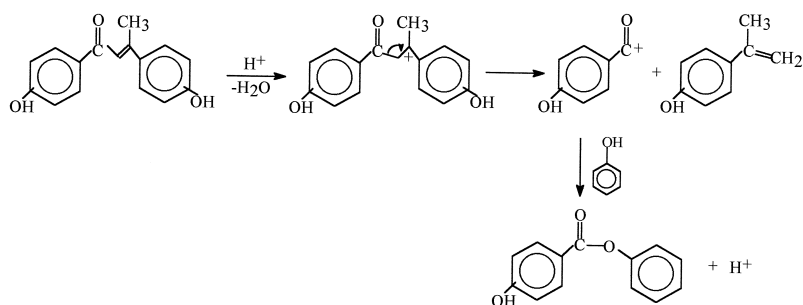
Only a small amount of β-methyl styrene is observed in the reaction products, probably due to its rapid polymerization.

The modes of formation of 2-methylchromone (2MC) and 4-methylcoumarine (4MC) have been previously described [21]. Both compounds would result from cyclization-dehydration of *o*-acetoxyacetophenone blocked inside the zeolite pores, hence not observed in RM.
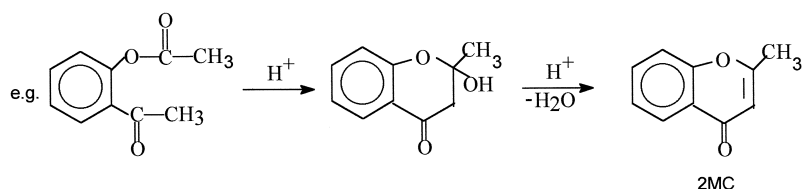
3.3. Origin of catalyst deactivation

As shown in Fig. 2 whatever the solvent there is a very rapid decrease in the reaction rate. This decrease cannot be due to the blockage of the pores by heavy products. Indeed, the amount of heavy products retained in coke after 2 h reaction is negligible, approximately 1% of the coke i.e. less than 0.5 mg for 500 mg catalyst, thus 0.1% of the catalyst. This deactivation could be due to the strong adsorption of these products at the pore mouth. Indeed, the elimination of the Ext fraction by soxhlet treatment with methylene chloride results in regeneration of a large part of the activity of catalysts used during 2 h or 7 h (Fig. 4). Moreover, this experiment confirms that the rapid initial deactivation is not due to heavy products of coke.

However, if the heavy products of Ext would be responsible for the rapid initial deactivation observed, a large difference in stability should be found in sulfolane and in dodecane. Indeed, with sulfolane as a solvent, the percentage of heavy products in Ext after 2 h reaction is 10 times lower than with dodecane.

Another hypothesis for explaining the rapid initial deactivation is related to the quasi absence of phenylacetate (PA) in the zeolite pores after 2 h or 24 h reaction. Thus, in the case of dodecane as solvent, phenol (P) and reaction products (which generally contain a phenol group) are practically the only components of coke. The polar sulfolane is also present in coke. However, its percentage in coke is equivalent to that found in RM after 2 h reaction, becomes much smaller after 24 h, which could indicate that more polar products limit the adsorption of the solvent in the zeolite pores.
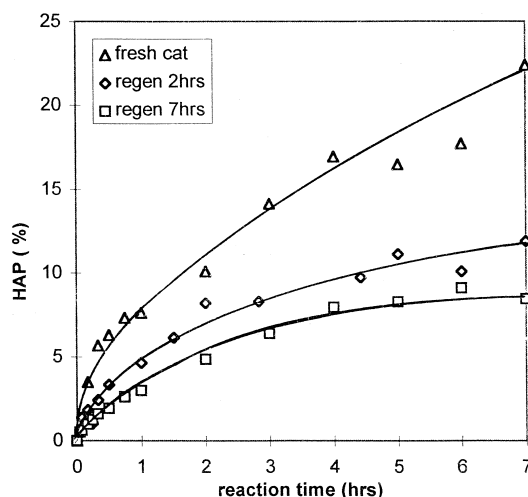
Fig. 4. HAP yield (%) as a function of time (h) in dodecane for fresh catalyst and catalyst regenerated after 2 h and 7 h reaction.

It can therefore be suggested that the initial decrease in the reaction rate is due to a great difficulty in the entrance of phenylacetate in the zeolite pores containing phenol compounds, hence in the replacement of the phenylacetate molecules consumed by reaction. To confirm this proposal the initial reaction rate obtained at 160°C under standard conditions i.e. stirring of the P–PA–solvent (S) mixture at 50°C, then rapid increase of the temperature up to 160°C, was compared to the initial rate obtained for addition of P–S to PA–S + zeolite and also for addition of PA–S to P–S + zeolite. For practical reasons dodecane was chosen as the solvent: contrary to sulfolane it is liquid even at low temperatures. Fig. 5 shows that the rate of HAP formation, depends very much on the experimental procedure. As expected for limitations in the entrance of PA in the zeolite pores the rate is very low when PA is added to the zeolite impregnated with P, the higher rate being obtained when P is added to the zeolite impregnated with PA. A critical effect of the order of introduction of the reactants has already been shown in the acylation of benzofuran with acetic anhydride [22].
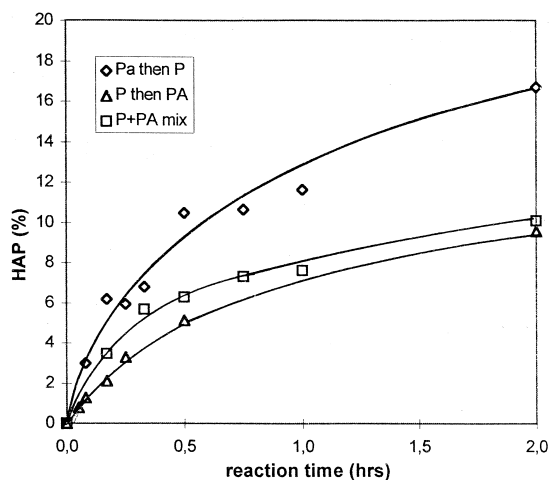

Fig. 5. Dependence of the rate of HAP formation in dodecane on the experimental procedure.

4. Conclusion

A rapid initial decrease in the rate of formation of hydroxyacetophenone is observed during the transformation of phenol and phenylacetate over a HBEA zeolite at 160°C in sulfolane or in dodecane solvents. This deactivation is not due to the formation of heavy reaction products but most likely to a limitation of the access of phenylacetate to the zeolite pores occupied by the very polar phenol. This explains the importance of the procedure used for the mixing of the reactants: a higher reaction rate is obtained when phenol is added to the zeolite impregnated with phenylacetate. The slightly better stability in the polar sulfolane could be due to the lower concentration of phenol in the zeolite pores, hence to a better access of phenylacetate to the acid sites.

References

[1] M.G. Franck, J.W. Stadelhofer, Industrial Aromatic Chemistry, Springer Verlag Berlin Heidelberg, 1987.
[2] H. van Bekkum, A.J. Hoefnagel, M.A. van Koten, E.A. Gunnewegh, A.H.G. Voght, H.W. Kouwenhoven, Stud. Surf. Sci. Catal., vol. 83, Elsevier, Amsterdam, 1994, p 379–390.
[3] Y. Pouilloux, N.S. Gnep, P. Magnoux, G. Pérot, J. Mol. Catal. 40 (1987) 231–233.
[4] C.S. Cundy, R. Higgins, S.A.M. Kibby, B.M. Lowec, R.M. Paton, Tetrahedron Lett. 30 (1989) 2281–2284.
[5] A.H.G. Vogt, H.W. Kouwenhoven, Collect. Czech. Chem. Commun. 57 (1992) 853–861.
[6] I. Neves, F. Jayat, P. Magnoux, G. Pérot, F.R. Ribeiro, M. Gubelmann, M. Guisnet, J. Mol. Catal. 93 (1994) 169–179.
[7] M. Guisnet, D.B. Lukyanov, F. Jayat, P. Magnoux, I. Neves, Ind. Eng. Chem. Res. 34 (1995) 1624–1629.
[8] A. Vogt, H.W. Kouwenhoven, R. Prins, Appl. Catal. A General 123 (1995) 37–49.
[9] K. Gaare, D. Akporiaye, J. Mol. Catal. 109 (1996) 177–187.
[10] K. Smith, Z. Zhenhua, L. Delaude, P.K.G. Hodgson, Book of Abstr. of 4th Int. Symp. on Heterogeneous Catalysis and Fine Chemicals, Basel, Switzerland, Sept. 1996.
[11] M. Spagnol, L. Gilbert, R. Jacquot, H. Guillot, P.J. Tirel, A.M. Le Govic, Book of Abstr. of 4th Int. Symp. on Heterogeneous Catalysis and Fine Chemicals, Basel, Switzerland, Sept. 1996.
[12] M. Spagnol, L. Gilbert, E. Benazzi, C. Marcilly, Patent PCT Int. Appl. WO 96 35,655, 1996.
[13] M. Spagnol, L. Gilbert, E. Benazzi, C. Marcilly, Patent PCT Int. Appl. WO 96 35,656, 1996.
[14] M. Guisnet, P. Magnoux, Appl. Catal. 54 (1989) 1–27.
[15] M. Guisnet, P. Magnoux, in: B. Delmon, G.F. Froment (Eds.), Catalyst Deactivation, vol. 88, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1994, pp. 53–68.
[16] H.G. Karge, in: H. van Bekkum, E.M. Flanigen, J.C. Jansen (Eds.), Introduction to Zeolite Science and Practice, vol. 58, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1991, pp. 531–570.
[17] P. Magnoux, P. Roger, C. Canaff, V. Fauche, N.S. Gnep, M. Guisnet, in: B. Delmon, G.F. Froment (Eds.), Catalyst Deactivation, vol. 34, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1987, pp. 317–330.
[18] F. Jayat, M.J. Sabater Picot, D. Rohan, M. Guisnet, Book of Abstr. of 4th Int. Symp. on Heterogeneous Catalysis and Fine Chemicals, Basel, Switzerland, Sept. 1996.
[19] B.C. Gates, Catalytic Chemistry, John Wiley and Sons, Canada, 1992.
[20] N. Lavaud, P. Magnoux, M. Guisnet, unpublished results.
[21] Y. Pouilloux, J.P. Bodibo, I. Neves, M. Gubelmann, G. Pérot, M. Guisnet, in: M. Guisnet et al. (Eds.), Heterogeneous Catalysis and Fine Chemicals II, vol. 59, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1990, pp. 513–522.
[22] F. Richard, J. Drouillard, H. Carreyre, J.L. Lemberton, G. Pérot, in: M. Guisnet et al. (Eds.), Heterogeneous Catalysis and Fine Chemicals III, vol. 78, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1993, pp. 601–606.