Liquid-phase acetylation of tetralin with acetyl chloride over zeolites: inhibition of the reaction by the products

Patrice Moreau, Annie Finiels, Sandrine Pelorgeas, Olivier Vigneau and Monique Lasperas

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, CNRS UMR 5618,
Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale,
34296 Montpellier Cedex 5, France

Received 30 September 1996; accepted 30 June 1997

HY and H-beta zeolites are efficient catalysts in the acetylation reaction of tetralin with acetyl chloride. Their activity depends largely on the experimental conditions and is restricted by the strong adsorption of organic species, either acetic acid or acetyltetralin formed in the reaction.

Keywords: acetylation, zeolites, tetralin, acetyltetralin, adsorption

1. Introduction

Friedel–Crafts acylation of aromatic derivatives has proved of great importance in fine chemical synthesis [1]. Nevertheless, present industrial processes generally involve acid chlorides as the acylating agents together with stoichiometric amounts of Lewis acids, mainly ferric and aluminum chlorides, as catalysts. The use of these soluble catalysts leads nowadays to more and more concern for the environment, so that their replacement by solid acid catalysts appears obvious [2,3]. The use of zeolites in the field of fine chemical synthesis has grown continuously in recent years [4]; besides their well-known shape-selective and acidic properties and their thermal stability, zeolites meet the essential requirements for industrial processing of organic chemicals taking into account their environmental advantages.

In the pioneering work of our group on the acylation of toluene and *p*-xylene by straight-chain aliphatic carboxylic acids over Y zeolites [5–7], it has been shown that excellent conversions and selectivities were obtained using long-chain aliphatic acids $C_nH_{2n+1}COOH$ ($n > 4$) as acylating agents, whereas acetic acid led only to very low conversions of aromatic substrates. Since this work, a large number of papers has appeared on the use of various zeolites in acylation reactions, in gas phase or liquid phase, not only of aromatic systems such as toluene and xylene [8–12], phenol and phenol derivatives [13–16], anisole [17–19], methoxynaphthalene [20], but also of heterocyclic-aromatic compounds, such as thiophene [21] or benzofuran systems [22–24].

In the continuation of our studies on the catalytic activities of zeolites in aromatic electrophilic substitution reactions, the present paper is concerned with the acylation reaction of tetralin over various zeolites in the liquid phase, and in particular with the acetylation reaction using acetyl chloride as acylating agent.

2. Experimental

(a) Materials. Tetralin, 2-acetyltetralin, acetyl chloride and 1,2-dichlorobenzene (99%) from Aldrich were used as supplied.

(b) Catalysts. The HY zeolites, HY 15 (Si/Al = 15, ZF 515) and HY 20 (Si/Al = 20, ZF 520) and the mordenite sample HM (Si/Al = 10.8, ZM 510) were from Zeocat, Montoir de Bretagne. The zeolite H-beta was synthesized according to a described procedure [25], and the mazzite sample was obtained in this laboratory [26]. Before reactions, the zeolite samples were activated according to the standard procedures, at various temperatures and times depending on the type of zeolite: HY 15, HY 20, mazzite: 400°C, 6 h; HM: 500°C, 6 h; H-beta: 200°C, 2 h, then 550°C, 6 h.

The typical properties of these catalysts are shown in table 1.

(c) Catalytic experiments. The reaction was carried out in a glass reactor equipped with a magnetic stirrer and heated in an oil bath. The standard procedure is the following: the freshly calcined catalyst is added to tetralin (0.1 mol/ℓ) in 50 ml 1,2-dichlorobenzene at 30°C, and the mixture is stirred; acetyl chloride (0.2 mol/ℓ) is then added and the mixture heated to reflux (180°C). Samples are withdrawn periodically and analyzed by gas chromatography (OV1 capillary column, 15 m). For experiments carried out under nitrogen atmosphere, a nitrogen flow swept the reaction medium during all the reaction time.

(d) Adsorption procedure. Adsorption experiments were carried out at 180°C (1,2-dichlorobenzene reflux)

Table 1
Properties of catalysts

Catalyst	Channel system dimensionality	Pore size largest channel (Å)	Si/Al molar ratio	Specific surface area ($m^2\ g^{-1}$)
HY	3	7.4	15	762
HY	3	7.4	20	780
Hβ	3	7.6×6.4	17	680
HΩ	1	7.4	20	440
HM	2	6.5	10.8	510

in a typical glass reactor. To 5 ml 1,2-dichlorobenzene were added 44 mg tetralin (0.33 mmol) or acetyltetralin (0.25 mmol); at $t = 0$, 100 mg activated HY 20 zeolite were added to the solution which was heated to the required temperature. Samples were taken periodically and analyzed by GC as above.

(e) Identification of the products. The structure of the different products was confirmed by GC-MS and ^1H and ^{13}C spectroscopy.

3. Results and discussion

3.1. Acylation of tetralin over HY zeolites: influence of the chain length of the acylating agent

In order to compare the catalytic activity of zeolites in the acylation of tetralin with that observed in our previous results [5–7], a preliminary study has been carried out on the influence of the chain length of the acylating agent. The HY 15 zeolite has been chosen for this reaction as a reference catalyst because of its known acidic properties in various acid-catalyzed reactions [21,23,27]. The results, given in figure 1, show that very good conversions (higher than 70%) of tetralin are obtained with respectively octanoyl chloride and butyroyl chloride, whereas acetyl chloride leads only to less than 20% conversion after 8 h reaction.

At the temperature of the reaction (180°C, reflux of 1,2-dichlorobenzene), octanoyl chloride (bp = 195°C) is totally in the liquid phase, whereas both butyroyl chloride (bp = 102°C) and acetyl chloride (bp = 52°C) are present in a gas–liquid equilibrium. Despite this, the conversion of tetralin is nearly the same with octanoyl and butyroyl chlorides as acylating agents (75% after 4 h reaction). Such a result leads to ascertain that the low conversion observed in the case of acetyl chloride is not due to the partial presence of the acylating agent in the gas phase, and is in agreement with recent papers related to the acetylation of various aromatics with either acetic anhydride or acetyl chloride at refluxing temperatures of high boiling solvents such as sulfolane [20] or chlorobenzene [28]. Thus, acylation reaction of aromatics over zeolites is much more difficult with acetic acid [5,18,29] or acetyl chloride than with the superior analogs, so that it can be said that zeolite-catalyzed acetylation constitutes a special case of acylation.

3.2. Acetylation of tetralin with acetyl chloride

3.2.1. Influence of the nature of the zeolite

Taking into account the above remark and the interest of acetylated derivatives in a variety of applications, a more extensive study of the acetylation reaction of tetralin with acetyl chloride has been carried out, first over various zeolites. Table 2 shows the results obtained under the same standard conditions described above.

From these results, it can be seen that tridimensional zeolites HY and H-beta are more efficient catalysts under those conditions. The dealuminated sample HY (Si/Al = 20) was then chosen as the catalyst for a more systematic study of the reaction:

$$\text{tetralin} + CH_3COCl \rightarrow \text{acetyltetralin}$$

Under the above experimental conditions, the acetylation of tetralin **1** with CH_3COCl leads to two products,

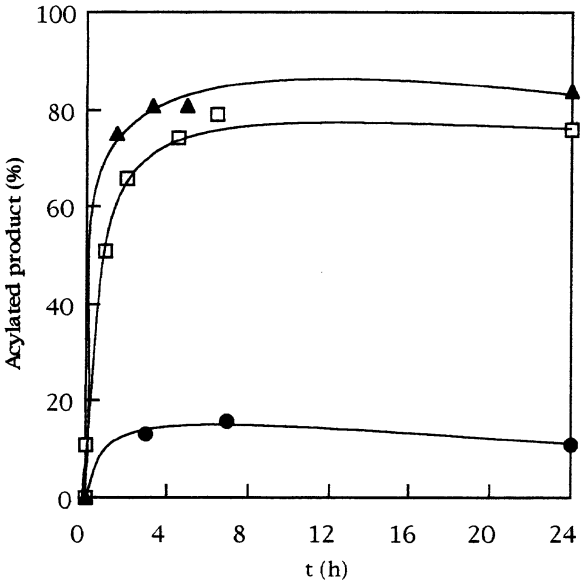


Figure 1. Acylation of tetralin with acetyl chloride (●), butanoyl chloride (□) or octanoyl chloride (▲). Formation of acylated products versus reaction time.

Table 2
Influence of the nature of the catalyst in the acetylation of tetralin with acetyl chloride

Catalyst			Tetralin (mol × 10^3)	CH_3COCl (mol × 10^3)	2-AcT[a] (mol × 10^3)
nature	quantity (g)	Si/Al			
HY 15	1	15	5	10	0.8
HY 20	1	20	5	10	1.5
H-beta	1	17	5	10	1.3
HM	1	11	5	10	0.1
HΩ	0.5	20	2.5	5	0.1

[a] Amount of 2-AcT (mol × 10^3) obtained after 24 h reaction.

identified as respectively the 2-acetyltetralin **2** as the main product and its isomer the 1-acetyltetralin **3**, as shown in scheme 1.

A typical evolution of the two isomers is shown in figure 2.

The ratio of the two isomers remains constant with time (isomer **2**/isomer **3** = 7.5); this implies that both isomers are obtained by parallel reactions, which could suggest, as in the case of acylation of toluene by long-chain aliphatic acids, the involvement of an electrophilic attack of the acylium ion CH_3CO^+ [5] on the positions 2 (more reactive) and 1 of the aromatic ring, and that no deacylation–reacylation process occurs. As shown in figure 2, the initial rates of the formation of the two isomers are high ($r_{02} = 6.1 \times 10^{-3}$ mol ℓ^{-1} min^{-1} g^{-1} and $r_{03} = 0.8 \times 10^{-3}$ mol ℓ^{-1} min^{-1} g^{-1}); nevertheless, after a few minutes, no more evolution is observed, which can be due to a loss of the catalyst activity.

3.2.2. Deactivation of the catalyst

Such a loss of the catalyst activity can be explained by a deactivation, due to the saturation of the active sites of the catalyst by organic products adsorbed, acetic acid and (or) acetyltetralin.

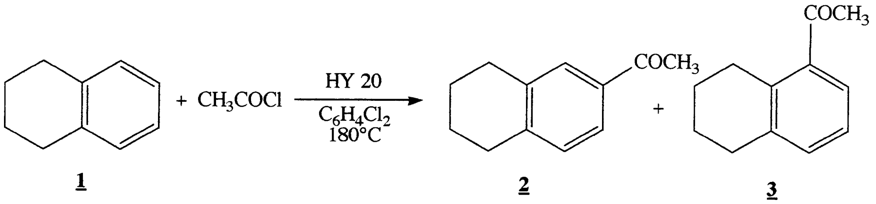
(a) Adsorption of acetic acid. It is known that acetic acid is generally strongly adsorbed on acidic sites of zeolites [30]. The total inhibition of the reaction observed when acetic acid is initially added together with acetyl chloride (1/4 ratio) confirms such an adsorption in the case of tetralin acetylation and is in agreement with a recent kinetic study of the acetylation of phenol with acetic acid over zeolites [31].

In our standard experimental conditions, acetyl chloride can be easily hydrolyzed into acetic acid, so that the observed deactivation could be explained by the formation of the acid during the reaction and its subsequent preferential adsorption. The number of active sites of the HY 20 zeolite sample (1 g) used in the reaction is 4.57×10^{20}; all these sites can be saturated by the acetic acid resulting from the hydrolysis of only 10% of the total amount of the acetyl chloride introduced (10 mmol, i.e. 6×10^{21} molecules). Such a behaviour explains that, under air, the catalyst is rapidly poisoned by acetic acid.

(b) Adsorption of acetyltetralin. In order to avoid such a deactivation, the reaction has been carried out under nitrogen atmosphere. Figure 3 shows the comparison of the results obtained under standard conditions and under nitrogen atmosphere, both for the conversion of tetralin and the formation of acetyl tetralin.

Under nitrogen conditions, the tetralin conversion is higher (50% after 1 h reaction), but, at the same time, the selectivity in 2-acetyltetralin decreases significantly; secondary products, mainly naphthalene, ethyltetralin and acetylnaphthalene, are obtained. Such a result shows that, under nitrogen, no acetic acid is formed, leading to a better availability of the active sites of the zeolite, not only for the reactants, but also for the formed acetyltetralin, which is preferentially adsorbed and leading to the various secondary products.

Adsorption and competitive adsorption of tetralin and acetyltetralin confirm these results. Under the conditions of the acetylation reaction (180°C), 2-acetyltetralin is quantitatively adsorbed after 1 h. Such an



Scheme 1. Reaction scheme of the acetylation of tetralin with acetyl chloride over zeolites.

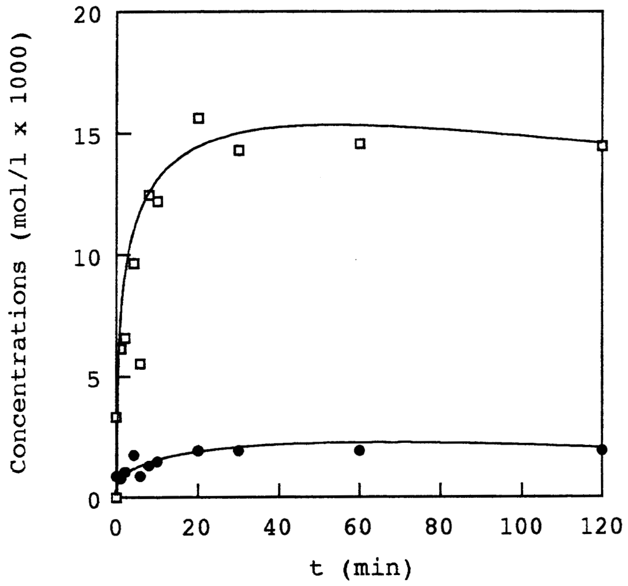


Figure 2. Acetylation of tetralin with acetyl chloride. Formation of 1-acetyltetralin (●) and of 2-acetyltetralin (□) versus reaction time.

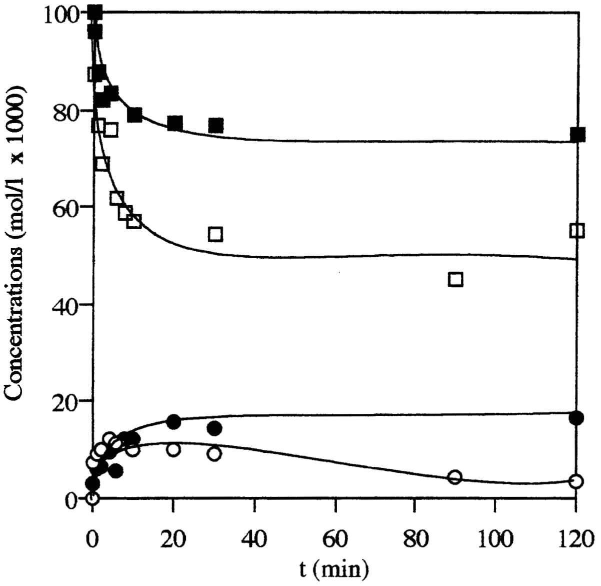


Figure 3. Influence of experimental conditions on disappearance of tetralin (□, ■) and on formation of 2-acetyltetralin (○, ●). The reaction is carried out under nitrogen (open symbols) flow or air (dark symbols).

adsorption is accompanied by the formation of secondary products, mainly ethyltetralin and acetylnaphthalene.

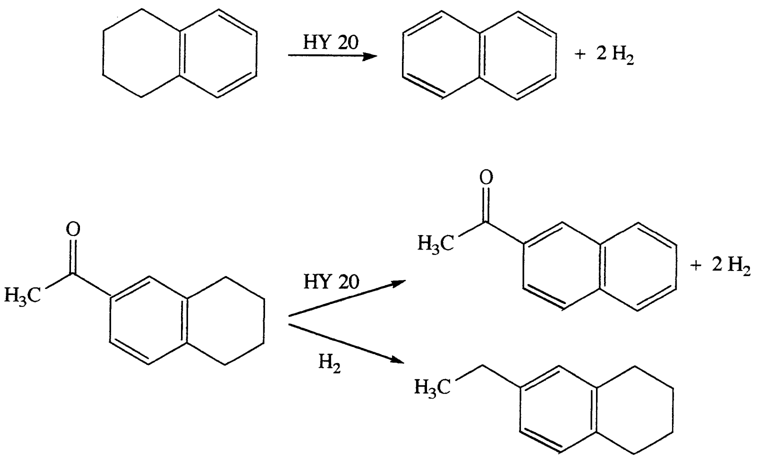
On the contrary, the same conditions for the tetralin lead to a very low adsorption of this substrate together with the formation of naphthalene (less than 5%). The competitive adsorption of the two substrates leads to the same results.

These results could be explained by a dehydrogenation of tetralin and acetyltetralin to respectively naphthalene and acetylnaphthalene followed by reduction of the carbonyl group of acetyltetralin by H_2 to give ethyltetralin, according to scheme 2.

3.2.3. Influence of the solvent

The same behaviour is observed when the reaction is carried out in the absence of solvent (15 ml tetralin and 9.4 ml CH_3COCl (1.2 equivalent) in the presence of 1 g catalyst at 190°C). Under nitrogen conditions, a very fast conversion is obtained leading to a maximum amount of acetyltetralin after only 30 min reaction; the acetyltetralin is then transformed into secondary products. Under air conditions, such a decomposition is not observed, but the same kind of saturation as in the presence of solvent occurs.

The existence of the consecutive reactions, observed under nitrogen conditions both in the presence and absence of solvent, has been confirmed by the study of the reactivity of 2-acetyltetralin under the same conditions (in the presence of tetralin, acetyl chloride and the catalyst) which leads to the same secondary products.



Scheme 2. Reaction scheme for the formation of the secondary products.

Table 3
Influence of the ratio tetralin/acetyl chloride on the formation of acetyltetralin

Tetralin (mol)	CH_3COCl (mol)	Tet/CH_3COCl	AcT (mol)	AcT/CH_3COCl
0.183	0.030	6.2	0.010	0.33
0.183	0.060	3.1	0.007	0.12
0.110	0.132	0.8	0.003	0.02

Under those conditions, only the decomposition of 2-acetyltetralin is observed; the concentration of tetralin remains constant, which means that the acetylation reaction is inhibited.

When the reaction is carried out in the absence of solvent, a better conversion of tetralin is obtained than in the presence of solvent. Such a result led us to study the influence of the ratio substrate/acetylating agent on the conversion; in order to avoid the decomposition of the 2-acetyltetralin formed, this study was made using standard conditions, i.e. under air. Figure 4 shows the evolution of the amount of acetyltetraline with time using various conditions.

The results obtained show that the more important the ratio tetralin/acetyl chloride is, the higher is the yield in acetyltetralin versus the amount of acetylating agent (table 3). This can be interpreted by the high amount of polar species (acetyl chloride and acetic acid), which totally occupy the porous volume of the zeolite, preventing the approach of tetralin into the pores.

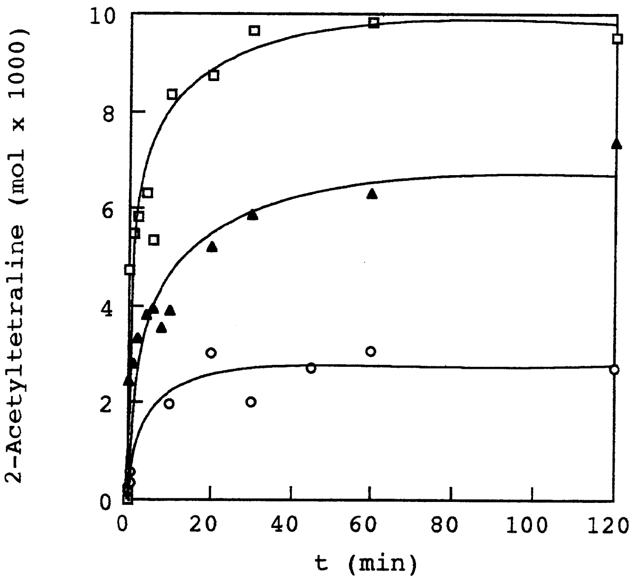


Figure 4. Influence of acetyl chloride amount on the formation of 2-acetyltetralin: (□) 0.183 mol tetralin and 0.030 mol acetyl chloride (tetralin/CH_3COCl= 6.2); (▲) 0.183 mol tetralin and 0.060 mol acetyl chloride (tetralin/CH_3COCl= 3.1); (○) 0.110 mol tetralin and 0.132 mol acetyl chloride (tetralin/CH_3COCl= 0.8). The reaction is carried out at 190°C in presence of 1 g HY 20.

4. Conclusion

Tridimensional zeolites, such as HY and H-beta, are active in the acetylation reaction of tetralin by acetyl chloride in liquid phase, leading to the corresponding 2- and 1-acetyltetralin in moderate yields. It is shown that the activity of the catalyst depends largely on the experimental conditions: air or nitrogen atmosphere, absence or presence of an organic solvent, reactants ratio. The observed deactivation is related to the strong adsorption of organic species, either acetic acid or 2-acetyltetralin formed in the reaction. In the latter case, secondary products are obtained which are due to consecutive reactions of the adsorbed acetyltetralin. Taking into account the overall results obtained, an order of preferential adsorption over zeolites can be proposed: acetic acid > acetyltetralin > acetyl chloride $\gg$ tetralin.

References

[1] G.A. Olah, *Friedel–Crafts and Related Reactions*, Vols. 1,3 (Wiley Interscience, New York, 1963/1964).

[2] W.F. Hölderich, M. Hesse and F. Naumann, Angew. Chem. Int. Ed. Engl. 27 (1988) 226.

[3] W.F. Hölderich and H. van Bekkum, in: *Introduction to Zeolite Science and Practice*, eds. H. van Bekkum, E.M. Flanigen and J.C. Jansen (Elsevier, Amsterdam, 1991).

[4] P.B. Venuto, Microporous Mater. 2 (1994) 297.

[5] B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Graille and D. Pioch, J. Org. Chem. 51 (1986) 2128.

[6] C. Gauthier, B. Chiche, A. Finiels and P. Geneste, J. Mol. Catal. 50 (1989) 219.

[7] C. Gauthier, B. Chiche, A. Finiels and P. Geneste, Appl. Catal. 30 (1987) 365.

[8] D.E. Akporiaye, K. Daastvan, J. Solberg and M. Stöcker, Stud. Surf. Sci. Catal. 78 (1993) 521.

[9] V. Paul, A. Sudalai, T. Daniel and K.V. Srinivasan, Tetrahedron Lett. 35 (1994) 67.

[10] R. Fang, G. Harvey, H.W. Kouwenhoven and R. Prins, Appl. Catal. A 130 (1995) 67.

[11] A.P. Singh, B. Bhattacharya and S. Sharma, J. Mol. Catal. A 102 (1995) 139.

[12] V. Bosacek, E.A. Gunnewegh and H. van Bekkum, Catal. Lett. 39 (1996) 57.

[13] Y.B. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, J. Chem. Soc. Chem. Commun. (1993) 1456; Appl. Catal. A 133 (1995) L1.

[14] I. Nicolau and A. Agiulo, US patent 4652683 (1987).

[15] B.B.G. Gupta, US patent 4668826 (1987).

[16] I. Naves, F.R. Ribeiro, J.P. Bodibo, Y. Pouilloux, M. Gibelmann, P. Magnoux, M. Guisnet and G. Pérot, *Proc. 9th Int. Zeolite Conf.*, Montreal 1992, eds. R. von Ballmoos et al. (1993) p. 543.

[17] A. Corma, M.J. Climent, H. Garcia and J. Primo, Appl. Catal. A 49 (1989) 109.

[18] Q.L. Wang, Y. Ma, X. Ji, H. Yan and Q. Qin, J. Chem. Soc. Chem. Commun. (1995) 2307.

[19] E.A. Gunnewegh, R.S. Downing and H. van Bekkum, Stud. Surf. Sci. Catal. 97 (1995) 447.

[20] G. Harvey and G. Mäder, Collect. Czech. Chem. Commun. 57 (1992) 862.

[21] A. Finiels, A. Calmettes, P. Geneste and P. Moreau, Stud. Surf. Sci. Catal. 78 (1993) 595.

[22] F. Richard, J. Drouillard, H. Carreyre, J.L. Lemberton and G. Pérot, Stud. Surf. Sci. Catal. 78 (1993) 601.

[23] P. Amouzegh, A. Finiels, P. Geneste, E. Ginestar and P. Moreau, Catal. Lett. 34 (1995) 389.

[24] F. Richard, H. Carreyre and G. Pérot, J. Catal. 159 (1996) 427.

[25] T.V. Whittam, Eur. patent 0055046 A1 (1981).

[26] B. Chauvin, P. Massiani, R. Dutartre, F. Fajula, F. Figueras and T. des Courières, Zeolites 10 (1990) 174.

[27] D. Mravec, M. Michvocik, M. Hronec, P. Moreau, A. Finiels and P. Geneste, Catal. Lett. 38 (1996) 267.

[28] E.A. Gunnewegh, S.S. Gopic and H. van Bekkum, J. Mol. Catal. A 106 (1996) 151.

[29] K. Gaare and D. Akporiaye, J. Mol. Catal. A 109 (1996) 177.

[30] P.S. Landis and P.B. Venuto, J. Catal. 6 (1966) 245.

[31] I. Neves, F. Jayat, D.B. Lukyanov, P. Magnoux, G. Pérot, F.R. Ribiero, M. Gubelman and M. Guisnet, in: *Catalysis of Organic Reactions*, eds. M.G. Scaros and M.L. Prunier (Dekker, New York, 1994) p. 515.