Kinetics of 2-methoxynaphthalene acetylation with acetic anhydride over dealuminated HY zeolites

Pascal Meric, Annie Finiels, Patrice Moreau*

UMR 5618 CNRS–ENSCM, Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, FR 1878 Institut Gerhardt, Ecole Nationale Supérieure de Chimie, 8 Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

Abstract

The Friedel–Crafts acetylation reaction of 2-methoxynaphthalene (2-MN) by acetic anhydride (Ac_2O) in liquid phase over HY zeolites as catalysts has been studied. This reaction leads to the selective formation of the sterically hindered 1-acetyl-2-methoxynaphthalene (1-Ac-2-MN). Among all HY zeolites tested, HY with a Si/Al molar ratio of 40 was the best catalyst in terms of initial activity, and was chosen for the kinetic study. Experimental data obtained by varying the reactant concentration allowed to propose a modified Eley–Rideal mechanism in which the acetic anhydride adsorbed on the catalyst reacts with 2-methoxynaphthalene present in the liquid phase, but in which 2-methoxynaphthalene is also competitively adsorbed on the active sites of the catalyst, acting in this case as a poison only. This kinetic study allowed to determine the adsorption equilibrium constants ratio of reactants, and to show that 2-methoxynaphthalene is more adsorbed than acetic anhydride, hence confirming the poisoning role of this aromatic species. Adsorption equilibrium constants of products, based on theoretical values of reaction rate as a function of conversion, was also determined and showed that products were more strongly adsorbed than reactants. The possible occurrence of an equilibrium between 2-methoxynaphthalene and 1-Ac-2-MN was also studied. In our reaction conditions, the acetylation reaction of 2-methoxynaphthalene with acetic anhydride does not lead to an equilibrium. The level-off observed in the conversion of 2-methoxynaphthalene was attributed to an inhibition of the reaction caused by adsorption of all of the products, i.e. acetylated products and acetic acid, on the active sites of the catalyst.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Friedel–Crafts acetylation; HY zeolites; 2-Methoxynaphthalene; 1-Acetyl-2-methoxynaphthalene; Equilibrium adsorption constants; Kinetics; Modified Eley–Rideal type mechanism

1. Introduction

Alkylation and acylation reactions of aromatics are particularly important steps in the formation of C–C bonds in organic chemistry. Alkylation is one of the most important reaction of petrochemical and chemical industries, and acylation often constitutes the fundamental step in the production of intermediates widely used in various areas of the fine chemical industry (pharmaceuticals, fragrances, dyes, insecticides, . . .) [1]. Lewis acids, such as $AlCl_3$, $FeCl_3$, $TiCl_4$, $SnCl_4$, BF_3, . . . , are generally used as catalysts for these Friedel–Crafts reactions. However, such conventional catalysts generate many problems as they are polluting, corrosive, and destroyed during the work-up. The advantages of the substitution

---

* Corresponding author. Tel.: +33-4-6714-4325;
fax: +33-4-6714-4349.
E-mail address: pmoreau@cit.enscm.fr (P. Moreau).

of these Lewis acids by environment-friendly catalysts, such as zeolites, are now well demonstrated [2], and have been especially emphasised for aromatic electrophilic substitution reactions in many papers and reviews [3–6]. The application of such an heterogeneous catalysis by zeolites has been described in the acylation of a number of aromatic and hetero-aromatic systems. In particular, C-acylation of aromatic ethers has been successfully carried out over various solid catalysts, including clays [7] and large pore zeolites, such as HY and HBEA [8]; an extent to an industrial scale of the use of the latter for the synthesis of 4-methoxyacetophenone and 3′,4′-dimethoxyacetophenone has been recently patented [9,10]. Acetylation reaction of 2-methoxynaphthalene is of particular interest due to the possible formation of 2-acetyl-6-methoxynaphthalene (2-Ac-6-MN) as a precursor of the anti-inflammatory drug Naproxen [11,12], and could constitute an interesting model to test shape-selective properties of large pore zeolites. Such a reaction has been carried out over various acidic zeolites, HY, HBEA and HZSM12 [13–23], MCM-41 molecular sieves [24,25], clays [7] and sulphated zirconia [26,27]. Acylation of 2-methoxynaphthalene generally occurs at the kinetically controlled 1-position, leading to the 1-acetyl-2-methoxynaphthalene (1-Ac-2-MN). Harvey and Mäder [13] first reported differences in products distribution depending on the zeolites: 100% selectivity of 1-Ac-2-MN over HY zeolites, whereas over HBEA both 1-Ac-2-MN and the linear 2-Ac-6-MN were obtained; these differences have been interpreted in terms of shape-selective effects. Furthermore, these authors first observed deacylation of 1-Ac-2-MN in the presence of HBEA zeolite, leading to the thermodynamically more stable 2-Ac-6-MN. This process was suggested to be a protiodeacylation mechanism as previously evidenced for the fluorenone rearrangement in phosphoric acid [28]. In order to understand the special behaviour of HBEA zeolites in the acetylation reaction of 2-methoxynaphthalene, the contributions of both the inner and outer surfaces of such catalysts have been examined [14], and it was suggested that 1-Ac-2-MN could be mainly formed on the external surface, whereas 2-Ac-6-MN in the microporous volume.

Recently, several groups reported results about acetylation reaction of 2-methoxynaphthalene, especially over HBEA catalysts. Effects of parameters, such as pre-treatment of the catalyst [15,16,18,21], crystal size [22,23], solvent polarity [16,20,21] or excess of reactants [19], on the activity and products distribution have been examined, and the mechanism of the 1-Ac-2-MN isomerisation process has been investigated [19].

As part of our interest in the study of acylation reactions over zeolites and the kinetics of such reactions under heterogeneous conditions, the present work deals with the study of the 2-methoxynaphthalene acetylation reaction with acetic anhydride in the liquid phase over HY zeolites, leading to the selective formation of 1-Ac-2-MN. The main purpose of this work is to determine the kinetics of such a reaction in order to propose a mechanism for this acetylation reaction, but also to investigate the possible occurrence of a deacylation–acylation equilibrium between 1-Ac-2-MN and 2-methoxynaphthalene, and/or deactivation process of the catalyst.

2. Experimental

2.1. Catalysts and reactants

The HY (Si/Al = 15) was from PQ Corporation (CBV 720); HY (Si/Al = 40) was a gift from Atochem (OPL109) and HY (Si/Al = 100) was from Degussa. The properties of the catalysts are listed in Table 1. Calcinations were performed at 773 K for 6 h with a heating rate of 60 K h^{-1}, in a dry air flow.

2-Methoxynaphthalene, acetic anhydride and undecane (internal standard) were commercially available from Aldrich (purity > 99%), 2-Ac-6-MN (98%) was provided by Acros Organics. Chlorobenzene (analytical grade from Aldrich) was used after being dried over molecular sieves.

2.2. Catalytic experiments and analytical methods

The reactions were performed under atmospheric pressure in a 100 ml round bottom flask equipped with a condenser, a dropping funnel, a thermometer and a stirring mechanism. A typical reaction was carried as follows: 1.90 ml (20 mmol, 0.4 mol l^{-1}) of acetic anhydride in 40 ml of chlorobenzene was introduced in the flask and magnetically stirred at 1000 rpm under

Table 1
Properties of HY zeolite samples

Si/Al ratio	BET specific area ($m^2 g^{-1}$)	Microporous volume ($cm^3 g^{-1}$)	Mesoporous volume ($cm^3 g^{-1}$)	Acidity ($meqH^+ g^{-1}$)	Elementary analysis (wt.%)		
					Si	Al	Na
15	762	0.25	0.215–0.211	0.64	37.80	2.64	0.06
40	749	0.30	0.184–0.185	0.15	39.20	1.00	0.10
100	644	0.28	0.101–0.092	0.062	44.80	0.39	0.08

nitrogen atmosphere. The freshly activated catalyst (0.5 g) was added and the reaction mixture was allowed to heat up to 353 K. Measured 1.58 g (10 mmol, $0.2 \, mol \, l^{-1}$) of 2-methoxynaphthalene in 10 ml of chlorobenzene was then added, and the mixture was stirred. Samples were periodically collected and analysed by gas chromatography (Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionisation detector, capillary column HP-1, 25 m × 0.2 mm, 0.33 mm thickness, carrier gas hydrogen).

2.3. Synthesis of 1-acetyl-2-methoxynaphthalene

The 1-Ac-2-MN was synthesised either according to [29] by reacting 1-acetyl-2-hydroxynaphthalene with Me_2SO_4 in the presence of K_2CO_3 using acetone as a solvent under stirring at room temperature for 24 h, or by reaction over HY catalysts. In the first case, 1-Ac-2-MN was recovered and recrystallised in petroleum ether (50% yield). In the second case, the catalyst was filtered after reaction and the products were concentrated by evaporation; products separation was carried out using silica gel chromatography, with petroleum ether/diethyl ether (90/10, volume) as the eluent.

The structure of 1-Ac-2-MN was established by GC–MS analysis (Hewlett-Packard 5890, with a 5970A series mass selective detector), uncorrected melting point (105–106 °C), ^1H and ^{13}C NMR: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 2.65 (3 H, s, –CH_3), 3.88 (3 H, s, –OCH_3), 7.26 (C_3–H, d, 9.12 Hz), 7.34–7.47 (C_5 or C_8–H, C_6–H, C_7–H, m), 7.8 (C_5 or C_8–H, d, 6.35 Hz), 7.85 (C_4–H, d, 9.12 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm): 32.61 (–$COCH_3$), 56.2 (–OCH_3), 112.71 (C_3), 123.53–123.96 (C_8–C_6), 124.86 (C_1), 127.56–128.14 (C_7–C_5), 128.74

(C_{10}), 130.22 (C_9), 131.44 (C_4), 153.95 (C_2), 204.9 (C=O); MS: 185 (M–CH_3), 200 (M$^+$), 142 (M–$COCH_3$–CH_3), 114 (M–CO–$COCH_3$–CH_3), 170 (M–CH_3–CH_3).

3. Results and discussion

3.1. Activity and products distribution

The acetylation reaction of 2-methoxynaphthalene has been carried out over three HY zeolite samples with a Si/Al molar ratio of 15, 40 and 100, respectively. Table 2 represents initial reaction rates, turnover frequencies (TOFs) and products distribution as a function of the Si/Al molar ratio of the samples. Initial reaction rates are deduced from the experimental curves of concentration versus time by determining the slope at the origin, and TOF are calculated by dividing the initial reaction rates by the number of acid sites determined by ammonia thermodesorption.

The highest initial activity is found with HY-40 sample ($r_0 = 1.25 \times 10^{-3} \, mol \, min^{-1} \, g^{-1}$). As can be seen in Fig. 1, which represents profile curves of ammonia desorption as a function of temperature for the three samples, normalised for the same weight of catalyst, a large peak of ammonia desorption is centred at around 350–400 °C, and is assigned to strong acid sites. The identical temperature of this ammonia desorption peak for the three samples indicates that there is no increase of the strength of the acid sites between HY-15 and HY-100, which is in agreement with previous conclusions of Barthomeuf [30]. Thus, the increase of the initial activity from HY-15 to HY-40 does not come from an increase of the strength of the acid sites. Furthermore, Corma et al. [31] proposed for the acylation reaction of anisole

Table 2
Initial reaction rates, turnover frequencies (TOFs) and products distribution as a function of the Si/Al molar ratio of the catalyst

Si/Al	$r_0 \times 10^3$ (mol min^{-1} g^{-1})	TOF (min^{-1})	Products distribution (%)		
			1-Ac-2-MN	2-Ac-6-MN	1-Ac-7-MN
15	1.1	1.72	95	4	1
40	1.25	8.5	95	4	1
100	0.58	9.3	95	4	1

Reaction conditions: solvent, chlorobenzene, 50 ml; [2-MN]$_0$ = [Ac$_2$O]$_0$ = 0.2 mol l^{-1}; catalyst = 0.5 g; T = 353 K.

that all the acid sites of the zeolite are able to catalyse the reaction. 2-Methoxynaphthalene is, as anisole, an activated aromatic system. HY-15 which contains a greater number of acid sites (Table 1) should be the most active catalyst for the 2-methoxynaphthalene acetylation reaction: it is not observed. Such results suggest that the better initial activity of HY-40 cannot be directly related to the number and/or the strength of the acid sites, and that another parameter seems to influence the reaction.

As can be seen in Table 2, the TOF increases till Si/Al molar ratio of 40, and remains almost constant in the range of Si/Al molar ratio 40–100. Such an evolution of the TOF, which is conventional for zeolites is, however, shifted to higher Si/Al molar ratios in our case. This displacement could be related to a more hydrophobic character of HY-40 zeolite, as already men-

tioned in the literature [31–33], which could promote the 2-methoxynaphthalene approach inside the zeolite framework, due to van der Waals interactions between the zeolite structure and 2-methoxynaphthalene. These favourable interactions could explain the better initial activity of the HY-40 sample. Hence, the following studies have been carried out using HY-40 catalyst.

Fig. 2 presents the evolution of the 2-methoxy-naphthalene acetylation reaction with acetic anhydride as a function of time, using dealuminated HY-40 zeolite in chlorobenzene as solvent. The reaction leads to the formation of 1-Ac-2-MN as major product, 2-Ac-6-MN and traces of 1-acetyl-7-methoxy-naphthalene (1-Ac-7-MN), with a distribution in favour of 1-Ac-2-MN (95%, kinetic product, Table 2). 2-Ac-6-MN, which is the thermodynamic product, is obtained only up to 4%. Furthermore, Fig. 2 shows
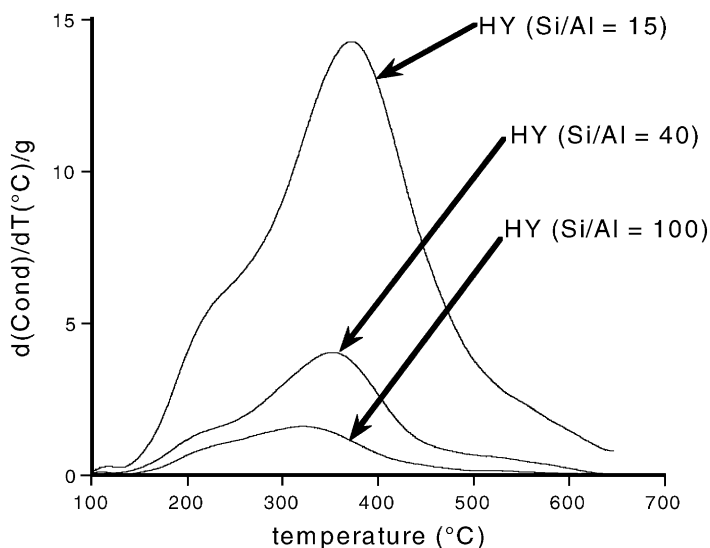

Fig. 1. Profile curves of ammonia desorption as the function of temperature for the three HY samples.
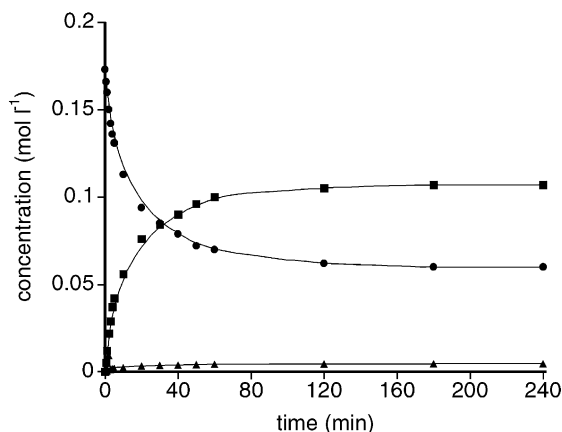
Fig. 2. Run profile for acetylation of 2-methoxynaphthalene by acetic anhydride over HY-40 zeolite (solvent, chlorobenzene, 50 ml; $[2\text{-MN}]_0 = [\text{Ac}_2\text{O}]_0 = 0.2\,\text{mol}\,l^{-1}$; catalyst = 0.5 g; $T = 353\,\text{K}$; (●), 2-MN; (■), 1-Ac-2-MN; (▲), 2-Ac-6-MN).

that the [1-Ac-2-MN]/[2-Ac-6-MN] ratio remains constant with time to a value of 24, even after 24 h reaction (not shown in this figure). Such a constant ratio indicates that products are formed by parallel reactions. This behaviour (products distribution and constant ratio of products) was also observed for the two other HY zeolites.

On the other hand, a level-off appears after 2 h of reaction (Fig. 2). Such a level-off could be attributed either to a protiodeacylation process of 1-Ac-2-MN, as evidenced by Harvey and Mäder [13], and confirmed by other authors [17–20], or to an inhibition of the reaction by product(s) adsorption on the acid sites of the catalyst [8,34–38]. The origin of this level-off will be more discussed later.

3.2. Kinetic study

The conditions required to ensure the absence of diffusion limitations have been first determined. The effect of the catalyst weight on the initial rate indicates a linear dependence up to 1 g. Further experiments were then achieved in the presence of 0.5 g of zeolite, and under stirring (1000 rpm).

3.2.1. Influence of initial concentration of reactants
Initial reaction rates have been measured at different initial concentrations of acetic anhydride whilst the 2-methoxynaphthalene concentration was kept

constant, and vice-versa, using HY-40 as catalyst. Figs. 3 and 4 represent the initial reaction rates as a function of initial concentrations of acetic anhydride and 2-methoxynaphthalene, respectively. As can be seen from these curves, when the initial concentration of 2-methoxynaphthalene is kept constant, the initial reaction rate first increases with an increase of the acetic anhydride concentration up to $0.4\,\text{mol}\,l^{-1}$ (first-order toward acetic anhydride), and then reaches a plateau (zero-order) for initial concentrations higher than $0.4\,\text{mol}\,l^{-1}$ (Fig. 3). The same trend is obtained when the initial concentration of acetic anhydride is kept constant and the initial concentration of 2-methoxynaphthalene is increased. In this latter case, the plateau is obtained for a concentration of 2-methoxynaphthalene of $0.2\,\text{mol}\,l^{-1}$ (Fig. 4). Thus, the following studies were carried out under the conditions where the initial activity is maximum, i.e. with 0.2 and $0.4\,\text{mol}\,l^{-1}$ of 2-methoxynaphthalene and acetic anhydride, respectively.

3.2.2. Kinetic law proposition
For a bimolecular heterogeneous reaction, either a Langmuir–Hinshelwood or an Eley–Rideal type kinetic mechanisms are generally considered. The Langmuir–Hinshelwood mechanism includes two types of mechanisms which depend on the adsorption of the reactants: adsorption over the same type of sites, or adsorption over different types of sites. The latter mechanism, called non-competitive Langmuir–Hinshelwood mechanism is reported for hydrogenation reactions [39]. Figs. 3 and 4 are similar to those corresponding to a non-competitive Langmuir–Hinshelwood mechanism, and could represent a reaction between acetic anhydride and 2-methoxynaphthalene adsorbed over different types of sites. However, if the reaction takes place between the two adsorbed species, an adsorption of 2-methoxynaphthalene on another type of sites than protonated sites already occupied by acetic anhydride seems difficult to operate. This leads us to consider that the reactants are adsorbed on the same type of acid sites, i.e. protonated sites. Such a mechanism is proposed by Derouane et al. [34,40] for acetylation reactions of anisole and toluene. However these authors [34] mentioned that: "a Langmuir–Hinshelwood model can describe this situation as discussed earlier. Although only one reactant may be activated at the
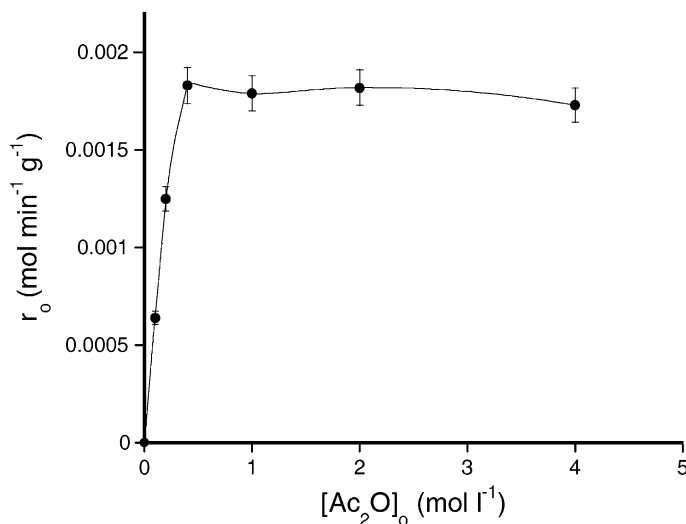
Fig. 3. Plot of initial rate of disappearance of 2-methoxynaphthalene vs. initial concentrations of acetic anhydride over HY-40 (solvent, chlorobenzene, 50 ml; $[2\text{-MN}]_0 = 0.2\,\text{mol}\,\text{l}^{-1}$; $[Ac_2O]_0 = 0$–$4\,\text{mol}\,\text{l}^{-1}$, catalyst = 0.5 g, $T = 353\,\text{K}$).

catalytic sites, it is obvious that the other reactant(s) and product(s) will block its access to the catalytic sites considering the atomic size of the zeolite pores, channels, and cavities". Furthermore, these authors consider, from the Langmuir–Hinshelwood kinetic law, that the adsorption terms of the aromatic system

represents only a physisorption process rather than a chemisorption. This could be interpreted as that the reaction does not occur between the two adsorbed species. From our part, we consider that the adsorption of the reactants on the same type of acid sites, leading to two positively charged species, cannot be
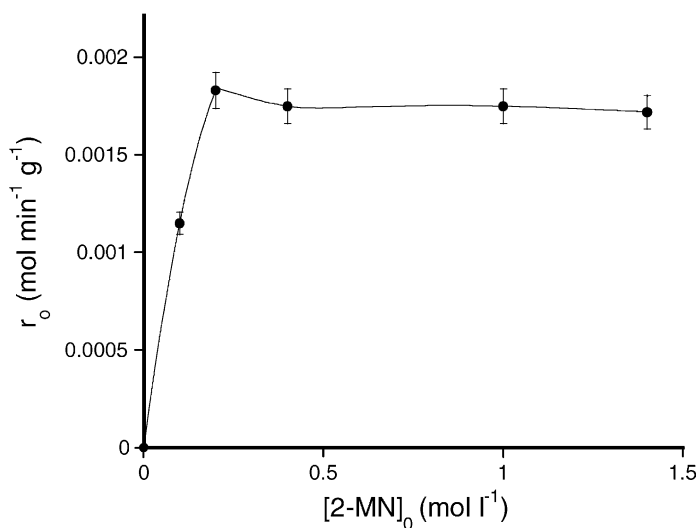

Fig. 4. Plot of initial rate of disappearance of 2-methoxynaphthalene vs. initial concentrations of 2-methoxynaphthalene over HY-40 (solvent, chlorobenzene, 50 ml; $[2\text{-MN}]_0 = 0$–$1.4\,\text{mol}\,\text{l}^{-1}$; $[Ac_2O]_0 = 0.4\,\text{mol}\,\text{l}^{-1}$; catalyst = 0.5 g, $T = 353\,\text{K}$).

satisfactorily envisaged for an electrophilic aromatic substitution.

A pure Eley–Rideal mechanism, in which the aromatic in the liquid phase reacts with the adsorbed acetylating agent, was first proposed by Venuto et al. [41] and Venuto and Landis [42], and recently by other authors [27,31,43]. However, Pérot and colleagues [43], who proposed such a mechanism for the benzofuran acetylation reaction, considered a strong physisorption of benzofuran on the acid sites in order to explain the kinetic partial order 1/2 for this reactant. On the other hand, Corma et al. [31] proposed a kinetic law based on an Eley–Rideal mechanism for the acylation reaction of anisole. However, these authors introduced a chemisorption terms of anisole at the denominator of the kinetic law in order to get a better interpretation of their results. Indeed, for acylation reactions of polar substrates, a pure Eley–Rideal mechanism does not seem to be satisfactorily envisaged for the reasons described: due to the polarity of the reactant (substituted aromatic), a chemisorption of the latter must necessarily be taken into account in the kinetic law.

Our experimental data shown in Figs. 3 and 4 do not correspond to the theoretical curves obtained for a pure Eley–Rideal mechanism. We propose a similar approach as that of Corma et al. [31] in order to explain our results, and suggest a modification of this mechanism, which could be named "modified Eley–Rideal mechanism".

3.2.3. Modified Eley–Rideal mechanism

Such a mechanism best accounts for the present results in the acetylation of 2-methoxynaphthalene, as already evidenced for various zeolite catalysed reactions studied in our group [8,44]. Following this mechanism, an adsorbed molecule of acetic anhydride should react with a non-adsorbed 2-methoxynaphthalene, within the porous volume of the catalyst. However, 2-methoxynaphthalene is also competitively adsorbed on the active sites of the zeolite, acting as a poison.

The corresponding equation can be written as follows:

$$r_0 = k\theta_A[MN]_0 \tag{1}$$

where MN is 2-methoxynaphthalene and A is acetic anhydride.

Under this assumption, the degree of occupation of the surface can be expressed as follows:

$$\theta_A = \frac{\lambda_A[A]_0}{1 + \lambda_A[A]_0 + \lambda_{MN}[MN]_0} \tag{2}$$

where λ_A and λ_{MN} are the equilibrium adsorption constants for acetic anhydride (A) and 2-methoxynaphthalene (MN), respectively.

As the reaction operates in the liquid phase, $\lambda_A[A]_0 + \lambda_{MN}[MN]_0$ is far higher than 1 so that (1) can be written as:

$$r_0 = k\frac{\lambda_A[A]_0[MN]_0}{\lambda_A[A]_0 + \lambda_{MN}[MN]_0} \tag{3}$$

Our proposition is not fundamentally different from that of Derouane et al. [34,40] who proposed a Langmuir–Hinshelwood type mechanism. We consider that the 2-methoxynaphthalene chemisorption process reduces the number of acid sites available for acetic anhydride, but also that the reaction does not proceed between the two adsorbed species. In this way, the physisorption (or chemisorption) terms of 2-methoxynaphthalene at the numerator does not appear in our proposed equation law, compared with Derouane equation.

3.2.4. Equilibrium adsorption constants determination

3.2.4.1. Reactants. At the very early stages of the reaction, product adsorption can be neglected as little product is present. The equation is (3). The λ_{MN}/λ_A ratio can be determined from Figs. 3 and 4. Indeed, in the conditions where the initial order of acetic anhydride is 0 (Fig. 3), the constant rate k of the reaction can be determined. We obtain:

$$k = \frac{r_0}{[MN]_0} = 9.15 \times 10^{-3}$$

On the other part, when the initial order of the reaction for 2-methoxynaphthalene is 0 (Fig. 4), the λ_{MN}/λ_A ratio is obtained after introduction of the constant rate k into the equation which is written as follows:

$$\frac{\lambda_{MN}}{\lambda_A} = \frac{k[A]_0}{r_0} = 2$$

The value of 2 indicates that 2-methoxynaphthalene is indeed more adsorbed than acetic anhydride, which

confirms the importance of the poisoning effect of 2-methoxynaphthalene. It is interesting to notice that this ratio could also be obtained using the Langmuir–Hinshelwood formalism. Indeed, in such a mechanism, the reaction rate is maximal when the $[MN]_0/[A]_0$ concentration ratio leads to equal occupancies of the intracrystalline volume of the zeolite by 2-methoxynaphthalene and acetic anhydride, i.e. $\theta_{MN} = \theta_A$, corresponding to a 1:1 stoichiometry of the reactants inside the zeolite porosity.

3.2.4.2. Product(s). Reaction rates measured at the quasi-stationary state can be used to determine an approximate value of λ_P. In this case, (3) becomes:

$$r = k \frac{\lambda_A[A][MN]}{1 + \lambda_A[A] + \lambda_{MN}[MN] + \lambda_P[P]}$$

where λ_P is the equilibrium adsorption constant for product(s) (P).

In order to analyse effects of product inhibition and competition between the reactants, Derouane [45] plotted the theoretical variations of the reaction rate as a function of the conversion, for a Langmuir–Hinshelwood model, and showed that the stronger the equilibrium adsorption coefficient of product is, the higher the reaction rate decreases with conversion.

We have used the same approach as that of Derouane [45] and plotted theoretical curves of reaction rate as a function of the conversion of 2-methoxynaphthalene, assuming that $k = 1$, $2\lambda_A = \lambda_{MN}$, $\lambda_A = 1$, $[2\text{-MN}]_0 = 0.2\,mol\,l^{-1}$, and $[Ac_2O]_0 = 0.4\,mol\,l^{-1}$, for a modified Eley–Rideal mechanism. These curves are represented in Fig. 5 and showed that an increase of the value of λ_P leads to a dramatic decrease of the reaction rate with conversion, hence to an enhancement in product inhibition. Under the conditions described in the experimental part, we reported the experimental curve of reaction rate with conversion, and compared it with the theoretical curves. As can be seen in Fig. 5, our experimental curve is close to the theoretical curve for which $\lambda_P = 20\,\lambda_{MN}$. This comparison indicates that, under our conditions, the products are more adsorbed than the reactants, so that the reaction could be inhibited by the adsorption of the products.

3.3. Equilibrium/deactivation study

As shown in Fig. 2, the 2-methoxynaphthalene conversion is not complete, and the reaction is stopped after 2 h. This level-off could be either due to a 1-Ac-2-MN protiodeacylation process or to a catalyst deactivation.
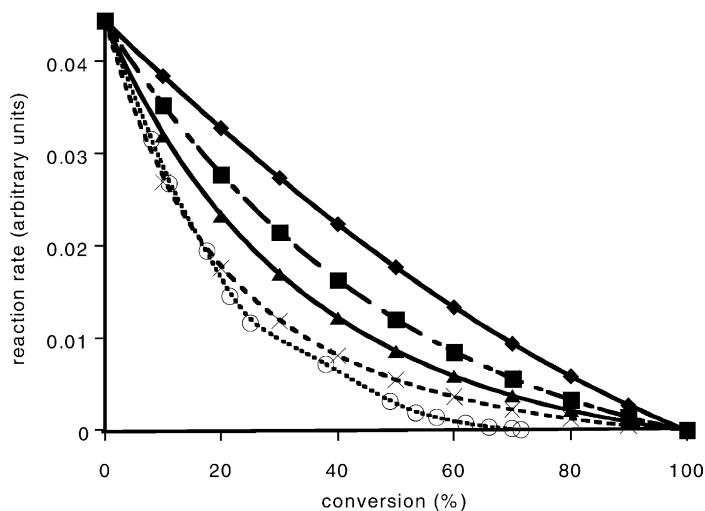

Fig. 5. Plot of experimental and theoretical curves of reaction rate vs. conversion of 2-methoxynaphthalene, using a modified Eley–Rideal mechanism ($k = 1$, $2\lambda_A = \lambda_{MN}$, $[2\text{-MN}]_0 = 0.2\,mol\,l^{-1}$, $[Ac_2O]_0 = 0.4\,mol\,l^{-1}$; $2\lambda_A = \lambda_{MN}$; (◆), $\lambda_{MN} = \lambda_P$; (■), $5\lambda_{MN} = \lambda_P$; (▲), $10\lambda_{MN} = \lambda_P$; (○), experimental data; (×), $20\lambda_{MN} = \lambda_P$).
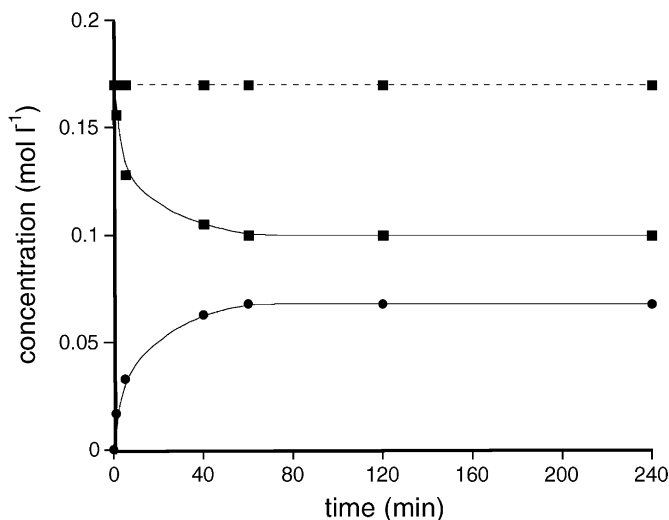
Fig. 6. Stability of 1-acetyl-2-methoxynaphthalene as a function of time over HY-40, in absence (straight line) or in presence (dotted line) of acetic anhydride (solvent, chlorobenzene, 50 ml; $[1\text{-Ac-2-MN}]_0 = 0.2\,\text{mol}\,l^{-1}$; $[\text{Ac}_2\text{O}]_0 = 0$ or $0.4\,\text{mol}\,l^{-1}$; catalyst $= 0.5\,\text{g}$; $T = 353\,\text{K}$; (●), 2-MN; (■), 1-Ac-2-MN).

3.3.1. Products stability

In order to investigate the possible occurrence of a protiodeacylation equilibrium between 1-Ac-2-MN and 2-methoxynaphthalene, the stability of the prod-ucts under standard conditions has been studied. Figs. 6 and 7 show the behaviour of 1-Ac-2-MN and 2-Ac-6-MN in the absence or presence of acetic anhydride, respectively, over HY-40 sample.
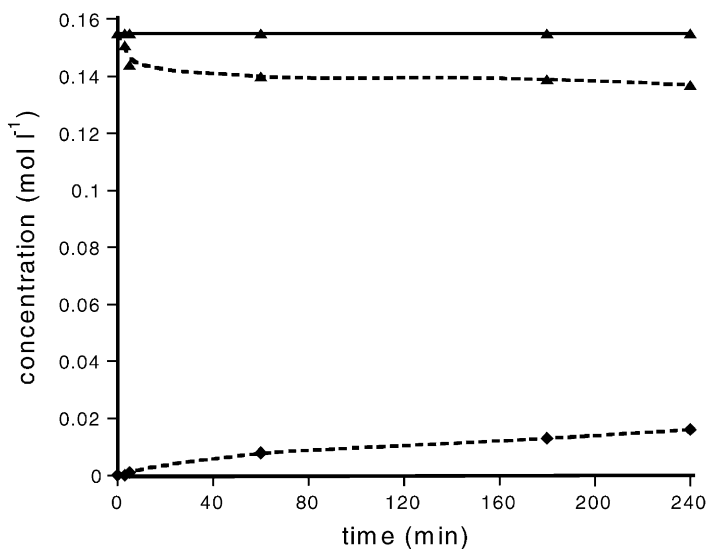

Fig. 7. Stability of 2-acetyl-6-methoxynaphthalene as a function of time over HY-40, in absence (straight line) or in presence (dotted line) of acetic anhydride (solvent, chlorobenzene, 50 ml; $[2\text{-Ac-6-MN}]_0 = 0.2\,\text{mol}\,l^{-1}$; $[\text{Ac}_2\text{O}]_0 = 0$ or $0.4\,\text{mol}\,l^{-1}$; catalyst $= 0.5\,\text{g}$; $T = 353\,\text{K}$; (▲), 2-Ac-6-MN; (◆), diacetylated product).

In the presence of catalyst, the concentration of 1-Ac-2-MN, without acetic anhydride (Fig. 6), decreases to partially give 2-methoxynaphthalene. The conversion remains constant at about 40% after 4 h reaction time. Such a behaviour shows that, under these conditions, a deacylation–acylation equilibrium exists between the sterically hindered 1-acetyl isomer and the 2-methoxynaphthalene. The corresponding equilibrium constant for the [1-Ac-2-MN]/[2-MN] ratio, has a value of 1.5. The 2-acetyl isomer is not formed. However, when acetic anhydride is initially added to the 1-Ac-2-MN in the presence of the zeolite (Fig. 6), no reaction occurred. Such a result means that under our experimental conditions, i.e. in the presence of acetic anhydride, the protiodeacylation equilibrium does not occur over HY zeolite.

As already reported in other papers, we have confirmed that such an equilibrium does not exist under our conditions, with the linear 2-Ac-6-MN, in presence or in absence of acetic anhydride (Fig. 7). However, the formation of a diacetylated product, characterised by mass spectrometry as 1,6-diacetyl-2-methoxynaphthalene previously observed in the literature [46], was obtained in the presence of acetic anhydride.

Catalytic test has been performed with AlCl₃ (5.34 g) and compared with the same reaction performed over HY-40 zeolite, under the standard conditions described. A nearly complete conversion of 2-methoxynaphthalene (98%) is obtained after 1 h reaction with AlCl₃, whereas only 70% of 2-methoxynaphthalene is converted after 4 h reaction over HY-40. It is well known that a reversible reaction is not affected by the presence of a catalyst. Such results indicate that under our conditions the acetylation reaction of 2-methoxynaphthalene is not governed by an equilibrium over HY zeolites. This has been confirmed by acetic anhydride addition at the level-off conversion of 2-methoxynaphthalene (not shown). There was no more conversion of 2-methoxynaphthalene, which would be the case for a reversible reaction. All these results clearly indicate that the level-off observed in the 2-methoxynaphthalene conversion is not due to an equilibrium under our conditions, but more probably due to a catalyst deactivation, and more especially to a reaction inhibition caused by product(s) adsorption on the acid sites of the catalyst.

3.3.2. Deactivation phenomenon

Reasons for the deactivation of zeolites during Friedel–Crafts catalysis are a matter of debate, and recent publications have dealt with this topic. It was suggested that the deactivation process could be attributed to the formation of heavy organic residues, like in acetylation reaction of anisole over HBEA zeolite [36,47]. However, for the same reaction, other authors suggested that the catalyst deactivation should be most probably due to strong (and reversible) adsorption of the acetylated product [34] on the active sites, or by adsorption of acetic acid formed as by-product [37].

In order to check if the level-off observed (Fig. 2) is caused by the formation of heavy organic products, regeneration tests of used catalyst have been performed over HY-40 catalyst, under the standard conditions. Table 3 presents initial reaction rates and 2-methoxynaphthalene conversions as a function of the number of cycles of the catalyst. The catalytic activity, which is retained after a third use of the catalyst, indicates that the deactivation process of the catalyst is reversible, thus, that no heavy organic residues are formed, but also that acetic acid formed as by-product does not seem to lead to a dealumination of the zeolite.

The possible occurrence of an inhibition of the reaction caused by product(s) adsorption has been studied by initial addition of products into the reaction mixture. Under the standard conditions, acetic acid or acetylated products (1-Ac-2-MN or 2-Ac-6-MN), or a mixture of acetic acid and 2-Ac-6-MN, were initially added. Table 4 presents initial reaction rates, 2-methoxynaphthalene conversions and initial rate ratios, as a function of the procedure.

As can be seen from the table, initial reaction rates and final conversions of 2-methoxynaphthalene are

Table 3

Initial reaction rates and 2-methoxynaphthalene conversions as a function of the number of cycle of HY-40

Cycle number	$r_0 \times 10^3$ (mol min^{-1} g^{-1})	Conversion (%)
1	1.83	71.5
2	1.76	65.0
3	1.91	72.0

Reaction conditions: solvent, chlorobenzene, 50 ml; $[2\text{-MN}]_0 = 0.2$ mol l^{-1}; $[\text{Ac}_2\text{O}]_0 = 0.4$ mol l^{-1}; catalyst = 0.5 g; $T = 353$ K.

Table 4
Influence of the addition of acetic acid or acetylated products on the initial rate and the final conversion of 2-methoxynaphthalene over HY-40

Conditions	$r_0 \times 10^3$ (mol min^{-1} g^{-1})	$r_{0A}/r_{0(A+X)}$	Conversion (%)
Standard	1.83	–	71.5
Standard + AcOH	1.07	1.71	64.0
Standard + 2-Ac-6-MN	0.95	1.93	52.0
Standard + 1-Ac-2-MN	1.42	1.29	50.0
Standard + 2-Ac-6-MN + AcOH	0.35	5.23	47.0

Reaction conditions: solvent, chlorobenzene, 50 ml; $[2\text{-MN}]_0 = 0.2\,\text{mol}\,l^{-1}$; $[Ac_2O]_0 = 0.4\,\text{mol}\,l^{-1}$; $[AcOH]_0 = 0.2\,\text{mol}\,l^{-1}$; $[1\text{-Ac-2-MN}]_0 = [2\text{-Ac-6-MN}]_0 = 0.1\,\text{mol}\,l^{-1}$; catalyst = 0.5 g; $T = 353\,\text{K}$.

sensitive to initial product(s) addition into the reaction mixture. Final conversions are reduced in the range from 10.5 to 34% and initial reaction rates from a factor of 1.29, 1.71 and 1.93 when 1-Ac-2-MN, acetic acid or 2-Ac-6-MN are, respectively, initially added. This decrease is more pronounced when a mixture of products is initially added (5.23). Such results confirm that the level-off observed after 2 h reaction time is caused by products adsorption on the active sites of the catalyst, which leads to an inhibition of the reaction, and also confirms the stronger equilibrium adsorption constant of product than that of reactants, estimated by comparing experimental data with theoretical values (Fig. 5). This inhibition seems to be due to the adsorption of all of the products, i.e. acetic acid and acetylated products. Furthermore, initial reaction rates presented in Table 4 are relatively close when each product is added separately. This trend could indicate that the equilibrium adsorption constants of the products are close to each other.

The inhibition process of the reaction by adsorption of the products is consistent with results reported in the literature for other acylation reactions, in which it was suggested that the reaction inhibition could be due to the preferential adsorption of acetic acid [8,37,38] or acylated products [34,36].

4. Conclusion

HY zeolites have been confirmed to be efficient catalysts for the acetylation reaction of 2-methoxynaphthalene, with acetic anhydride, under liquid phase conditions. A 95% selectivity towards 1-Ac-2-MN (hindered acetylated product) was always observed. In the range of HY zeolites studied (Si/Al from 15 to 100), HY with a Si/Al molar ratio of 40 was shown to be the most active catalyst for this reaction. The higher activity of HY-40, as compared with HY-15, does not seem to be directly related to the number and/or the strength of the acid sites of the catalyst, and was attributed to an increase of the hydrophobic character from HY-15 to HY-40, which could favour the 2-methoxynaphthalene approach in the zeolite framework, hence the reaction process.

The kinetic study of this reaction with acetic anhydride over HY-40 zeolite allowed to propose a modified Eley–Rideal mechanism, where the adsorbed acetic anhydride reacts with 2-methoxynaphthalene in the liquid phase, but in which 2-methoxynaphthalene is also competitively adsorbed on the active sites, acting somehow as a poison of the acid sites.

The λ_{MN}/λ_A ratio was determined and the higher adsorption of 2-methoxynaphthalene as compared with that of acetic anhydride confirmed the poisoning effect of 2-methoxynaphthalene. The ratio of equilibrium adsorption constants of products and reactant was also estimated by comparing experimental data and theoretical values of reaction rates versus 2-methoxynaphthalene conversion, using the modified Eley–Rideal kinetic law. This comparison allowed to evidence a higher adsorption of products than reactants.

The level-off in the conversion of 2-methoxynaphthalene, observed after 2 h reaction, was shown not to be caused by a protiodeacylation equilibrium between 1-Ac-2-MN and 2-methoxynaphthalene. This conclusion is supported by the stability tests of the products, which showed that under our conditions, the 1-acetyl isomer does not react over time. Furthermore, addition of acetic anhydride at the level-off does not lead to any further conversion.

Initial additions of the products in the reaction mixture lead to a reduction of the catalytic activity and allow to suggest that the level-off is due to a reaction inhibition caused by products adsorption onto the acid sites. This proposition is also supported by the stronger adsorption of products as compared with that of reactants, evidenced theoretically.

References

[1] P.H. Gore, in: G.A. Olah (Ed.), Friedel–Crafts and Related Reactions, Vol. III, Wiley-Interscience, New York, 1964.

[2] J.H. Clark, Green Chem. 1 (1999) 1.

[3] W. Hölderich, M. Hesse, F. Näuman, Angew. Chem. Int. Ed. Engl. 27 (1988) 226.

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

[5] A. Corma, Chem. Rev. 95 (1995) 559.

[6] A. Corma, H. Garcia, Catal. Today 38 (1997) 257.

[7] B.M. Choudary, M. Sateech, M. L Kantam, K.V.R. Prasad, Appl. Catal. A: Gen. 171 (1998) 155.

[8] P. Moreau, A. Finiels, P. Meric, J. Mol. Catal. A: Chem. 154 (2000) 185.

[9] M. Spagnol, L. Gilbert, E. Benazzi, C. Marcilly, Patent PCT Int. Appl. WO 96,35,655 (1996).

[10] M. Spagnol, L. Gilbert, E. Benazzi, C. Marcilly, Patent PCT Int. Appl. WO 96,35,656 (1996).

[11] K.T. Wan, M.E. Davis, J. Catal. 152 (1994) 25.

[12] M.E. Davis, Microporous Mesoporous Mater. 21 (1998) 173.

[13] G. Harvey, G. Mäder, Collect. Czech. Chem. Comm. 57 (1992) 862.

[14] G. Harvey, G. Binder, R. Prins, Stud. Surf. Sci. Catal. 94 (1995) 397.

[15] H.K. Heinichen, W. Hölderich, J. Catal. 185 (1999) 408.

[16] S.D. Kim, K.H. Lee, J.S. Lee, Y.G. Kim, K.E. Yoon, J. Mol. Catal. A: Chem. 152 (2000) 33.

[17] D. Das, S. Cheng, Appl. Catal. A: Gen. 201 (2000) 159.

[18] A. Berrhegis, P. Ayrault, E. Fromentin, M. Guisnet, Catal. Lett. 68 (2000) 121.

[19] E. Fromentin, J.M. Coustard, M. Guisnet, J. Catal. 190 (2000) 433.

[20] E. Fromentin, J.M. Coustard, M. Guisnet, J. Mol. Catal. A: Chem. 159 (2000) 377.

[21] M. Casagrande, L. Storaro, M. Lenarda, R. Ganzerla, Appl. Catal. A: Gen. 201 (2000) 263.

[22] P. Andy, J. Garcia-Martinez, G. Lee, H. Gonzalez, C.W. Jones, M.E. Davis, J. Catal. 192 (2000) 215.

[23] P. Botella, A. Corma, G. Sastre, J. Catal. 197 (2001) 81.

[24] H. Hitz, R. Prins, J. Catal. 168 (1997) 194.

[25] E.A. Gunnewegh, S.S. Gopic, H. van Bekkum, J. Mol. Catal. A: Chem. 171 (1998) 155.

[26] G.D. Yadav, M.S. Krishnan, Stud. Surf. Sci. Catal. 113 (1998) 259.

[27] G.D. Yadav, M.S. Krishnan, Chem. Eng. Sci. 54 (1999) 4189.

[28] I. Agranat, Y. Bentor, Y. Shan-Shi, J. Am. Chem. Soc. 99 (1977) 7068.

[29] P. A Sommai, O. Kamuzi, M. Masahiro, M. Satoru, N. Masakatsu, J. Chem. Soc. Perkin Trans. I 13 (1994) 1703.

[30] D. Barthomeuf, Mater. Chem. Phys. 17 (1987) 49.

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

[32] M.A. Camblor, A. Corma, S. Iborra, S. Miquel, J. Primo, S. Valencia, J. Catal. 172 (1997) 76.

[33] A. Finiels, P. Geneste, J. Lecomte, F. Marichez, C. Moreau, P. Moreau, J. Mol. Catal. A: Chem. 148 (1999) 165.

[34] E.G. Derouane, G. Crehan, C.J. Dillon, D. Bethell, S.B. Derouane Abd-Hamid, J. Catal. 187 (1999) 209.

[35] I. Neves, F.R. Ribeiro, J.P. Bodibo, Y. Pouilloux, M. Gubelmann, P. Magnoux, P. Magnoux, M. Guisnet, G. Pérot, in: R. von Ballmoos, J.B. Higgins, M.M.J. Treacy (Eds.), Proceedings of the 9th International Zeolite Conference, Montreal, 1992, p. 543.

[36] D. Rohan, C. Canaff, E. Fromentin, M. Guisnet, J. Catal. 177 (1998) 296.

[37] K. Smith, Z. Zhenhua, P.K.G. Hodgson, J. Mol. Catal. A: Chem. 134 (1998) 121.

[38] P. Moreau, A. Finiels, S. Pelorgeas, O. Vigneau, M. Laspéras, Catal. Lett. 47 (1997) 161.

[39] M.V. Rajashekharam, I. Bergault, P. Fouilloux, D. Schweich, H. Delmas, R.V. Chaudhari, Catal. Today 48 (1999) 83.

[40] E.G. Derouane, G. Crehan, C.J. Dillon, D. Bethell, H. He, S.B. Derouane Abd-Hamid, J. Catal. 194 (2000) 410.

[41] P.B. Venuto, L.A. Hamilton, P.S. Landis, J. Catal. 5 (1966) 484.

[42] P.B. Venuto, P.S. Landis, J. Catal. 6 (1966) 237.

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

[44] N. Barthel, A. Finiels, C. Moreau, R. Jacquot, M. Spagnol, J. Mol. Catal. A: Chem. 169 (2001) 163.

[45] E.G. Derouane, J. Mol. Catal. A: Chem. 134 (1998) 29.

[46] N.P. Buu Hoï, D. Lavit, J. Collard, Croat. Chem. Acta 29 (1957) 291.

[47] U. Freese, F. Heinrich, F. Roessner, Catal. Today 49 (1999) 237.