

HY zeolite-promoted electrophilic acylation of methoxyarenes with linear acid chlorides

Franca Bigi^a, Silvia Carloni^a, Cristina Flego^b, Raimondo Maggi^a,
Alessandro Mazzacani^a, Massimo Rastelli^a, Giovanni Sartori^{a,*}

^a Dipartimento di Chimica Organica e Industriale dell'Università, Parco Area delle Scienze 17A, I-43100 Parma, Italy

^b EniTecnologie S.P.A., Via F. Maritano 26, I-20097 San Donato Milanese (MI), Italy

Received 16 March 2001; received in revised form 11 June 2001; accepted 22 June 2001

Abstract

The reaction of *ortho*-, *meta*- and *para*-dimethoxybenzene with linear acyl chlorides under acid zeolite catalysis was examined. Zeolites HY with different SiO₂/Al₂O₃ molar ratio (6, 14 and 390, respectively) were tested and their activity correlated with the acid site distribution (density, nature). It has been postulated that their catalytic performances could be explained in terms of a delicate balance between Brønsted and Lewis acid sites.

The chain length of the acyl chloride seems also to play an important role in enhancing the process efficiency. The ketone yield initially increases by increasing the carbon atom number of the chain (from C₂ to C₄) and subsequently falls down (from C₆ to C₁₀) probably due to the increase of the bulkiness of the reactive system.

To confirm the crucial role of the pore dimension of the catalyst even in the liquid-phase system, zeolite HZSM-5, with smaller pore diameter than that of HY (5.1 Å × 5.6 Å versus 7.4 Å × 7.4 Å), was applied in the same reaction, resulting inactive. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: HY zeolites; Acylation reactions; Aromatic ketones; Surface acidity

1. Introduction

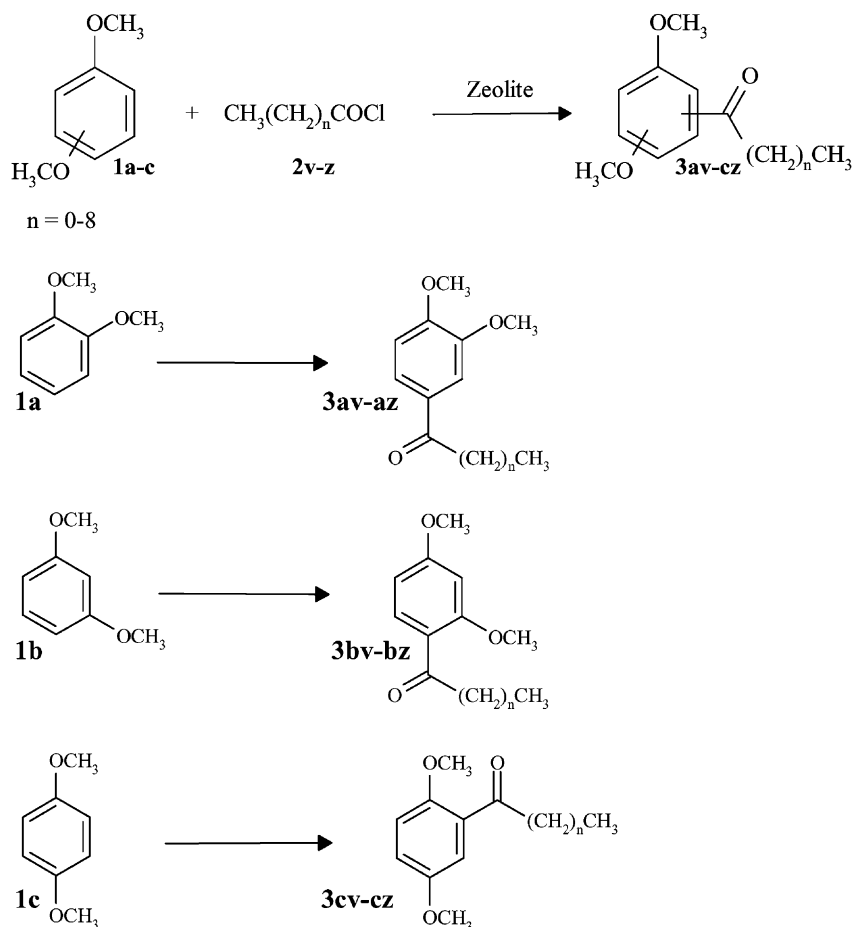
The development of methodologies for the functionalisation of aromatics under heterogeneous catalysis continues to be an important goal in industrial organic chemistry [1,2]. Since decades, the alkylation of aromatic substrates and isomerisation of alkylarenes under solid acid catalysis has been extensively studied by different academic and industrial groups and it is now recognised as a useful methodology for many refining and basic fine chemicals processes

[3,4]. More recently, various heterogeneous catalysts were efficiently utilised in the analogous aromatic electrophilic acylation. The use of highly acid Ce–Y zeolite was early reported for production of aromatic ketones from arenes and carboxylic acids by Geneste and co-workers [5]. Acylation of aromatic and heteroaromatic compounds with carboxylic acids, anhydrides and chlorides over Y and Y-modified zeolites was further reported [6–12]. Particular attention was paid to the acylation of alkyl–aryl ethers due to the great interest of the corresponding ketones which represent important intermediates in the production of fine chemicals and pharmaceuticals [13–15]. Beta zeolite was applied in this reaction [16–21].

* Corresponding author. Tel.: +39-0521-905551;

fax: +39-0521-905472.

E-mail address: sartori@unipr.it (G. Sartori).



Scheme 1. Reaction scheme and products.

However, further studies are needed to clarify the characteristic feature of the zeolite-promoted electrophilic aromatic acylation. In this work, the study is reported on the reaction of dimethoxybenzenes (**1a–c**) with linear chain carboxylic acid chlorides (**2v–z**) (see Scheme 1), in the presence of acid zeolites. Three differently dealuminated HY zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 6, 14 and 390) and one HZSM-5 zeolite are applied with the aim to clarify the effects of steric bulkiness of reactants and zeolite pores dimension on the reactivity. A correlation between the surface acidity of the catalysts and the yield of the acylation process is proposed.

2. Experimental

2.1. Reagents and catalysts

All organic reagents (1,2-, 1,3- and 1,4-dimethoxybenzenes, acetyl chloride, butanoyl chloride, hexanoyl chloride, octanoyl chloride, decanoyl chloride) were commercial products (Aldrich, Fluka). Acid chlorides were distilled under nitrogen before use. The products were separated by flash column chromatography (Merck silica gel 60, 70–230 mesh) using appropriate hexane–ethyl acetate mixtures as eluant.

HY zeolites (HFAU-6, HFAU-14 and HFAU-390) were purchased by Tosoh Corp.; zeolite HZSM-5 was

purchased by Zeolyst International. Before reaction, the zeolites were activated by heating at 500 °C for 5 h in N₂ flow.

2.2. Catalyst characterisations

The surface area was measured by BET method [22]. The surface areas of HFAU-6, HFAU-14 and HFAU-390 zeolites were of 460, 500 and 590 m²/g, respectively.

Particles of HY zeolites HFAU-6 and HFAU-14 were arranged in clusters with variable diameters. High magnification SEM investigations revealed that the clusters had a fine structure made of prismatic crystals with the same morphology and dimension ($\leq 0.5 \mu\text{m}$). This allow to exclude the influence of internal diffusion on relative reactivity.

The total surface acidity of the catalysts was measured by NH₃ TPD (temperature programmed desorption) [23]. After adsorption of NH₃ at 25 °C, the desorption (heating rate 2 °C/min up to 600 °C, He flow 50 ml/min) was performed trapping the ammonia with a 0.1 N HCl aqueous solution; the total amount of adsorbed ammonia was determined by titration of the residual acid. The experimental error is ca. 10%.

The acid sites distribution was determined by pyridine adsorption–desorption method, monitored by FT-IR spectroscopy [24]. A thin wafer of pure powder (around 5–10 mg cm⁻² thickness) was pre-treated at 500 °C for 1 h under dynamic vacuum (residual pressure lower than 2×10^{-3} mbar) in the optical cell. Then it was contacted with 10 mbar of pyridine at 200 °C for 1 h and evacuated at increasing temperatures (from 200 to 500 °C) for 1 h under dynamic vacuum. After each treatment, an IR spectrum was recorded at 21 °C with a mod. 2000 (Perkin-Elmer), taken a resolution of 1 cm⁻¹. The density of acid sites was evaluated from the peak area of the IR signals at 1455 (co-ordinately bonded pyridine to Lewis sites) and 1545 cm⁻¹ (pyridinium ion after reaction with Brønsted sites), taken the extinction coefficients as reported in [25]. The error in peak area determination was around 10%. The acid strength of one site is defined as the capacity of that site to retain the probe (pyridine) during the evacuation procedure: the higher the temperature necessary to desorb the probe, the higher is the acid strength of the site. In this way, the

weak acid sites are those able to retain pyridine after evacuation at 200 °C and that desorb it after treatment at 300 °C; the sites with medium acid strength retain pyridine up to 300 °C and desorb it during evacuation at 400 °C; the sites with medium–strong acid strength retain pyridine up to 400 °C and desorb it during evacuation at 500 °C; the strong acid sites retain pyridine beyond evacuation at 500 °C.

2.3. Reaction procedure

All reactions were carried out in a glass flask equipped with a magnetic stirrer, a thermometer and a condenser. In a typical experiment, the catalyst (1.0 g) was stirred with the aromatic substrate (0.05 mol) and the acyl chloride (0.01 mol) without solvent at 65 °C for 1 h under dry N₂ atmosphere. The mixture was then cooled to 25 °C, methylene chloride (50 ml) was added and the slurry was filtered on Büchner funnel, the catalyst was washed with additional methylene chloride (5 × 10 ml). The reaction mixture was analysed by GC in a capillary column (methyl silicone gum, 25 m × 0.2 mm × 0.33 μm film thickness). Conversion and yield were calculated as moles of ketone per mole of starting acyl chloride, using the internal standard method.

3. Results and discussion

In a first series of experiments, the model electrophilic acylation of 1,2-, 1,3- and 1,4-dimethoxybenzenes (**1a–c**) with the linear acyl chlorides (**2v–z**) containing an increasing number of carbon atoms (see Scheme 1) was studied in the presence of HY zeolite HFAU-14. The reaction was carried out in batch conditions at 65 °C for 1 h without solvent to avoid competitive adsorption and interaction of solvent molecules with the active sites of the catalyst. Reagents and products are shown in Scheme 1. The aromatic compounds show the molecular diameter (at the level of the ring plane) increasing from $6.13 \pm 0.02 \text{ \AA}$ for 1,4-dimethoxybenzene to $6.96 \pm 0.02 \text{ \AA}$ for 1,2-dimethoxybenzene to $7.53 \pm 0.02 \text{ \AA}$ for 1,3-dimethoxybenzene. The acyl chlorides present the common diameter of 2.39 \AA and the length increasing from 6.17 \AA with the length of the carbon chain.

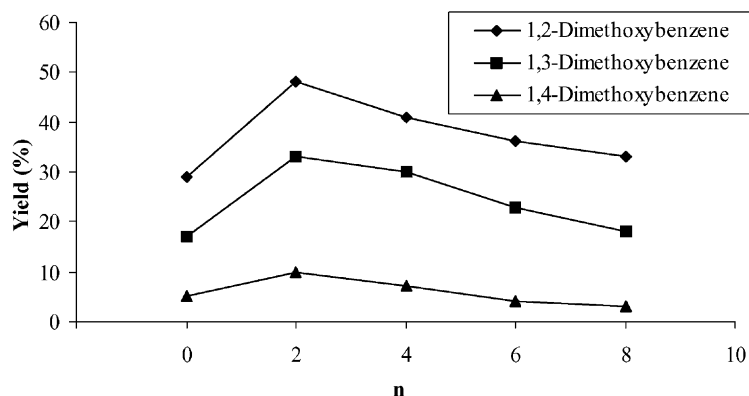


Fig. 1. Yield as a function of chain length (n -value) of the dimethoxybenzenes in the presence of HY zeolite HFAU-14.

The system was highly selective towards the product of monoacylation. By contrast with the homogeneous catalysed reaction, any demethylation at the methoxy group *ortho* to the carbonyl moiety was not observed [26–28]. Only traces (<2%) of hydrolysis of the acyl chloride utilised were present.¹

The dependence of the reactivity upon the arrangement of the two methoxy groups on the aromatic ring is depicted in Fig. 1. Hydroquinone dimethyl ether (**1c**) yields a low amount of the corresponding ketones, while 1,2-dimethoxybenzene (**1a**) is the most reactive substrate. The products are less sterically hindered with the latter reactant than with the other two isomers, where both positions *ortho* to the carbonyl group are free. In addition, if we consider that the aromatic substrate must approach the catalyst surface-acyl chloride complex, it is clear that compound **1a** is the more facilitated bearing the two methoxy groups far off its reactive site. From these evidences, it is possible to deduce that the reaction mainly occurs in the pores of the catalyst.

The carbon chain length of the acyl chloride (n -value) is also significant in determining the reactivity (Fig. 1). Indeed, a marked enhancement in the ketone yield is noted for *ortho*- and *meta*-dimethoxybenzene with increasing the number of carbon atoms of the acyl chloride from 2 to 4. For

longer acyl chlorides, the yield drops off sharply. A similar trend with maximum yield for C₁₂–C₂₀ acid was early observed in the acylation of *para*-xylene with carboxylic acids over Ce–NaY zeolite [5].

The higher activity with acyl chloride chain length increasing from two to four carbon atoms could be related to the favoured interaction of the relatively more lipophilic reagent **2** with the cavities of the HY zeolite, considered hydrophobic [29].² As the chain became bulkier, the difficult release of the products could explain the gradual lowering of the activity.

In a second series of experiments, the influence of the catalyst physico-chemical parameters was examined. Three HY zeolites with different SiO₂/Al₂O₃ molar ratio (HFAU-6, HFAU-14 and HFAU-390) were tested in the reaction between *ortho*-dimethoxybenzene and the series of acyl chlorides (**2v–z**). The best results were obtained with zeolite HFAU-14 (Fig. 2).

As the main physical difference among these samples is the SiO₂/Al₂O₃ molar ratio and consequently the acidity, the evaluation of the acid sites distribution becomes important. The overall surface acidity was determined by TPD of ammonia, the most used method for characterising acidity in solid catalysts. The higher SiO₂/Al₂O₃ molar ratio, the lower was the acid sites density. The highest acid sites density was observed in zeolite HFAU-6 (1.39 mmol/g), an inter-

¹ In a comparison experiment, all the acyl chlorides (**2v–z**) were treated with zeolite HFAU-14 under similar conditions giving only traces (~2%) of the corresponding acid suggesting that under the present conditions, all acyl chlorides are not noticeably hydrolysed.

² It has been demonstrated that the cyclohexane sorption capacity of different zeolites raises the maximum value when the SiO₂/Al₂O₃ molar ratio is ~15.

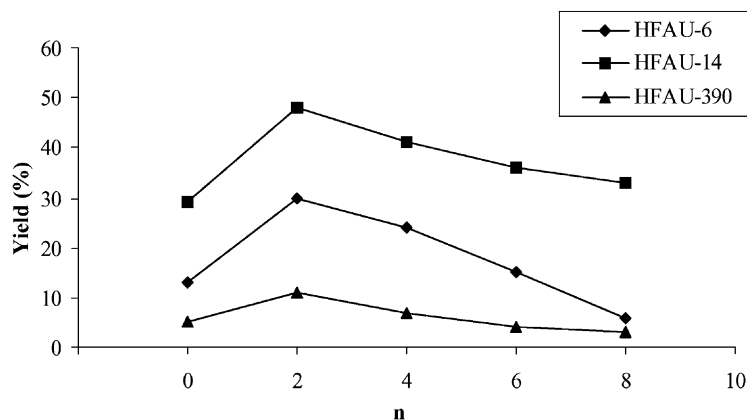


Fig. 2. Yield as a function of chain length (n -value) of *ortho*-dimethoxybenzene in the presence of the HY zeolites (HFAU-6, HFAU-14 and HFAU-390).

mediate acidity was found in HFAU-14 (0.51 mmol/g), whereas in HFAU-390 the acid sites drastically decreased (0.10 mmol/g). The comparison between reactivity and overall surface acidity shows that the more acidic HY zeolite HFAU-6 proved to be less active than the HY zeolite HFAU-14 characterised by a lower acidity. Finally, the too high $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio resulted in the marked decrease in both the activity and acidity.

However, to get more detailed information on the acid sites distribution, the pyridine adsorption–desorption method was applied. It is important to note that although pyridine is not small enough to enter the cages of HY zeolite, its molecular diameter ($d = 5.8 \text{ \AA}$) is comparable or lower than that of the reactants. Also this determination confirms the increase of the acid site density in agreement with the content of Al in the HY zeolites (Table 1). The sample HFAU-6 shows a large amount of acid sites both of Lewis and Brønsted type and a wide range of acid strength from

weak to strong. By contrast in the HFAU-390 sample only few weak Lewis acid sites are detected by pyridine. An intermediate behaviour is observed with HFAU-14: the acid density is lower than in HFAU-6, with a comparable wide range of acid strength from weak to strong, but with a large number of Lewis acid sites with respect to the Brønsted ones.

Beside the acidity, also the hydroxyl distribution may vary with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of zeolites. The IR spectra of the $3800\text{--}3200 \text{ cm}^{-1}$ region (Fig. 3) clearly show differences in the OH groups of these zeolites related to their Al content. IR signals are detected at 3736 cm^{-1} assigned in literature [30] to terminal silanols, at 3600 cm^{-1} assigned to some structural defects, at 3625 cm^{-1} attributed to AlOH groups located inside the supercage, at 3561 cm^{-1} observed for bridged hydroxyls located in small cavities. The last two signals are related to the presence of Brønsted acid sites and more intensive in HFAU-6 sample, in agreement with the above results of the acidity.

Table 1
Acid sites density (mmol/g) determined by FT-IR spectroscopy of absorbed pyridine

Acid strength	HFAU-6		HFAU-14		HFAU-390	
	Lewis	Brønsted	Lewis	Brønsted	Lewis	Brønsted
Weak	50	112	25	10	50	0
Medium	22	144	17	11	–	–
Medium–strong	30	102	7	14	–	–
Strong	46	22	8	4	–	–

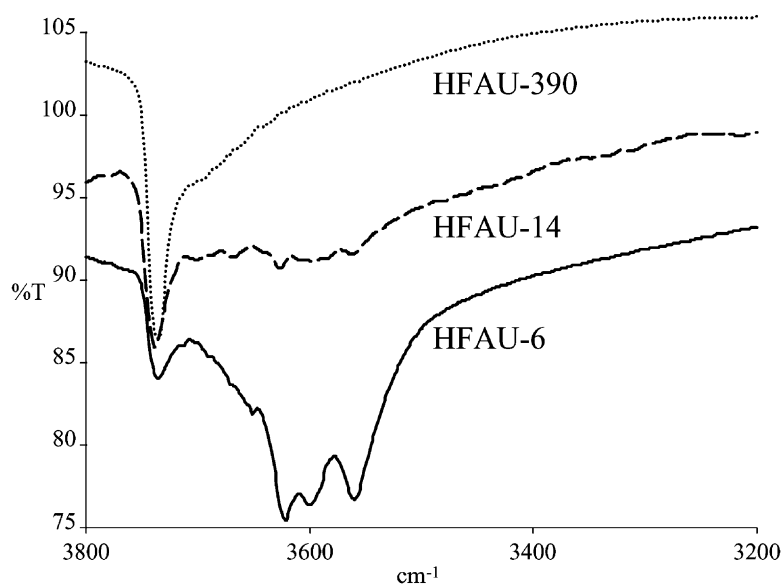


Fig. 3. IR spectra in the 3800–3200 cm^{-1} region of the HY zeolites (HFAU-6, HFAU-14 and HFAU-390).

As the direct correlation between catalytic acidity and framework composition was already observed and discussed [31], in this reaction the nature of the acid sites results to be more important in the reactivity than their amount. In particular, the HY zeolite (HFAU-14) with high Lewis/Brønsted ratio in the range of medium–high strength seems to be active in the reaction between *ortho*-dimethoxybenzene and acyl chlorides (2v–z). In the more acidic zeolite HFAU-6, the competitive interaction of the strong Brønsted acid surface of the catalyst (hydrophilic character) with the lone electron pairs of the methoxy groups could reduce the electrophilic reactivity of the aromatic ring as early observed by Rapoport and co-worker in the acylation of alkyl–aryl ethers promoted by Lewis acids [32].

Despite the different reactivity observed in the reactions promoted by the three HY zeolites, the shapes of the three diagrams are quite similar (Fig. 2). In all cases, butanoyl chloride shows the maximum of activity, the two minima corresponding to acetyl and decanoyl chlorides. The influence of the nature of the HY zeolite concerns the second part of the diagram, which slope decreases in the order: HFAU-390 < HFAU-14 < HFAU-6. The different reactivity depends on the different hydrophobic nature and acidity,

as the similar trend could be related to the shape and dimension of the zeolitic channels.

To confirm the crucial role of the pore dimension of the catalyst even in the present liquid-phase system, the model reaction between 1,2-dimethoxybenzene and butanoyl chloride was performed in the presence of HZSM-5 and HY zeolites. The HZSM-5 zeolite was chosen with similar surface acidity (0.57 and 0.51 mmol/g, respectively), but different pore dimension (bi-dimensional channels of $5.1 \text{ \AA} \times 5.5 \text{ \AA}$ and $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ with respect to mono-dimensional channels of $7.4 \text{ \AA} \times 7.4 \text{ \AA}$) than HFAU-14 sample. HZSM-5 yielded only 2% of the corresponding ketone, as HY zeolite HFAU-14 gave the yield of 48%. The very low activity of HZSM-5 zeolite is caused by the large dimension of both the aromatic substrate and ketonic products, that cannot enter in its pores. The formation of traces of product can be attributed to the reaction promoted by the external surface of the catalyst [33]. On the other hand, the difference in surface area (500 and 425 m^2/g for HFAU-14 and HZSM-5, respectively) cannot explain the highly different reactivity.

The reaction of butanoyl chloride with 2,6-ditert-butylanisole in the presence of HY zeolite HFAU-14 gave another confirm that the reaction happens in the

pores of the zeolite. No traces of the ketonic product were observed, because the aromatic substrate (kinetic diameter: 7.5 Å) can enter the pore of the catalyst but its ketone eventually formed (kinetic diameter: 8.9 Å) cannot exit from the zeolitic channels.

4. Conclusions

The catalytic properties of different HY zeolites in the electrophilic acylation of isomeric dimethoxybenzenes with acyl chlorides were studied as a function of both their physical characteristics (surface acidity, hydrophobic nature) and the dimension and lipophilic nature of reactants. The results of the catalytic tests confirm that the best catalyst for this system is HY zeolite HFAU-14, characterised by an optimum ratio between Lewis and Brønsted acid sites, whereas stronger or weaker acidic materials (HFAU-6 and HFAU-390) gave lower yields. These evidences suggest that this reaction requires both a delicate balance between Lewis and Brønsted acid sites and a low density of hydrophilic hydroxyl groups, that interact strongly with the methoxy groups in the reactants. This strong interaction gives rise before to poisoning of the active sites and subsequently to deactivation of the zeolitic channels by pore blockage.

The chain length of the acyl chloride also plays an important role in the efficiency of the process. In fact the ketone yield initially increases by increasing the carbon atom number of the chain (from C₂ to C₄), due to the favoured interaction between the lipophilic reactant and the hydrophobic zeolite, and subsequently drops down (from C₆ to C₁₀), probably due to the increase of the bulkiness of the reactive system.

Finally, HZSM-5 zeolite with smaller pore dimension than HY gives rise to products only in traces (2%). This very partial activity can be attributed to the presence of few active sites on the external surface of the crystallites.

Acknowledgements

The authors are grateful to Prof. Avelino Corma (University of Valencia, Spain) for helpful suggestions and to Dr. Giancarlo Salviati (Istituto MASPEC, CNR, Parma) for the SEM investigation. Thanks are

due to the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Italy, the Consiglio Nazionale delle Ricerche (CNR), Italy and the University of Parma (National Project "Processi Puliti per la Chimica Fine") for financial support.

References

- [1] A. Corma, Chem. Rev. 95 (1995) 559.
- [2] E.G. Derouane, J. Mol. Catal. A 134 (1998) 29.
- [3] E. Armengol, A. Corma, H. García, J. Primo, Appl. Catal. A 149 (1997) 411.
- [4] J.A. Martens, W. Souverijns, P.A. Jacobs, in: J.L. Atwood (Ed.), Comprehensive Supramolecular Chemistry, Vol. 7, Pergamon Press, Oxford, 1996, pp. 621–645.
- [5] B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Graille, D. Pioch, J. Org. Chem. 51 (1986) 2128.
- [6] A. Corma, M.J. Climent, M. García, J. Primo, Appl. Catal. 49 (1989) 109.
- [7] F. Richard, H. Carreyre, G. Pérot, J. Mol. Catal. A 103 (1995) 51.
- [8] R. Fang, G. Harvey, H.W. Kouwenhoven, R. Prins, Appl. Catal. A 130 (1995) 67.
- [9] F. Richard, H. Carreyre, G. Pérot, J. Catal. 159 (1996) 427.
- [10] A.P. Singh, D. Bhattacharya, S. Sharma, J. Mol. Catal. A 102 (1995) 139.
- [11] D. Barthomeuf, Catal. Rev. (1996) 521.
- [12] C. De Castro, J. Primo, A. Corma, J. Mol. Catal. A 134 (1998) 215.
- [13] K. Arata, M. Hino, Appl. Catal. 59 (1990) 197.
- [14] V. Quaschnig, J. Deutsch, P. Druska, H.-J. Niclas, E. Kemnitz, J. Catal. 177 (1998) 164.
- [15] K. Arata, H. Nakamura, M. Shouji, Appl. Catal. A 197 (2000) 213.
- [16] K. Smith, Z. Zhenhua, P.K.G. Hodgson, J. Mol. Catal. A 134 (1998) 121.
- [17] D. Rohan, C. Canaff, E. Fromentin, M. Guisnet, J. Catal. 177 (1998) 296.
- [18] E.G. Derouane, C.J. Dillon, D. Bethell, S.B. Derouane-Abd Hamid, J. Catal. 187 (1999) 209.
- [19] P. Moreau, A. Finiels, P. Meric, J. Mol. Catal. A 154 (2000) 185.
- [20] M. Casagrande, L. Storaro, M. Lenarda, R. Ganzerla, Appl. Catal. A 201 (2000) 263.
- [21] E. Fromentin, J.-M. Coustard, M. Guisnet, J. Mol. Catal. A 159 (2000) 377.
- [22] S. Brunauer, P.G. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
- [23] P. Berteau, B. Delmon, Catal. Today 5 (1989) 121.
- [24] C. Flego, I. Kiricsi, C. Perego, G. Bellussi, Catal. Lett. 35 (1995) 125.
- [25] J. Take, T. Yamaguchi, K. Miyamoto, H. Ohyama, M. Misono, Stud. Surf. Sci. Catal. 28 (1986) 495.
- [26] I.M. Hunsberger, H.S. Gutowsky, W. Powell, L. Morin, V. Bandurco, J. Am. Chem. Soc. 80 (1958) 3294.

- [27] R.B. Girdler, P.H. Gore, J.A. Hoskins, *J. Chem. Soc. (Sect. B)* (1966) 181.
- [28] M.H. Palmer, G.J. McVie, *J. Chem. Soc. (Sect. C)* (1968) 742.
- [29] N.Y. Chen, *J. Phys. Chem.* 80 (1976) 60.
- [30] J.W. Ward, *J. Catal.* 9 (1967) 225.
- [31] R.A. Beyerlein, G.B. McVicker, L.N. Yacullo, J.J. Ziemiak, *J. Phys. Chem.* 92 (1988) 1967.
- [32] T.F. Buckley III, H. Rapoport, *J. Am. Chem. Soc.* 102 (1980) 3056.
- [33] E.G. Derouane, J.-M. Andre, A.A. Lucas, *J. Catal.* 110 (1988) 58.