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Isomerisation of styrene oxide to phenylacetaldehyde by fluorinated mordenites using microwaves

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Abstract

In this paper, we studied the acidity of several mordenite samples, which were modified to have 1% (HM1F) and 10% (HM10F) in fluorine w/w, through their catalytic behaviour in the isomerisation of styrene oxide to phenylacetaldehyde in liquid phase. The catalytic experiments were performed by using microwaves as a new method and with a conventional heated batch reactor for comparison. We detect new stronger acid sites for sample HM1F by using NH_3 TPD and FTIR techniques, whereas for sample HM10F some dealumination, and therefore, loss of Brönsted acidity was observed by ^{29}Si, ^{27}Al NMR and X-ray fluorescence. Catalyst HMF1 is the most active at batch reaction conditions, but undergoes faster deactivation when using microwaves. Fluorination in low amounts gives to accessible stronger Brönsted acid sites due to the fluorine located in the external structure framework. This explains the higher activity in the batch reactor and the acceleration of condensation and coke products formation in microwaves experiments. When methanol is used as a solvent, the epoxide ring of styrene oxide opens catalysed by Lewis and Brönsted acid sites. In this case, the existence of high amounts of Lewis acid sites for sample HM10F explains its highest activity.

Keywords: Styrene oxide isomerisation; Mordenite; Fluorination; Acidity

1. Introduction

The isomerisation of styrene oxide to β-phenylacetaldehyde is used at industrial scale in fine chemistry for the production of fragrances (which give a narcissus-like smell in floral perfumes), pharmaceuticals, insecticides, fungicides and herbicides [1].

Epoxide reactivity has been widely studied, because of its versatility as intermediate in organic chemistry [2,3]. In the isomerisation reaction, the use of conventional catalysts often results in the formation of a mixture of ketones and aldehydes, and also by-products such as aldol condensation products, diols and dioethers. The high-weight molecules formed by aldol condensation are the first step in the formation of 1,3,5-triphenylbenzene and coke, which are responsible for the fast deactivation of the catalysts, limiting their lifetime [1].

The rearrangement of different styrene oxides has been studied under gas and liquid conditions using several solid catalysts [4,5]. The main products of the styrene oxide isomerisation are the corresponding aldehyde and ketone depending on the properties of the catalyst [6]. This reaction can be catalysed by Brönsted acids (addition of a proton to the epoxide oxygen), by Lewis acids (coordination of the epoxide oxygen to a multivalent cation) as well as by bases [7], although the first are the most active [1]. On the whole, by increasing acidity, the transformation of

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these oxides increases, and the formation of the aldehyde is favoured [8].

Recently, the use of zeolites as catalysts for this reaction is of increasing interest because of their capacity to suppress the formation of by-products by stabilising the α-carbocation intermedium, and by their shape selectivity which favours the selectivity to the aldehyde [9]. Zeolites show good acidic properties for their use as catalysts in isomerisation reactions. The synthesis of zeolites with very strong acid sites is one of the goals of catalysis at the moment [10].

Mordenite is one of the zeolites catalogued as a strong acid zeolite [11]. Several studies, found in the literature, show the FTIR technique, among others, as an interesting tool for the study of the acidity of zeolites. Few of these studies made with mordenite report the existence of several types of Brönsted acid sites with different acidity strength located on different positions of its structure [12,13].

The modification of zeolites and clay-type structures with fluorine as a way to modify their acidic properties has been intended by different authors [14–18]. Several authors reported changes in the structure of mordenite after activation under mild conditions (treatment with KF or NH_4F), or using more aggressive conditions like treatment with HF or F_2. The use of these fluorinated mordenites changes the catalytic activity as observed in some reactions catalysed by acids, such as cumene cracking or transformation of alkylaromatics [14,16]. However, it has not been clearly demonstrated if these fluorine atoms are located in the framework or in the extraframework structure, generating Brönsted or Lewis acid sites, respectively [16,18,19].

This work aims to study the acidity of different mordenite-type samples, which were modified by fluorination treatment under mild conditions, by testing them in the acidic catalysed transformation of styrene oxide to phenylacetaldehyde. Additionally, we also propose the use of microwaves as a new method to perform the catalytic experiments. The use of microwaves has been reported from 90s applied to the synthesis of materials [20–22] and also to several catalytic reactions such as Diels–Alder cycloadditions [23], oxidations [24,25], etc. The main advantages of using this technology are the faster preparation rate and the high yields and purity of the obtained products.

2. Experimental

2.1. Starting materials

The starting material was a commercial Na-Mordenite (Si/Al = 6.5, CBV 10A Lot No. 1822-50), designated as NaM, which was supplied by Zeolist as hydrated powder with a SiO_2/Al_2O_3 mole ratio of 13 and a Na_2O wt% of 6.6. Ammonium chloride (NH_4Cl, 99% minimum, Prolabo) and ammonium fluoride (NH_4F, high purity, Probus) were used for samples preparation.

Styrene oxide (C_8H_8O, 97% minimum, Aldrich) and phenylacetaldehyde (C_8H_8O, 90% minimum, Aldrich) were used as reactants, whereas hexane (C_6H_{14}, 95% minimum, SDS) and methanol (CH_3OH, 99.5%, Prolabo) were used as solvents in the catalytic experiments.

2.2. Catalyst preparation

Commercial mordenite (NaM) was modified to its acidic form (HM) by complete cation exchange with a NH_4Cl 2.2 M solution and later calcination at 673 K for 12 h. Afterwards, HM was treated with different amounts of NH_4F in order to obtain 1% (HM1F) or 10% (HM10F) w/w of fluorine with respect to the amount of zeolite used. After fluorine treatment, samples were calcined again at 673 K for 12 h. Samples were kept all the time in a dissecator in dry conditions.

2.3. Characterisation techniques

^{27}Al and ^{29}Si MAS-NM, NH_3 TPD, FTIR spectroscopy and X-ray fluorescence techniques were used in order to determine the location and the effect of fluorine for the modified samples.

TPD experiments were carried out on a TPD/R/O 1100 Thermo Finnigan equipment equipped with a temperature programmable oven and with a TCD and a PFEIFFER GSD 301 02 Mass Spectrometry detector. For the pre-treatment, samples were activated in situ by flowing Ar at 20 cm^3/min between room temperature until 673 K at 10 K/min. Afterwards, ammonia 3%/He was adsorbed at 313 K and desorbed by flowing He 20 cm^3/min from 373 K to 873 K at 5 K/min. The desorbed ammonia was detected using both detectors.

^{27}Al and ^{29}Si, MAS NMR spectra were obtained at a frequency of 400 MHz by spinning at 5 kHz. The pulse duration was 2 µs and the delay time was 5 s. The chemical shift references for aluminum and silicon were high purity octahedral hexahydrated aluminum chloride $AlCl_3 \times 6H_2O$ and silicon nitride Si_3N_4, respectively.

Infrared spectra were recorded using a Nicolet Magna 750 Fourier Transform instrument in the frequency range of 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1}. Acetonitrile was used to characterise the different samples. Pressed disks of pure zeolite powders were activated in situ in the IR cell by outgassing at 773 K before the adsorption experiments. A conventional gas manipulation/outgassing ramp connected to the IR cell was used.

The acetonitrile adsorption/desorption process has been studied by transmission FT-IR. The adsorption procedure involves contact of the activated sample disk with vapors at room temperature at a pressure not higher than 2.5 kPa. The desorption process at increasing temperatures was performed in vacuum at temperatures compressed in the range 298 to 573 K.

X-ray fluorescence was used to determine the atomic distribution maps and the Si/Al ratio of the fluorinated and non-fluorinated samples. Experiments were performed on a scanning electron microscope, JEOL JSM6400, operating at accelerating voltage of 15 kV and work distances of 15 mm. All samples were covered with a graphite layer. Accumulating time for mapping experiments was around 120 s.

2.4. Determination of the catalytic activity

Isomerisation reactions were carried out in liquid phase at atmospheric pressure using batch reactors by conventional heating and microwaves. The microwaves experiments were performed in a Milestone ETHOS-TOUCH CONTROL equipped with a temperature controller.

The catalysts were first activated at 673 K. The catalytic experiments were performed using 0.04 g of catalyst, 25 ml of solvent (n-hexane or methanol) and 0.3 ml of reactant (styrene oxide or phenylacetaldehyde). Solvents were dried with activated molecular sieves. In the case of n-hexane (95% purity), it was previously distilled with sodium.

The reaction products were analysed by GC on a Shimadzu GC-2010 instrument equipped with a 30 m capillary column RTX-5 coated with phenylmethylsilicon and a FID detector.

Conversion was defined by the following equations:

$$\Big[[\text{area PA}/\text{area SO}]_{\text{after reaction}} - [\text{area PA}/\text{area SO}]_{\text{before reaction}}\Big] \quad \mathrm{g}_{\text{cat}}^{-1}, \tag{1}$$

$$\Big[[\text{area MPE}/\text{area SO}]_{\text{after reaction}}\Big] \quad \mathrm{g}_{\text{cat}}^{-1}, \tag{2}$$

where PA denotes phenylacetaldehyde; SO, styrene oxide and MPE, 2-methoxy-2-phenylethanol.

For a more exhaustive characterisation of some reaction products, Mass spectrometry, ^{1}H and ^{13}C NMR have been used. Mass spectrometer results were obtained on a quadrupolar mass spectrometer Hewlett Packard 5989A equipped with a double injection font for electronic impact and chemical ionisation (EI/CI) and connected to a Gas chromatograph Hewlett Packard 5890. ^{1}H and ^{13}C NMR spectra were obtained on a Mercury 400 MHz equipment.

3. Results and discussion

3.1. Samples characterisation

Figs. 1 and 2 show the ^{27}Al and ^{29}Si MAS NMR spectra, respectively, for several samples. ^{27}Al NMR spectra of the starting mordenite (NaM or HM) and the low fluorinated mordenite (HM1F) reveal that the aluminium is mainly tetrahedrally coordinated since we only observe one peak at 50 ppm. However, for the highly fluorinated material (HM10F), besides this tetrahedral aluminium, a broad band around 0 ppm indicates the presence of some octahedral aluminum. Therefore, fluorination in mild conditions (using NH_4F) does not cause an appreciable dealumination of the structure when the amount of fluorine used is low (1% w/w). This has also been suggested by Kowalak et al. [16]. Otherwise, when the amount of fluorine is higher (10% w/w), part of the tetrahedral aluminium becomes octahedrally coordinated.

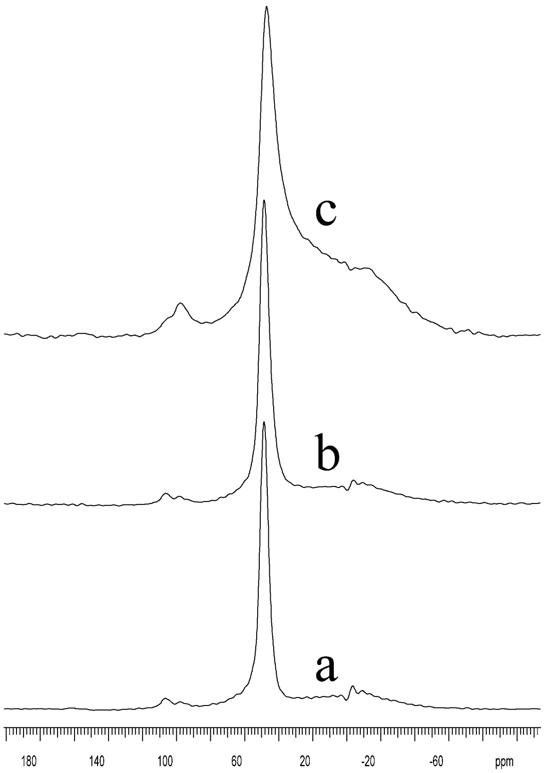

Fig. 1. ^{27}Al MAS NMR spectra for (a) NaM, (b) NaMF1, (c) NaMF10 samples.

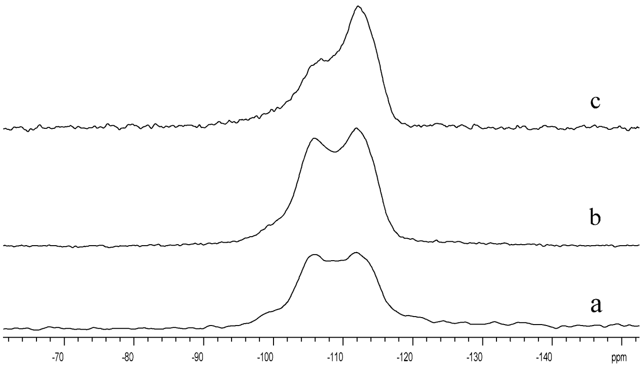

Fig. 2. ^{29}Si MAS NMR of (a) NaM, (b) NaM1F and (c) NaM10F.

From the ^{29}Si NMR results (Fig. 2), the non-fluorinated mordenites (NaM and HM) and the low fluorinated mordenite (HM1F) show three bands at −115 ppm, −105 ppm, and −100 ppm (less intense) which correspond to the Si coordinated to 0 Al, 1 Al and 2 Al, respectively. The band at −105 ppm has a slightly lower intensity for the HM1F sample, which indicates some dealumination not observed before by ^{27}Al NMR. For the HM10F sample three bands were also observed, but in that case, the band at −105 ppm tends to disappear, increasing the band at −115 ppm. From these

Table 1
NH_3 TPD results for all samples

Sample	NH_3 T_D (K)[a]	
NaM	475	–
HM	490	–
HM1F	513	770
HM10F	495	775

[a] T_D, maxima of NH_3 desorption temperature peaks.

results, we can suggest that the dealumination observed in this sample is mainly produced by the initial attack of fluorine to the SiO(H)Al groups of the mordenite on its acidic form (HM).

Table 1 shows the NH_3 TPD results obtained for all samples. Only one band was observed for NaM and HM samples at 475 K and 490 K, respectively. However, HM1F and HM10F show two bands with different relative intensities. Thus, for the HM1F sample, the first band at 513 K is much more intense than the second band at 770 K, whereas the sample HM10F shows two bands with similar intensity at 495 and 775 K, respectively. The bands in the range 465–515 K can be assigned to the initial SiO(H)Al groups while the bands in the range 770–775 K, only observed for the fluorinated samples, should be associated to the presence of some new Lewis acid sites, according to the other characterisation results reported in this paper.

Referring to the first band, the highest NH_3 desorption temperature observed for sample HM1F involves the existence of very strong acid sites for this sample. Meanwhile, the sample with higher amount of fluorine (HM10F) presents this band around the same temperature than the non-fluorinated acidic sample (HM). This could indicate that the stronger Brönsted acid sites observed for HM1F sample should be probably generated by the presence of fluorine atoms in the framework structure. The second desorption band has slightly higher desorption temperature and higher intensity for the most fluorinated sample. Therefore, HM10F presents higher amounts of Lewis sites than HM1F but with similar acidic strength.

In order to confirm this behaviour, the FTIR spectra of HM, HM1F and HM10F samples were also registered. Fig. 3 shows the FTIR spectra in the region compressed between 3900 and 3000 cm^{-1}. Spectra have been normalised to the weight of zeolite used for the spectra collection. The non-fluorinated sample (HM) shows two peaks with the main maxima at 3743 and 3609 cm^{-1}. The first corresponds to SiOH terminal groups, and the second to SiO(H)Al groups [26]. After fluorination, some changes are observed in the FTIR spectra of that region, especially regarding the band at 3609 cm^{-1} since the band at 3743 cm^{-1} almost does not change for both fluorinated samples. The band intensity of the bridging silanol groups decreases when increasing the amount of fluorine introduced, confirming the attack of fluorine ions on the starting mordenite structure. For HM10F, we observe the appearance of new bands, with absorption wavenumbers between 3650 and 3750 cm^{-1}. These bands correspond to some new species whose nature can be related to different extraframework aluminium formed as a consequence of the dealumination detected by ^{27}Al RMN for this sample. This agrees with the data found in the literature [16].

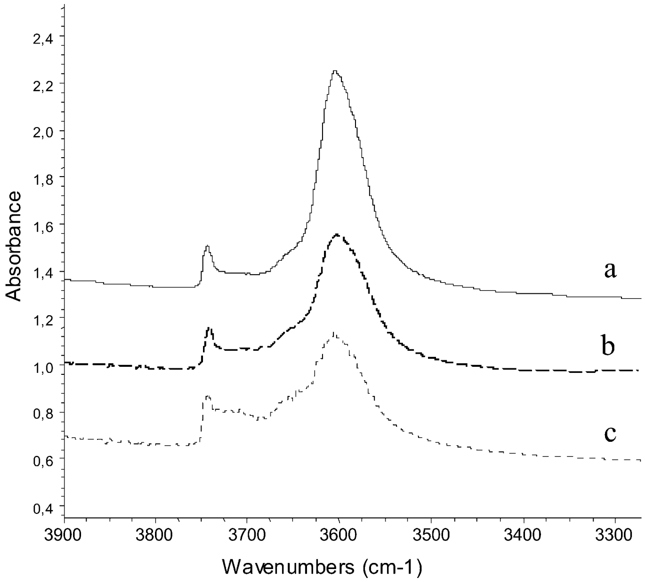

Fig. 3. FTIR spectra of (a) HM, (b) HM1F and (c) HM10F samples.

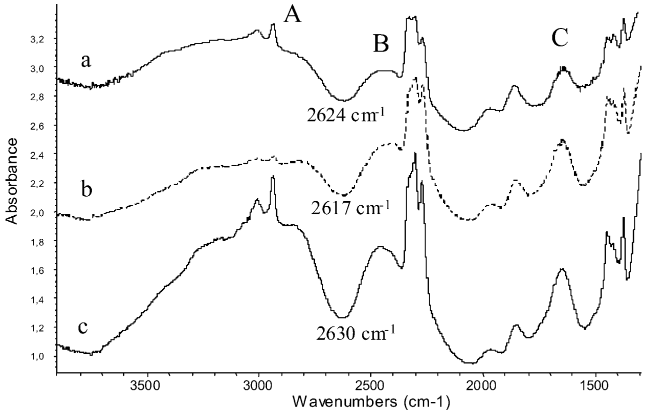

Fig. 4. FTIR spectra of acetonitrile interacting with HM (a), HM1F (b) and HM10F (c) at room temperature.

In order to evaluate the acidity of these bridged SiOHAl groups, the so-called *hydrogen-bond method* was used, in which the acid strength measure is based on the red shift that the OH stretching modes undergo as a result of interaction with bases, like acetonitrile.

The IR spectra taken for all acidic mordenite samples in the presence of acetonitrile at room temperature (shown in Fig. 4) agrees with the expected behaviour for acidic-mordenite-like samples [12]. The so-called A, B, C bands with maxima around 2800, 2450 and 1670 cm^{-1} are the result of the bridged OH groups interacting with acetonitrile molecules. Additionally, a component at 3400 cm^{-1} can also be observed corresponding to the result of silanol terminal groups interacting with acetonitrile. The OHs band shifts ob-

Table 2
IR frequencies of fluorinated mordenites and Si/Al ratio determined by X-ray fluorescence

Sample	IR frequencies (cm^{-1})		Si/Al ratio
	ν_{as}(T–O)	ν_s(T–O)	
HM	1064	630	7.0
HMF1	1065	629	7.4
HMF10	1072	637	8.2

served when interacting with acetonitrile with respect to the OHs bands observed on HMOR (3743 and 3609 cm^{-1}) confirm that bridging OHs groups are strong Brönsted acid sites, while terminal SiOH groups are weak Brönsted acid sites. The position of the minimum between A and B components corresponds to the first overtone of the in-plane bending band of the hydrogen-bonded OHs, and allows us to evaluate the strength of the interaction between the OH groups and acetonitrile. The strength of this interaction can easily be related to the strength acidity [13]. Thus, from Fig. 4 we observe that HM1F sample shows the frequency of that minimum at the lowest frequency ($\Delta\nu = 13$ cm^{-1} respect to HM sample), indicating the existence of the strongest Brönsted acid sites for this sample. However, HM10F sample shows this minimum also at lower frequencies than HM sample ($\Delta\nu = 6$ cm^{-1}), so the still remaining acidic groups after fluorination (Fig. 3) have slightly higher acidity than HM sample.

Moreover, the shift in the position for symmetric and asymmetric TO_4 tetrahedral bands in the mid-IR region (see Table 2), is almost the same for the non-fluorinated (HM) and the low fluorinated (HM1F) structures, but shifting towards higher frequencies for the highly fluorinated sample (HM10F). This confirms the dealumination of the structure.

Finally, to complete the characterisation of these samples, element map distributions (not shown here) of Si, Al and Na were also performed and Si/Al ratio was determined by X-ray fluorescence for the modified mordenites (Table 2). Si, Al and Na maps distribution exhibited a homogeneous atomic distribution in all cases. Quantification results, expressed as Si/total Al (framework + extraframework) ratio, show that there is an initial loss of aluminium during the fluorination treatment, which is higher when a higher amount of NH_4F is used, confirming what was observed by other techniques.

3.2. Catalytic results

Figs. 5 and 6 show the catalytic activity results in the isomerisation of styrene oxide, with hexane as a solvent, for the four samples using microwaves and conventional heating, respectively. Conversion results are expressed as commented in the Experimental.

From the results obtained by using microwaves at 353 K at different reaction times (Fig. 5), we observe a very low activity for the NaM sample in all cases. Modified mordenites present higher activity than the NaM sample, but

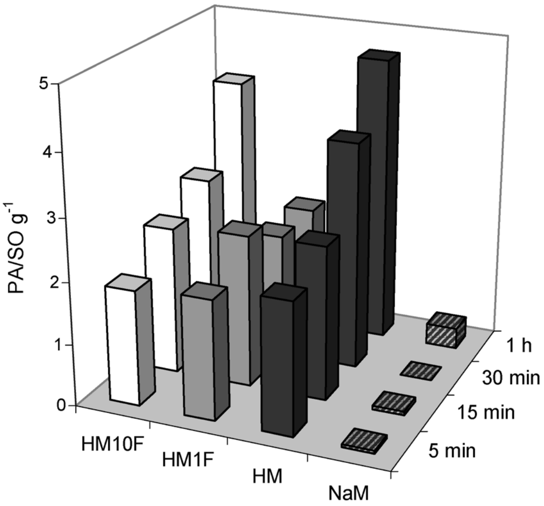

Fig. 5. Catalytic results in a microwave heated batch reactor at 353 K using hexane as a solvent.

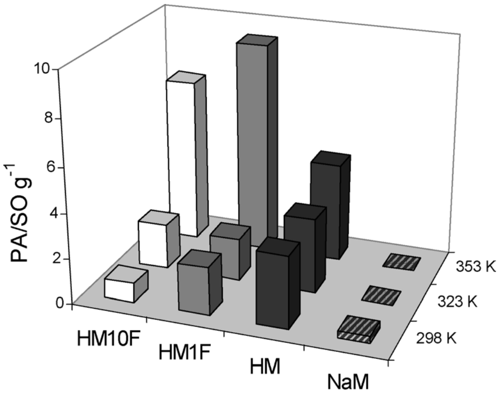

Fig. 6. Catalytic results in a conventional heated batch reactor at atmospheric pressure at different temperatures using hexane as a solvent.

their catalytic behaviour with time is different. Thus, HM and HM10F show a similar behaviour, which is an increase of the conversion as reaction time increases for all conditions tested, but sample HM10F has lower catalytic activity than sample HM, probably associated to the loss of some Brönsted acid sites in the fluorination process. This is in agreement with the characterisation results and with the fact that Lewis acid sites, present in higher amounts in sample HM10F, are less active for this isomerisation reaction [1]. Additionally, a slight deactivation of catalyst HM10F cannot be discarded, as we will see below for the HM1F sample, since HM10F contains also some strong acid sites, as observed by FTIR. Surprisingly, HM1F, for which larger conversions would be expected according to the presence of stronger Brönsted acid sites, shows a very different behaviour with an increase of the conversion at the beginning of reaction, which then decreases and remains practically constant after 30 min. For the modified mordenites (HM, HM1F, HM10F) a blackish colour was observed after reaction, which could be related to the formation of coke on the surface of the catalyst. We think that these facts could be ascribed to a typical behaviour of very strong acid catalysts: first, the formation of condensation products, which deposit on the catalytic surface and, consecutively, the coke formation is favoured provoking a fast deactivation of the catalyst [1]. Thus, the catalyst with the strongest Brönsted acid sites (HM1F) shows the fastest deactivation (Fig. 5).

Additional experiments were carried out in order to try to avoid the formation of deactivation products by varying the amount of catalyst in HM and HM1F samples, at 353 K for 1 h using $\frac{1}{4}$, $\frac{1}{2}$ and 2 times the catalyst amount tested in the previous catalytic experiments. Samples became also blackish after reaction. The results indicate that, for both catalysts, it was not possible to avoid the formation of condensation products by varying the catalyst amount. Although an increase on the activity was observed when using higher amounts of catalyst, also a few increase of deactivation was observed, especially for HM1F, which corroborates the stronger acidity observed for this catalyst.

In order to compare the influence of using microwaves in this reaction, catalytic experiments using batch reactors with conventional heating were also performed at different temperatures (298, 323 and 353 K) for 1 h. From the results shown in Fig. 6 we observe at 353 K an increase on the activity respect to the microwave conditions for all samples except for NaM, as expected, since this sample almost does not contain acidic groups which are necessary to catalyse this reaction, as commented above. Catalyst HM1F shows the best conversion, but now the catalytic activity of sample HM10F is higher than that of sample HM, contrarily to the results obtained with microwaves. This can be probably associated to the presence of strong acid sites in both fluorinated samples, which are present in lower amounts in sample HM10F. We can conclude that the use of microwaves accelerates the catalyst deactivation, especially for the fluorinated samples, although in less extension for sample HM10F. This confirms again that these samples contain very strong acid sites, which favour the formation of condensation products that impede the interaction of the styrene oxide molecules with the Brönsted acidic centres, deactivating the catalyst. When lower temperatures were used (298 and 323 K), lower activities were observed for the HM, HM1F and HM10F catalysts, meanwhile for NaM the activity was practically null.

In order to see the influence of the solvent in this catalytic reaction, a more polar solvent, methanol, was chosen since it has already been used for this reaction [27]. The experiments were performed using the microwaves at 333 K for 1 h. From the results shown in Fig. 7 some differences were observed. In this case, a new major product was obtained besides the aldehyde. This new product, identified by ^{1}H and ^{13}C NMR, corresponds to the formula 2-methoxy-2-phenylethanol (MPE) showing signals (400 MHz, CD_3OD) at 3.25 (s, 3H, OCH_3), 3.6 (m, 2H, CH_2OH), 4.20 (dd, 1H, Ar-CH), 4.91 (s, 1H, OH), 7.20 (m, 5H, Ar) for ^{1}H NMR, and (100.6 MHz, CD_3OD) at 57.24 (s, 1C, OCH_3), 67.82 (s, 1C, CH_2OH), 86.36 (s, 1C, Ar-CH), 129.10, 129.26, 129.58 and 140.32 (4s, 6C, Ar) for ^{13}C NMR. The identification of this product was also confirmed by mass spectrometry.

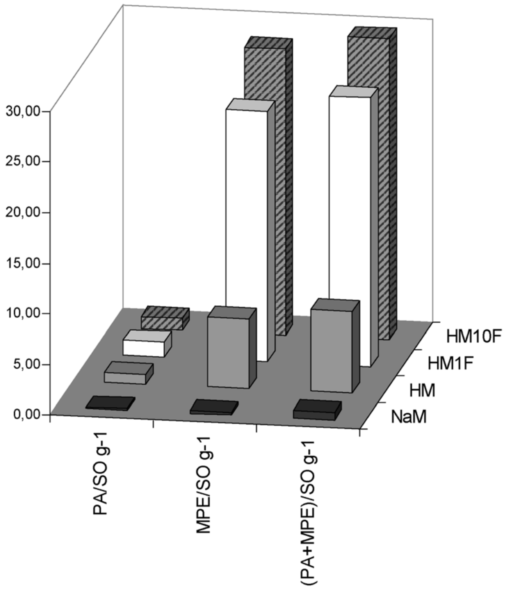

Fig. 7. Catalytic results in a microwave heated batch reactor at 333 K using methanol as a solvent.

In order to check the origin of that product, whether it comes from the reactant (styrene oxide) or the isomerisation product (phenylacetaldehyde), additional catalytic experiments were carried out using phenylacetaldehyde as the starting reactant but maintaining the same reaction conditions. The reaction products were also identified by GC, ^{1}H NMR, ^{13}C NMR, and Mass Spectrometry techniques. Phenylacetaldehyde dimethyl acetal was the main product, and also small amounts of condensation products were observable by ^{1}H and ^{13}C NMR techniques. This let us think that the formation of 2-methoxy-2-phenyletanol comes from the aperture of the oxide ring in styrene oxide and not from the aldehyde.

The catalytic activity, expressed as the sum of Eqs. (1) and (2) ($(\mathrm{PA} + \mathrm{MPE})/\mathrm{SO}\,\mathrm{g}^{-1}$), and the conversion to MPE ($\mathrm{MPE}/\mathrm{SO}\,\mathrm{g}^{-1}$) increase when the percentage of fluorine increases (Fig. 7). This indicates that the formation of 2-methoxy-2-phenylethanol is a reaction catalysed by both Brönsted and Lewis acid sites. However, the conversion to the isomerisation product ($\mathrm{PA}/\mathrm{SO}\ \mathrm{g}^{-1}$) follows the same tendency than that observed when hexane was used (Fig. 6), but in this case the conversions are lower because the opening of the oxide ring is the most favoured reaction.

4. Conclusions

The introduction of fluorine in the mordenite structure framework is found to have a remarkable effect on its acidic properties as demonstrated in this study. Introducing low amounts of fluorine, the Brönsted acidity of the catalyst increases as concluded from the catalyst characterisation and also from the comparison of the catalytic results obtained on the microwaves and batch reactors with conventional heating under the same reaction conditions. The results confirm that the use of microwaves accelerates the condensation and coke products formation, which are responsible for the catalyst deactivation. This makes evident the importance of using microwaves as a radiation font for catalytic reactions, especially those showing low yields and/or low reaction rates.

Besides this, fluorine must be mainly located on the more external structure positions, and therefore without the shape restriction expected for this zeolite. This explains the higher and faster catalyst deactivation observed in the microwave reactor when mordenite is modified using low amounts of NH_4F (HM1F catalyst). Consequently, only the more accessible positions are fluorinated and materials are easily deactivated during the styrene oxide isomerisation reaction.

Otherwise, when methanol is used as a solvent, the styrene oxide ring breaks to give 2-methoxy-2-phenylethanol. This reaction is favoured by the presence of Brönsted and Lewis acid sites, and the conversion increases as the % of fluorine introduced increases.

Acknowledgments

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