Catalysis Letters 53 (1998) 103–106

Preparation of HNaY zeolite by ion exchange under microwave treatment. A preliminary study

J.M. Lopes, F.N. Serralha, C. Costa, F. Lemos and F. Ramôa Ribeiro

Grupo de Zeólitos, Centro de Engenharia Biológica e Química, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

Received 24 March 1998; accepted 14 May 1998

Acidic samples of Y zeolite were prepared by ion exchange promoted using microwave irradiation. Interesting exchange levels were obtained with only a few minutes of irradiation. The catalytic properties of these samples were evaluated using the transformation of iso-octane; the observed conversions lie in the same range as those for the samples prepared by the conventional ion-exchange method of stirring the mixture of the sodium form with an ammonium salt solution for several hours; the deactivation with time-on-stream was significantly reduced for the catalysts prepared by the irradiation method in the cases of highest activity.

Keywords: ion exchange, microwave treatment, zeolites, Y zeolite, catalytic cracking

1. Introduction

The dielectric heating effect of microwave irradiation in a material is a consequence of the polarization of the charges which is induced in that material; the dipoles rotate to try to align themselves in phase with the oscillating electric field, but the inability of this polarization to follow the high frequencies of the field results in heating the system. The extent of the effect depends on the power of the field, strength of the dipole moment and its mobility.

The wide application of the microwave radiation interaction with materials was reviewed by Jacob et al. [1]. Despite the fact that the mechanism of interaction of microwave radiation with a material has not been completely understood, it is comprehensible that a microwave-treated material may present some different properties when compared to a conventionally heated one, as a consequence of an activation process by hot spots, molecular agitation and improved transport properties of molecules.

Zeolites have been the object of several studies in this field. The synthesis of zeolitic materials in a microwave environment has been successfully achieved in many cases, with shortened nucleation and crystal growth periods [2–7]. Interesting results were also obtained by microwave activation of zeolitic catalysts. Namely, it is thought that microwaves have a potential use in the preparation of highly dispersed metal salts in the channels or cages of zeolites [8,9].

In this work, the efficiency of the ion-exchange process, under microwave irradiation, has been tested with the NaY zeolite/ammonium salt solutions system. Some parameters, such as the salt solution concentration, duration and power of the irradiation, were changed. The catalytic properties of the acidic Y zeolite forms obtained were tested in the iso-octane transformation and were compared with those from acidic samples prepared by the conventional process of stirring of the mixture zeolite/salt solution using a conventional heat source.

2. Experimental

The sodium form of Y zeolite was obtained from Union Carbide. Each sample of NaY zeolite ($\approx$2.5 g) was then contacted with an ammonium nitrate solution, with concentrations 0.5, 1 and 2 M, and a (solution volume)/(mass of zeolite) ratio of 4, under microwave irradiation. The mixtures were introduced in closed vessels, with an optical fibre temperature sensor. The treatment was performed in a Milestone MLS-1200 MEGA microwave oven equipped with a temperature-monitoring system, operating at 2.45 GHz. The power of the microwave radiation was varied between 250 and 500 W and the duration of the treatment between 5 and 20 min. After the irradiation, the mixtures were rapidly cooled down, filtrated, and the resulting NH_4NaY samples were dried at 100 °C. The corresponding acidic samples were prepared by calcination at 480 °C during 8 h under a flow of dry air.

Another sample series was prepared by the traditional successive exchange treatments of the NaY zeolite with the same salt solution, 2 M concentration, stirring the mixtures for 5 h in each step, in reflux conditions. Samples were collected after 1, 2 and 5 steps. An extra exchange treatment was performed over the initial NaY form, at room temperature, with salt concentration of 0.45 M, in order to obtain a lower exchange level. The procedure to obtain the final acidic forms was the same.

All the samples were characterised by X-ray diffraction, in order to check for their macroscopic crystallinity, and by chemical analysis, for determination of the resulting exchange levels.

The catalytic properties were evaluated by the iso-octane cracking reaction, carried out in a flow reactor at 350 °C, total pressure 1 bar, nitrogen/hydrocarbon ratio of 9, reactant flow 3 ml/h, and 400 mg of catalyst.

3. Results and discussion

Figure 1 shows the temperatures measured inside the mixtures under irradiation as a function of the irradiation time for experiments at 250, 350 and 500 W. These temperatures are substantially higher than those obtained in reflux conditions and are achieved in only a few minutes.

Table 1 lists the exchange levels of the NH_4NaY samples (percentage of sodium removal) resulting from 5, 10 and 20 min of irradiation at 250 W. In the case of the salt concentration 0.5 M, the amount of the ammonium cations present in the solution was approximately 50% of the total cationic positions in the zeolite sample; its maximum exchange level was then achieved after 10 min. In the other cases, the increase of the irradiation time beyond 10 min did not improve the efficiency of the ion exchange.

The results obtained for the experiments performed at different irradiation power and fixed irradiation time (10 min) are collected in table 2. Irradiating at 350 and 500 W did not induce any improvement in the results relative to those obtained at 250 W, in spite of the higher temperatures that are achieved in these cases, which indicates that this sodium exchange is not strictly a temperature-dependent process.

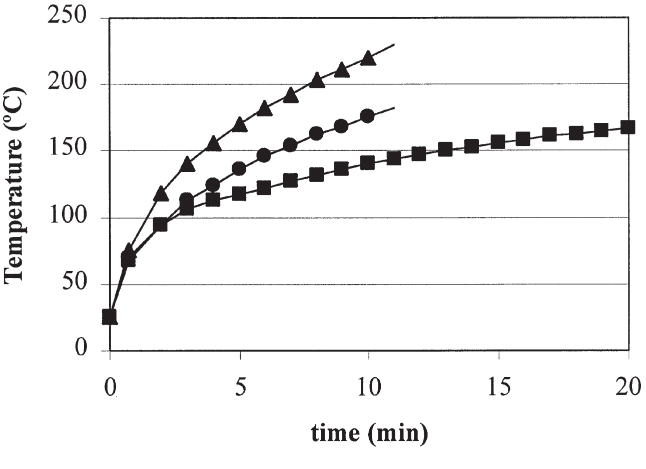

Figure 1. Bulk temperature, measured in the irradiated mixtures as a function of the irradiation time, at 250 W (■), 350 W (●) and 500 W (▲).

Table 1
Exchange levels (% of sodium removal) obtained in the NH_4NaY samples for different irradiation time at 250 W.

Salt conc. (M)	Time (min)		
	5	10	20
0.5	25	49	51
1	45	61	60
2	–	73	71

Table 2
Exchange levels (% of sodium removal) obtained in the NH_4NaY samples for different irradiation power levels and duration of the treatment of 10 min.

Salt conc. (M)	Power (W)		
	250	350	500
0.5	49	50	51
1	61	58	63
2	73	69	72

The exchange levels reached by the traditional successive exchange treatments at reflux conditions were 56, 73 and 87% after 1, 2 and 5 steps, respectively. The experiment at room temperature, with 0.45 M solution, produced a 40% exchange level.

It is known that in faujasitic zeolites an exchange of the sodium cations close to the 100% level is not easily obtained, due to the particular location of some of the cations in the intra-crystalline micropores. The results obtained clearly show that microwave irradiation can easily and with quite a short operating time promote the cation exchange process to interesting levels, although the single treatments used here did not cross the 75% threshold which is usually observed for Y zeolite [10]. Possible explanations are: the bulk temperatures of the irradiated mixtures that were measured during the treatment may not be representative of the actual temperature near the zeolite crystals. The nature of the heating effect can induce the generation of localized “hot spots”, since the heat is produced at the molecular level, inside the mixture. The bond distance and bond angle oscillations inside the zeolite framework may be raised with the pore dimensions oscillating in a wider range. Some other studies pointed out that the microwave irradiation may enhance the diffusion relative to the conventional heating at the same temperature, for example, in the diffusion of various cations in Pyrex glasses [11] and ethylene oxide in polyvinyl chloride [12].

The X-ray diffraction characterization did not reveal any change in the macroscopic crystallinity of the irradiated materials.

The catalytic properties of the two acidic series of HNaY, prepared by the microwave treatment and by the conventional procedure, are presented in figures 2 and 3 for the transformation of iso-octane at 350 °C.

Figure 2 displays the conversion level obtained as a function of time-on-stream. Similar initial catalytic activities were attained for the most acidic samples of both HNaY zeolite series, but with a significantly lower deactivation with time-on-stream observed in the microwave-irradiated samples. Possibly, different changes in the micro-environment of the active site might be induced, namely in what concerns the proximity of acid/base pairs and acid site density; these could contribute to explain the observations, but additional work will have to be carried out to inspect this findings.

The cracking product distributions, always presenting a large preponderance of branched C_4 species, clearly re-

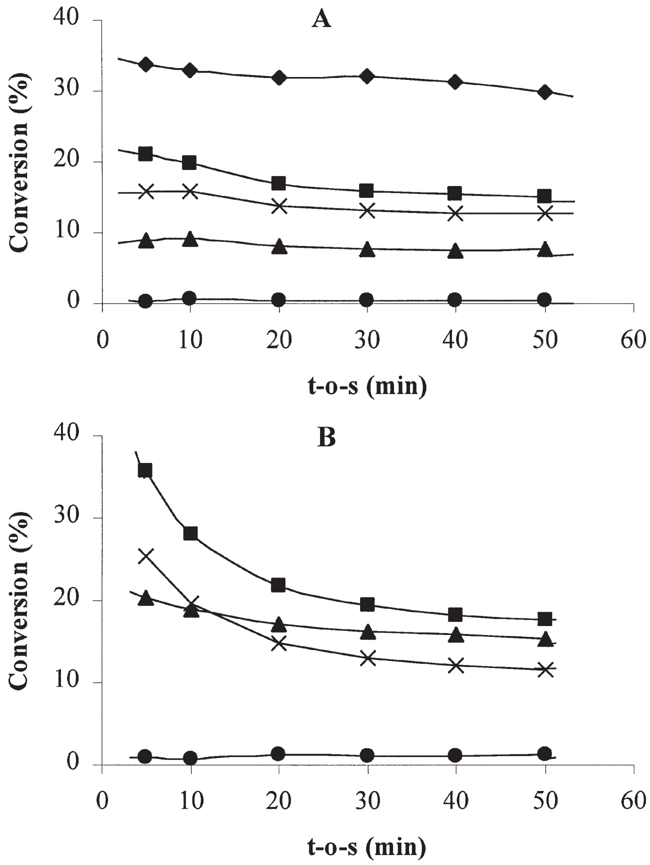

Figure 2. Iso-octane conversion as a function of time-on-stream for the irradiation-prepared samples (A) with exchange levels of 25% (●), 45% (▲), 50% (×), 61% (■) and 73% (◆), and for the conventionally exchanged samples (B) with exchange levels of 40% (●), 56% (▲), 73% (×) and 87% (■).

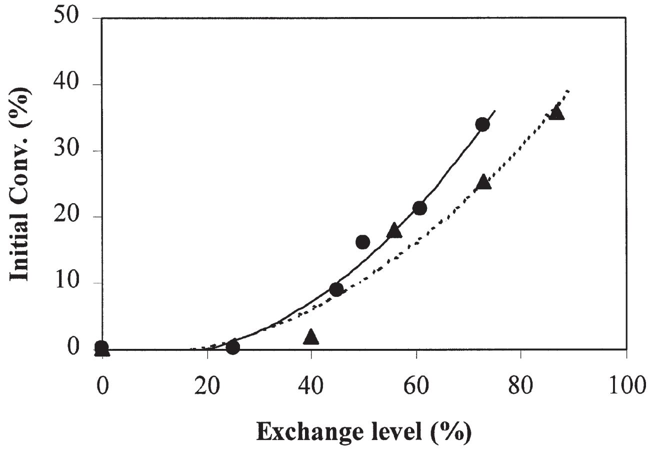

Figure 3. Initial conversions (time-on-stream = 5 min) as a function of the exchange level (% of sodium removed) for the irradiation-prepared samples (●) and for the conventionally exchanged samples (▲).

flects the effectiveness of the classical β-scission mechanism [13]; the olefin/paraffin ratio was similar for all of the most active samples at the beginning of the reaction, ranging from 0.2 to 0.4, but after 50 min time-on-stream this ratio increased to values near to 0.8 in the catalytic tests with the conventionally prepared samples paralleling its deactivation pattern, while in the irradiated samples this parameter showed only a slight modification.

The initial conversion (time-on-stream = 5 min) as a function of the exchange level, as presented in figure 3, is not significantly changed by the preparation method of the samples. The observed behaviour is that expected for such a system, where the reaction demands catalytic acid sites with moderate to strong acidity, but where the first acid sites to be generated are the weakest ones. Similar results have been obtained in other studies with this and similar reactions [14,15]. Nevertheless, a trend can be observed, in which the microwave-treated samples show, for the same exchange levels, a slightly higher activity than the conventionally exchanged ones.

4. Conclusions

Microwave irradiation, applied to a mixture of a zeolite sample and a salt solution, can be effective in promoting the ion-exchange process, leading to processing times of only a few minutes, as reported in this study for the preparation of acidic forms of Y zeolite from its sodium form. High exchange levels were achieved and the samples that were prepared present very interesting catalytic properties in the acid-catalysed transformation of iso-octane. The major difference between these samples and those prepared by the conventional method for ion exchange is that the deactivation with time-on-stream was negligible for the former, unlike what would be expected. Also, a general trend was observed indicating that the microwave-prepared samples show, for the same exchange level, a higher activity than those that were conventionally prepared.

Acknowledgement

Financial support by the Junta National de Investigação Científica e Tecnológica (JNICT) of Portugal (Project PBIC/C/QUI/2378/95) is gratefully acknowledged.

References

[1] J. Jacob, L.H.L. Chia and F.Y.C. Boey, J. Mater. Sci. 30 (1995) 5321.
[2] J.P. Zhao, C. Cundy and J. Dwyer, in: *Progress in Zeolite and Microporous Materials*, Stud. Surf. Sci. Catal., Vol. 105, eds. H. Chon, S.-K. Him and X.S. Uh (Elsevier, Amsterdam, 1997) p. 181.
[3] C.-G. Wu and T. Bein, J. Chem. Soc. Chem. Commun. (1996) 925.
[4] S.L. Cresswell, J.R. Parsonage, P.G. Riby and M.J.K. Thomas, J. Chem. Soc. Dalton Trans. (1995) 2315.
[5] A. Arafat, J.C. Jansen, A.R. Ebaid and H. van Bekkum, Zeolites 13 (1993) 162.
[6] J.C. Jansen, A. Arafat, A.K. Barakat and H. van Bekkum, Synth. Micropor. Mater. 1 (1992) 507.
[7] X. Meng, W. Xu, S. Tang and W. Pang, Chin. Chem. Lett. 192(5,6) (1992) 69.
[8] F.-S. Xiao, W. Xu, S. Qiu and R. Xu, Mater. Res. Soc. Symp. Proc. 344 (1994) 139.
[9] L. Seyfried, F. Garin, G. Maire, J.-M. Thiébaut and G. Roussy, J. Catal. 148 (1994) 281.

[10] F. Lemos, J.M. Lopes and F. Ramôa Ribeiro, J. Mol. Catal. 53 (1989) 265.

[11] T.T. Meek, R.D. Blake, J.D. Katzs, J.R. Bradbury and M.H. Brooks, J. Mater. Sci. Lett. 7 (1988) 311.

[12] C. Gibson, I. Matthews and A. Samuel, J. Microwave Power Electromag. Energy 23 (1988) 17.

[13] J.M. Lopes, F. Lemos, F. Ramôa Ribeiro, N. Dewaele, E.G. Derouane and M. Guisnet, J. Mol. Catal. 48 (1988) 373.

[14] I.V. Mishin, A.L. Klyachko, T.R. Brueva, V.D. Nissenbaum and H.G. Karge, Kinet. Catal. 34(5) (1993) 835.

[15] J.M. Lopes, F. Lemos, E. Derouane and F. Ramôa Ribeiro, React. Kinet. Catal. Lett. 58(1) (1996) 33.