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Performance of Fe-BEA catalysts for the selective hydroxylation of benzene with N_2O

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Abstract

The catalytic performance and the formation of carbon in Fe-BEA and Fe-MFI catalysts prepared by three methods (hydrothermal synthesis, ion-exchange at room temperature with an iron-nitrate solution and ion-exchange at 80 °C with an iron ammonium sulfate solution) are analyzed with the aim to develop catalysts having larger dimensions of the cavities with respect to the MFI structure (such as ZSM-5 and silicalite) and which could be applied in the selective hydroxylation of molecules having larger kinetic diameters than benzene. The results show that, apart from minor differences, Fe-BEA catalysts have comparable catalytic performances in selective benzene hydroxylation to phenol with respect to Fe-MFI catalysts. However, all the Fe-BEA samples show a higher formation of carbon than the corresponding Fe-MFI samples as well as the formation of carbon having a higher degree of condensation. This is connected to the larger cavities in the BEA framework, especially at the intersections of the channels, with respect to the MFI framework. Highly active samples were obtained by ion-exchange at 80 °C with the iron ammonium sulfate solution. The phenol productivity in both Fe-MFI and Fe-BEA samples is about 60–70% higher than that of comparable samples prepared by hydrothermal synthesis.

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1. Introduction

Fe-MFI used for selective benzene oxidation to phenol with N_2O can be considered an interesting example of nanostructured catalysts, because the properties of the catalyst depend both on the presence of specific iron sites and the effects of the zeolite cage around the iron sites. These effects include confinement of the reactants, stabilization of the transition state and formation of the specific highly active iron sites themselves [1]. Therefore, the properties of the catalyst depend on the supramolecular structure (having nano dimensions) around the active centers. In fact, iron supported on oxides such as silica, alumina or zirconia is not active in the reaction and the catalytic performance depends considerably on the type of zeolite structure.

The one-step synthesis of phenol from benzene in the gas phase using N_2O or in the liquid phase using H_2O_2 as the oxidizing agent is attracting increasing interest, because the commercial process of phenol synthesis has the drawbacks of the formation of: (i) co-products such as acetone (in a 1:1 ratio) the market for which is decreasing, differently from the expanding market for phenol, and (ii) a hydroperoxide as intermediate which limits the productivity of the process (conversion should be low in this step) and poses severe safety problems (risk of explosion). For these reasons, development of a one-step synthesis of phenol is of particular interest.

In 1988, three groups of researchers (Suzuki et al. [2] in Japan, Gubelmann and Tirel [3] in France, and Panov and coworkers [4] in the former Soviet Union) independently discovered that ZSM-5 zeolites allow high selectivity to be obtained in the selective benzene oxidation to phenol. Panov and coworkers [4], in particular, further developed the catalyst (Fe-ZSM-5) and process, and in collaboration with Solutia developed a semi-commercial process [5] for the reuse of N_2O produced as a by-product in the adipic acid process in the synthesis of phenol which is then hydrogenated to intermediates for adipic acid synthesis.

Several articles and reviews [6–10] have discussed in detail the chemistry of the gas phase catalytic reaction of

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benzene hydroxylation with N_2O and the nature of the active sites. While initially it was supposed that acid zeolites (H-ZSM-5) were also active in the reaction, there is conclusive evidence [11,12] that the activity is instead related to iron impurities in the zeolite and that the catalytic behavior is related to the presence of extra-framework iron species. Different indications are instead given in the literature on the nature of the active sites, but there is no conclusive evidence to support one model over the other, due in part to the intrinsic difficulty in the study of these catalysts where the number of iron active sites is very limited (usually lower than 1% Fe, w/w). Recently it was also shown that the largest fraction of the extra-framework iron is only a spectator species (could be removed without affecting catalytic performance) and therefore only a very limited number of iron sites are active in benzene hydroxylation [13], pointing out that the iron species which could be characterized by spectroscopic methods are not necessarily the active species. This agrees with the fact that impurities in H-ZSM-5 catalysts (of the order of 100 ppm of iron) give catalysts having activities comparable with that of catalysts having about 100 times higher iron contents (about 1 wt.%) which are those that can be studied by spectroscopic methods. In addition, it has also been shown [13] that during the catalytic reaction a change in the nature and distribution of the iron species occurs, rendering difficult identification of defined relationships between the catalytic behavior and the nature of the iron species in Fe-ZSM-5 catalysts.

The reaction of phenol synthesis using N_2O as the oxidant has also been applied for the hydroxylation of substituted alkylaromatics [14,15], but one of the limitations was the accessibility of bulkier molecules than benzene to sites located inside the zeolite channels. The synthesis of substituted phenols is an interesting area of application, because the higher value of this class of intermediates with respect to phenol makes less critical the question of the cost of N_2O production (a main drawback in the direct synthesis of phenol).

Notwithstanding the relevant research activity on the direct synthesis of phenol, most of the data in the literature have been limited to Fe-MFI type zeolites (Fe-ZSM-5 and Fe-silicalite). On the other hand, the use of other types of Fe–zeolites having larger pore dimensions is made difficult by the cited dependence of the reactivity on the supramolecular effect of the zeolite cage around the active iron sites. Various Fe–zeolites such as Fe–Y and Fe–mordenite have been found inactive in the reaction. Fe-MCM-22 [16] and H-MCM-22 [17] have been reported as active in the reaction, but the performances are significantly lower than those of Fe-ZSM-5 or Fe-silicalite catalysts. We also found that Fe-MCM-41 catalysts show worse performances than Fe-ZSM-5 or Fe-silicalite catalysts. Hereinafter the ZSM-5 and silicalite-1 class of materials will be referred to with the more general indication of Fe-MFI zeolites, according to the common framework classification, and independent of the presence or absence of Al in the framework.

Beta (BEA framework class) is a well known class of zeolites the use of which is considerably expanding due to the interesting properties in the alkylation of aromatics (cumene synthesis), for example, [18]. The BEA framework is characterized by 12 member ring channels (the 12 member ring along the [1 0 0] direction has openings of 0.66 nm × 0.67 nm, and along the [0 0 1] direction openings of 0.56 nm × 0.56 nm) having significantly larger internal accessibility than the 10 member ring of the MFI framework (the 10 member ring along the [1 0 0] direction has opening of 0.51 nm × 0.55 nm, and along the [0 1 0] direction openings of 0.53 nm × 0.56 nm). On the other hand, BEA zeolites show analogies with MFI zeolites in terms of the other framework characteristics (three-dimensional pore network, topology) and therefore are suitable candidates to develop Fe/zeolite materials which may be used for the selective hydroxylation of substituted aromatics.

No detailed investigation has been reported on the performance of Fe-BEA catalysts in benzene hydroxylation. Tyrlov et al. [19] indicated that the catalytic activity of H-BEA zeolite with high Si content is similar to those of dehydroxylated HZSM-5 type zeolites. Panov [6] cited that BEA and ZSM-11 are other zeolite structures active in selective benzene hydroxylation, but data are not reported. Therefore, very limited information is available in the literature about the possible use of Fe-BEA catalysts in benzene hydroxylation, notwithstanding the potential interest of this class of materials.

The objective of the research reported here was to study the properties of Fe-BEA catalysts, synthesized either by post-synthesis addition of Fe or direct introduction during hydrothermal synthesis and consecutive partial migration to extra-framework positions induced by thermal treatments, in the benzene hydroxylation with N_2O. The performances of Fe-BEA samples are compared with those of analogous Fe-MFI samples, in order to have a more direct indication of the role of the zeolite structure in determining catalytic performance. Furthermore, the deactivation by carbon formation being a very important aspect of the catalytic chemistry of these materials, the amount of carbon formed and its temperature programmed oxidation (which provides indications on its characteristics [22,13]) are also analyzed. On the contrary, for the reasons outlined above, i.e., there is no clear relationship between iron species identified by characterization techniques and reactivity, and due to limitations in the length of the article, no data regarding characterization of the nature of the iron species in the Fe-BEA and Fe-MFI samples are reported here.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by either addition of Fe^{3+} ions to commercial zeolites or direct hydrothermal synthesis

Table 1
Characteristics of the Fe-MFI and Fe-BEA catalysts used for the tests of benzene hydroxylation

Sample code	Frame-work	Method of addition of Fe	Post-treatment	Si/Al	% Fe (wt.)	Note
$Fe_{2.0}$MFI-ht	MFI	Hydrothermal synthesis	700 °C (1 h), flow of He (in situ before the catalytic tests)	50	2.0	–
$Fe_{0.95}$BEA-ht	BEA	Hydrothermal synthesis	700 °C (1 h), flow of He (in situ before the catalytic tests)	28.1	0.95	–
$Fe_{1.85}$BEA-ht	BEA	Hydrothermal synthesis	700 °C (1 h), flow of He (in situ before the catalytic tests)	28.5	1.85	–
$Fe_{0.35}$MFI ie(N)	MFI	Ion-exchange, r.t. using aq. solution of $Fe(NO_3)_3$	700 °C (1 h), flow of He (in situ before the catalytic tests)	13	0.35	Parent zeolite: AlsiPenta SN27
$Fe_{0.85}$BEA ie(N)	BEA	Ion-exchange, r.t. using aq. solution of $Fe(NO_3)_3$	700 °C (1 h), flow of He (in situ before the catalytic tests)	13	0.85	Parent zeolite: Zeolist CP814E
$Fe_{0.35}$MFI ie (Mohr-80 °C)	MFI	Ion-exchange, 80 °C using aq. solution of Fe^{3+} ammonium sulfate (Mohr salt)	700 °C (1 h), flow of He (in situ before the catalytic tests)	13	2.5	Parent zeolite: AlsiPenta SN27
$Fe_{0.85}$BEA (Mohr-80 °C)	BEA	Ion-exchange, 80 °C using aq. solution of Fe^{3+} ammonium sulfate (Mohr salt)	700 °C (1 h), flow of He (in situ before the catalytic tests)	13	2.5	Parent zeolite: Zeolist CP814E

of the (Fe, Al)-zeolite. The characteristics of the samples and the code used for indicating them throughout the text are summarized in Table 1.

H-MFI was obtained from a commercial NH_4^+-MFI zeolite (SN27 from Alsi-Penta) with a SiO_2/Al_2O_3 ratio of 25. The acid form was obtained by calcination of the dried sample at 550 °C in air. Iron was present in this commercial sample in traces, estimated by atomic absorption spectroscopy as about 0.002 wt.% H-BEA was obtained from a commercial NH_4^+-Beta zeolite (CP 814E from Zeolist) with a SiO_2/Al_2O_3 ratio of 26. The acid form was obtained by calcination of the dried sample at 550 °C in air. Iron was present in this commercial sample in traces.

Two methods were used for the preparation of the samples made by ion-exchange: (1) ion-exchange at room temperature using an aqueous solution of iron-nitrate and (2) ion-exchange at 80 °C using an aqueous solution of iron ammonium sulfate (Mohr salt). Use in the latter case of an ion-exchange temperature of 80 °C was found to produce samples having a better dispersion of iron than those prepared at r.t. [20], but this was not found in the case of the iron-nitrate solution. In both cases, the ion-exchange was made by stirring (24 h) the zeolite suspended in a 250 ml flask containing the aqueous solution of the iron salt, recovering then the zeolite by filtration. The zeolite was washed with distilled water, dried at 100 °C overnight, and then calcined at 550 °C in air for 4 h with a heating rate of 5 °C/min. The same procedure was used for both MFI and BEA zeolite, but while the same loading of iron was found in the case of the second type of iron-exchange procedure (Mohr salt), the loading of iron in the case of MFI was about half of that for BEA using the iron-nitrate solution.

The (Fe, Al)-zeolites synthesized by the hydrothermal method were prepared in a static Teflon®-lined autoclave and under autogeneous pressure at 170 °C. The molar composition of the starting hydrogel was:

MFI: 0.175 Na_2O–0.08 TPABr–0.01 Al_2O_3–0.01 Fe_2O_3/1 H_3PO_4–1 SiO_2–20 H_2O
BEA1: 5 Na_2O–10 TEAOH–0 TEABr–1 Al_2O_3–0.50 Fe_2O_3/1.5 $H_2C_2O_4$–50 SiO_2–1000 H_2O.
BEA2: 5 Na_2O–5 TEAOH–5 TEABr–1 Al_2O_3–0.25 Fe_2O_3/0.75 $H_2C_2O_4$–50 SiO_2–1000 H_2O

where BEA1 indicates the composition for the $Fe_{0.95}$BEA-ht sample and BEA2 for the $Fe_{1.55}$BEA-ht sample.

The synthesis procedure was the following: sodium aluminate or $Al(OH)_3$ was added to a sodium-hydroxide solution and then after homogenization the organic compound (TPABr for MFI and TEAOH and/or TEABr for BEA) and the silica source (silica-gel BDH) were added (the latter was slowly added under stirring). A solution of an iron complex with oxalic or orthophosphoric acid, starting from iron-nitrate and the acid, prepared in another beaker was slowly added to the hydrogel. After 1 h of homogenization the mixture was transferred into the autoclave. Hydrothermal synthesis was made at 170 °C for MFI and 140 °C for BEA under static conditions. The template was removed by calcination in air up to 550 °C. The temperature was slowly increased up to the final value (from r.t. to 350 °C at a rate of 3 °C/min, then isothermal for 2 h, then a further increase in temperature at a rate of 5 °C/min to 550 °C followed by 5 h under isothermal conditions at 550 °C).

The solid products either after synthesis or after template removal were analyzed by powder X-ray diffraction (XRD), infrared spectroscopy (FT-IR), BET surface area measurements and scanning electron microscopy (SEM) to verify the synthesis procedure and crystallinity of the samples. Crystallization was good in all the samples, and no significant changes after pretreatment at 700 °C in a flow of He occurred. The treatment induces the partial migration of iron from framework to extra-framework positions. Characterization data indicate that about 60% of the iron migrates from framework to extra-framework positions as a result of the pretreatment.

2.2. Catalytic tests

The catalytic tests in selective oxidation of benzene to phenol using N_2O as the oxidant were made in a fixed-bed reactor at 400 °C feeding a mixture containing 20% benzene and 3% N_2O in helium. The total flow rate was 3 l/h and the amount of catalyst was 0.5 g (contact time of 0.6 s).

The feed was prepared using an already calibrated mixture of N_2O in helium and adding benzene using an infusion pump and a vaporizer chamber. The feed could be sent either to the reactor or to a by-pass for its analysis. The feed coming out of the reactor or from the bypass could be sent to vent or to one of the two parallel absorbers containing pure toluene as the solvent (plus calibrated amounts of tetrahydrofuran as the internal standard) cooled at about −15 °C in order to condense all organic products. The line to the absorbers was heated at about 200 °C in order to prevent condensation

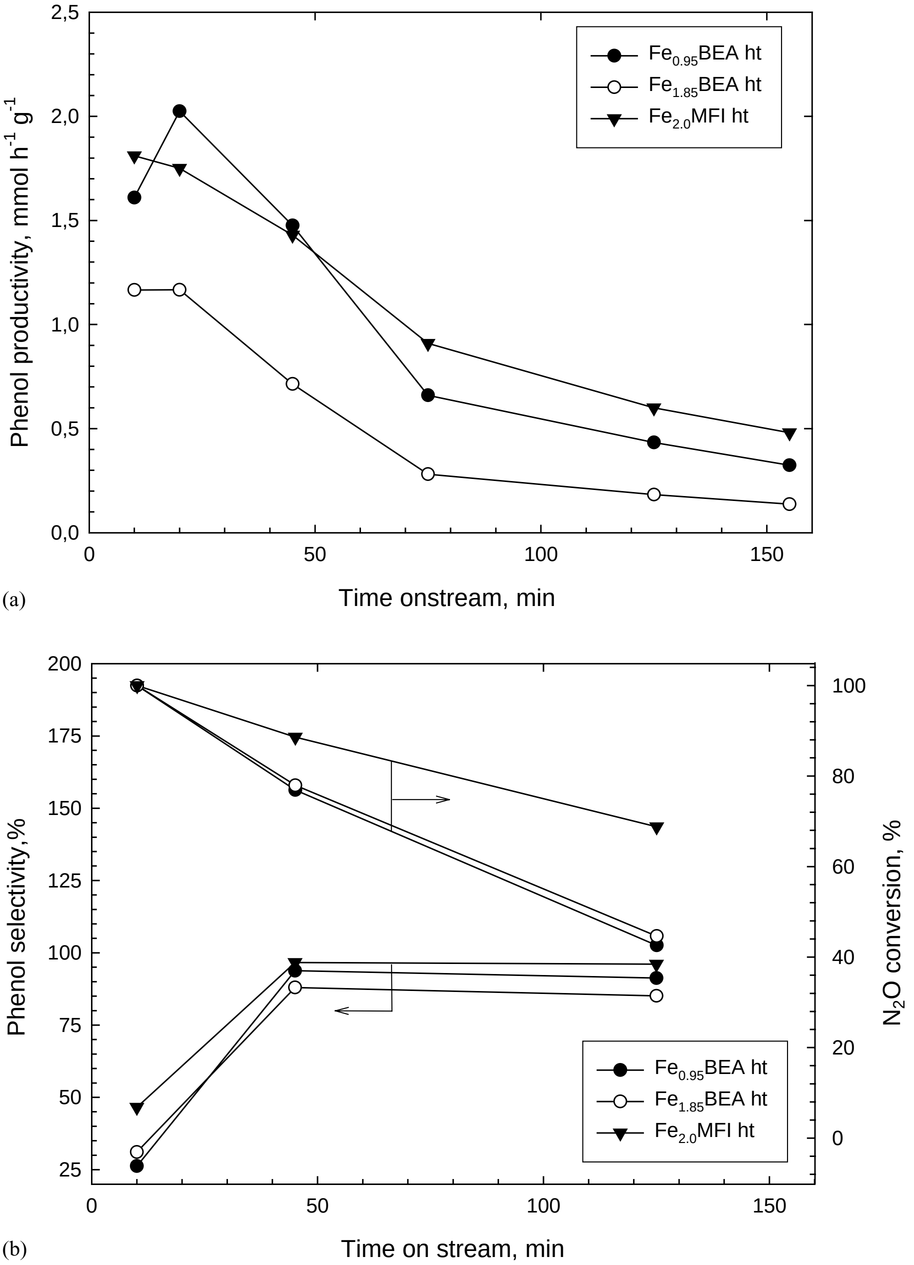

Fig. 1. Phenol productivity (mmol h^{-1} g^{-1}) as a function of time on stream (a) and corresponding phenol selectivity and N_2O conversion (b) in Fe-BEA and Fe-MFI catalysts prepared by hydrothermal synthesis.

of the products. The vent, after condensation of the organic products, was sent to a sampling valve for analysis of the residual gas composition. The reactor outlet stream was sent alternatively to the two parallel absorbers for a given time (typically 3 or 5 min), in order to monitor the change in the catalytic activity averaged over this time.

N_2O, O_2, N_2 and total oxidation products (CO and CO_2) were analyzed using TCD-Gas chromatography and a 60/80 Carboxen-1000 column, whereas benzene and phenol (as well as other minor aromatic by-products) were determined by FID-Gas chromatography using a ECONO-CAP SE-30 "wide bore" column or a Mass-GC equipped with a capillary Chrompack CP-Sil 5CB-MS fused silica column.

Before the reactivity tests the catalysts were activated in situ at 700 °C in a flow of water saturated helium.

2.3. Thermogravimetric tests

Thermogravimetric (TG) tests were made in a TGA Q50 apparatus (TA Instruments) on the samples discharged from the reactor for catalytic tests after flushing with helium for 5 min at the same temperature of the catalytic tests (400 °C), in order to remove weakly adsorbed species. TG tests were made in a flow of air (60 ml min^{-1}) which passes tangential to the pan of the TG apparatus containing approximately 3–4 mg of sample. The heating rate was 5 °C/min from r.t.

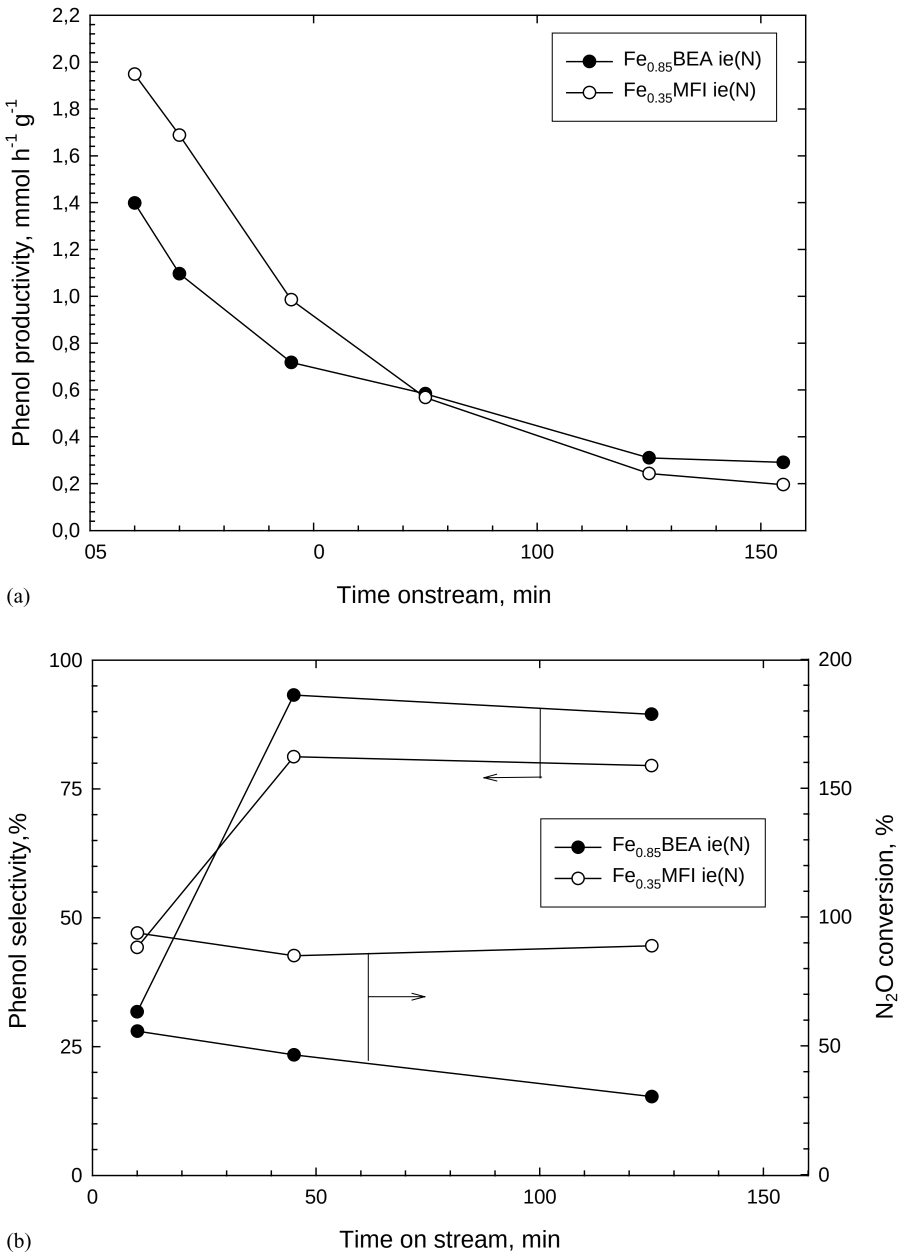

Fig. 2. Phenol productivity (mmol h^{-1} g^{-1}) as a function of time on stream (a) and corresponding phenol selectivity and N_2O conversion (b) in Fe-BEA and Fe-MFI catalysts prepared by ion-exchange at room temperature with an iron-nitrate solution.

(25 °C) to 1000 °C. During the TG experiments, the samples turned from black to white, indicating complete removal of carbonaceous species.

3. Results and discussion

3.1. Catalytic behavior

The comparison of the catalytic behavior is reported in Fig. 1 as a function of time on stream for two Fe-BEA samples prepared by hydrothermal synthesis and containing different amounts of iron (the initial amount of framework iron was 0.95 and 1.85 wt.%, but after the in situ pretreatment at 700 °C about 60% of the framework iron migrated to extra-framework positions). Fig. 1a reports the change in the productivity to phenol as a function of time on stream, while Fig. 1b shows the change in the selectivity to phenol (on the basis of the gaseous products of reaction, i.e., excluding the carbon which remains on the catalyst) and in the conversion of N_2O (the limiting reactant, being benzene in large excess; the benzene to N_2O ratio in the feed was 20:3, similar to the conditions reported for the cited process by Solutia [5,21]). For comparison, the behavior of a representative sample of Fe-MFI catalysts prepared and pretreated in a similar way to the Fe-BEA-ht samples, is also shown in Fig. 1.

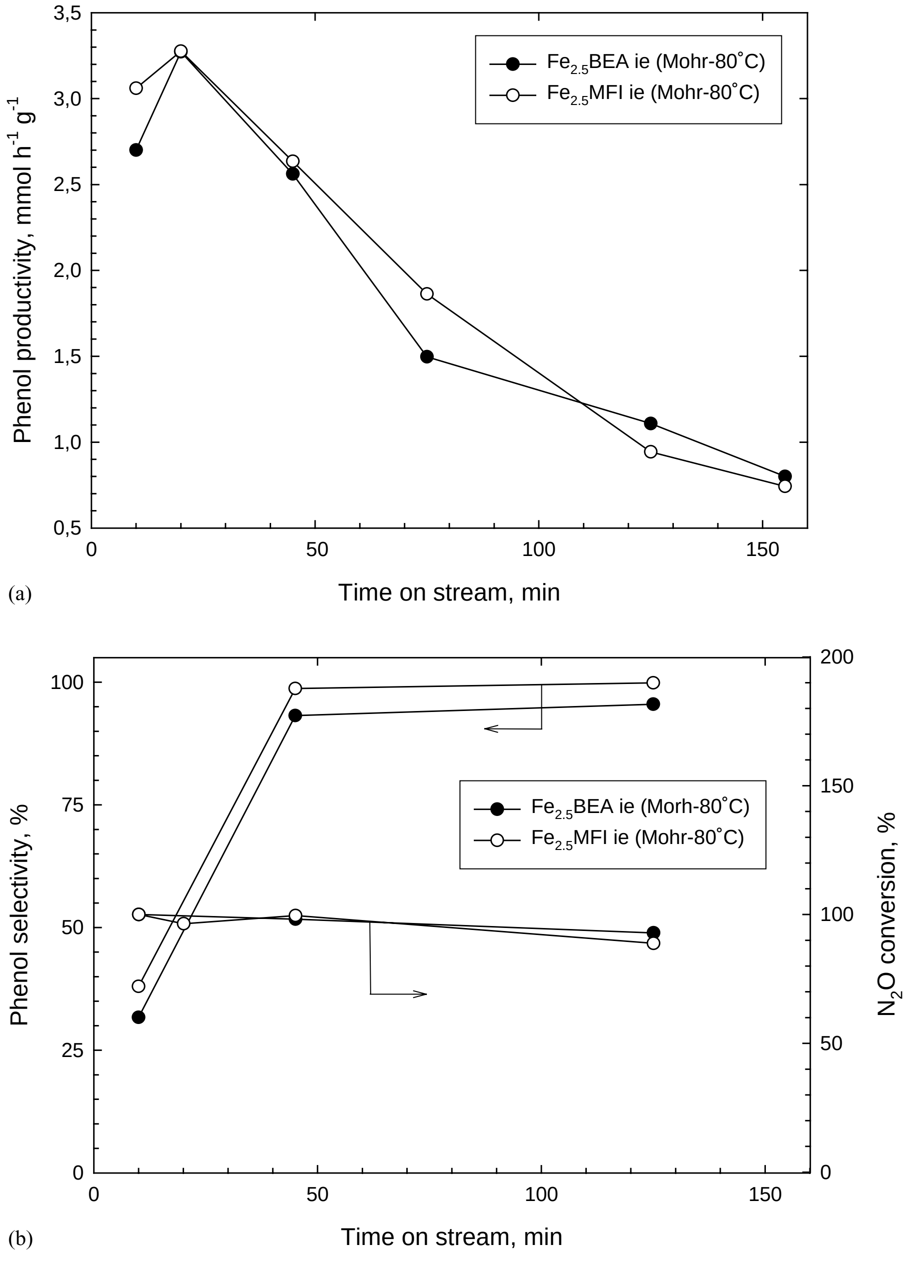

Fig. 3. Phenol productivity (mmol h^{-1} g^{-1}) as a function of time on stream (a) and corresponding phenol selectivity and N_2O conversion (b) in Fe-BEA and Fe-MFI catalysts prepared by ion-exchange at 80 °C with an iron ammonium sulfate solution.

For all reported samples, the productivity to phenol, after an initial slight increase, decreases significantly during the first 3 h of time on stream, reaching then a pseudo-constant activity, but with a phenol productivity about a quarter of the maximum productivity. This behavior is similar to that observed in the literature, although, usually, the change in the phenol formation as a function of the time on stream has not been followed in detail.

No considerable differences were observed between the Fe-BEA and Fe-MFI samples, although the latter shows a slightly lower rate of deactivation and the residual phenol productivity after about 3 h is slightly higher than that of the Fe-BEA sample having comparable loading of iron ($Fe_{1.85}$BEA-ht).

At the beginning of the reaction (during approximately the first half hour of time on stream) the selectivity to phenol increases significantly, due to a corresponding lowering of the formation of carbon oxides. After this initial stage, the selectivity reaches high values (above 90%) and remains constant. No significant differences were observed between the Fe-BEA-ht and Fe-MFI-ht samples, although the latter is slightly more selective to phenol.

The initial high formation of carbon oxides during the first half hour of time on stream explains the initial increase in the phenol productivity for two reasons. The first reason is based on the consecutive oxidation of phenol to carbon oxides. The second reason is related to the formation of steam as a by-product of the oxidation of benzene to carbon oxides. The steam may cause a further migration of iron from framework (FW) to extra-framework (EFW) positions, similar to that observed in the Fe-silicalite samples [13]. The increased amount of Fe^{EFW} determines an increase in the productivity to phenol.

The conversion of N_2O decreases with time on stream in all cases, although the decrease is less for the Fe-MFI samples than for the Fe-BEA samples. It should be noted that reactivity tests in N_2O decomposition under similar experimental conditions, but in the absence of benzene in the feed, indicate that the mean conversion of N_2O is about 13–15%, i.e., much lower than that observed in these tests. The removal of the oxygen produced by decomposition of N_2O on iron sites due to the benzene oxidation leaves further iron sites accessible for N_2O decomposition, increasing therefore its rate of conversion.

The comparison of the catalytic behavior of Fe-BEA and Fe-MFI samples is reported in Fig. 2 in which iron was introduced by ion-exchange at room temperature using an aqueous iron-nitrate solution. The behavior of these samples is comparable to that of the samples prepared by introduction of iron in the zeolite framework and then thermal displacement to EFW positions. This indicates that there are no special active sites which form in the FW → EFW iron migration, but similar sites (in terms of amount and probable nature) can be produced by a simple impregnation method. However, the selectivity to phenol (Fig. 2b) is lower than that of the samples prepared by hydrothermal synthesis (Fig. 1b), probably due to the presence of iron-oxide species (possibly hematite-type) which give rise to an increased rate of conversion as well as N_2O decomposition. In fact, there is a parallelism between lowering of the selectivity to phenol and increase in the N_2O conversion (Fig. 2b).

The behavior of the Fe-BEA and Fe-MFI samples prepared by ion-exchange is reported in Fig. 3, but using an aqueous solution of an iron ammonium sulfate salt (Mohr salt) and making the ion-exchange at 80 °C. The ion-exchange at 80 °C instead of room temperature as used in

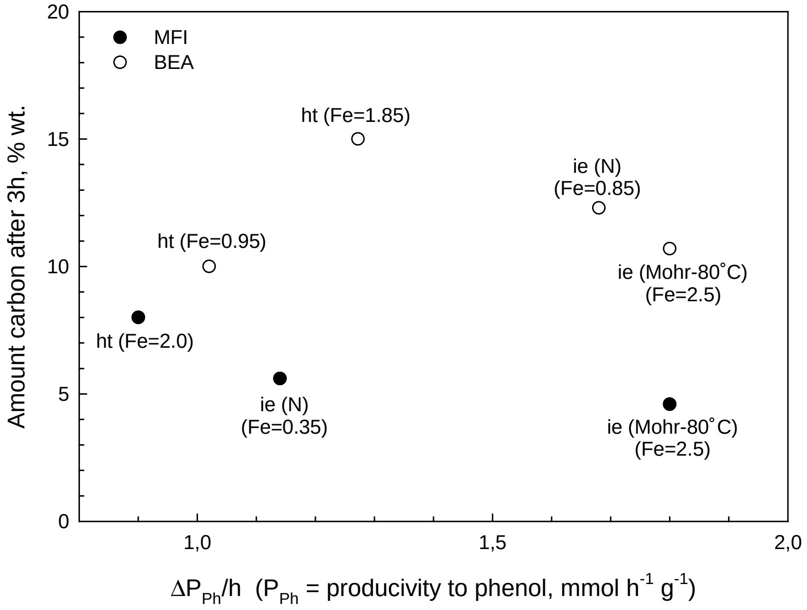

Fig. 4. Amount of carbon after 3 h of time on stream (wt.%) vs. initial rate of change of the productivity to phenol (see text) in all the samples studied. Black symbols: Fe-MFI; open symbols: Fe-BEA.

previous works [20] allows very good dispersion of iron to be obtained, even at high iron loadings. When iron-oxide forms during the preparation, the zeolite changes to a brown-yellow color and therefore it is simple to note when bulk-type iron-oxide forms. In the preparation at r.t. by ion-exchange with the Mohr salt, the zeolite turns brown-yellow above loadings of about 0.5%, while when the ion-exchange is carried out at 80 °C a loading of 2.5 wt.% is reached before the color change occurs. Also in the preparation of Fe-ZSM-5 catalysts for N_2O selective reduction with propane the method of ion-exchange with the Mohr salt at 80 °C allows more active catalysts to be obtained [22]. Data reported in Fig. 3 evidence that this method makes it possible to obtain catalysts having around 60–70% higher productivity than that of samples prepared by hydrothermal synthesis. These values of phenol productivity are among the highest values reported in the literature, when normalized to the same feed composition.

No relevant differences are observed between the Fe-BEA and Fe-MFI samples, in terms of the trend of the selectivity versus time on stream, selectivity to phenol and N_2O conversion. Also in this case an initial increase in the productivity to phenol is noted, probably as a consequence of the higher initial formation of carbon oxides.

3.2. Carbon formation during the catalytic tests

The formation of carbon as a by-product of the reaction is a critical aspect of the catalytic chemistry of Fe/zeolite samples for benzene hydroxylation with N_2O. A good

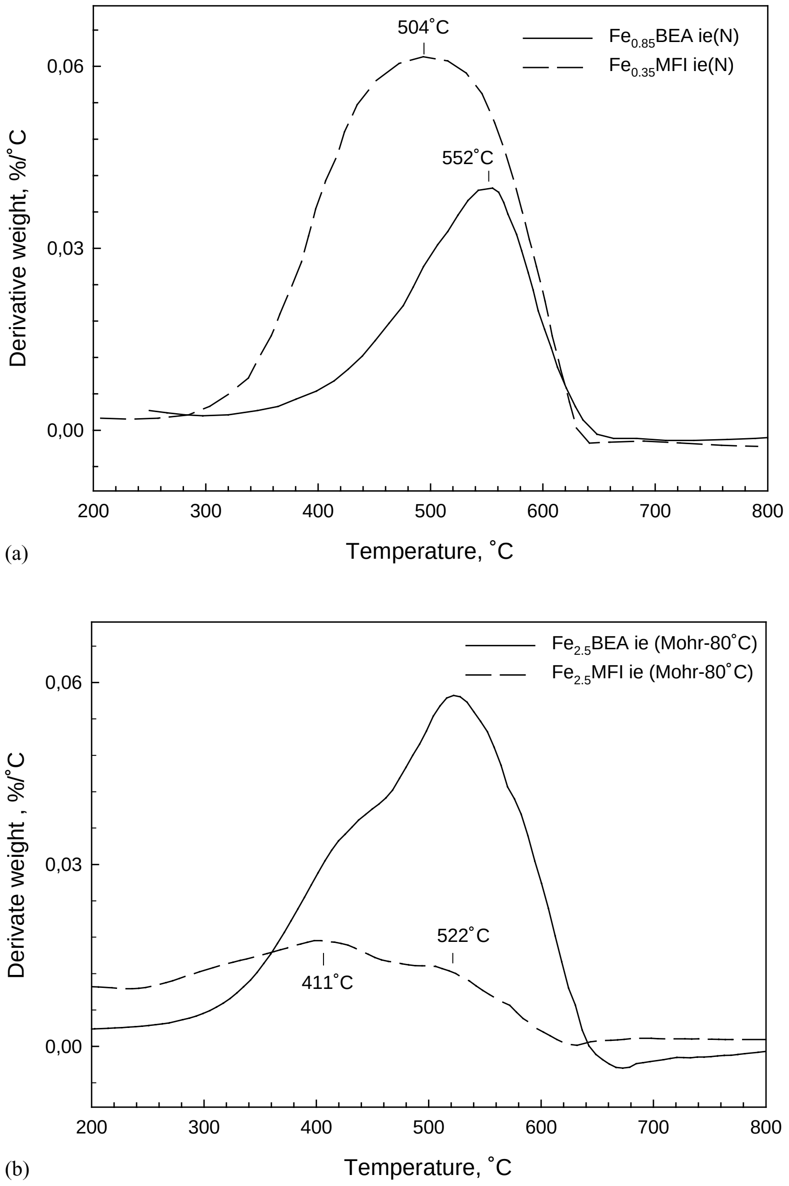

Fig. 5. TPO derivative weight (wt.%/°C) for coke formed in Fe-BEA and Fe-MFI samples prepared by ion-exchange: (a) at r.t. with an iron-nitrate solution and (b) at 80 °C with an iron ammonium sulfate solution.

method to analyze the amount of carbon as well as to have indications on its characteristics is to determine its temperature programmed oxidation (TPO) in a thermogravimetric apparatus (TG) [20]. Carbon is oxidized in a temperature range between about 300 and 700 °C. The shift of the maximum in the TG derivative weight change towards higher temperature is associated with the progressive formation of heavier polycondensated products. Two possible pathways of carbonaceous species were identified [20], the first through the intermediate further hydroxylation of phenol and the second through the coupling of phenol with benzene or another phenol molecule. This second pathway is the dominant mechanism of formation of carbonaceous species, although the relative rate of the two pathways depends on the zeolite characteristics and iron loading.

It is often supposed that the decrease in phenol productivity with increasing time on stream is related to the carbon formation. While certainly carbon formation is one of the factors causing this deactivation, it is not the only factor. Reported in Fig. 4 is the comparison of the amount of carbon observed in the various samples after 3 h of time on stream and the initial rate of change in the productivity to phenol, estimated from the data in Figs. 1–3 (after the maximum in phenol productivity, when present). Although this value is not the true rate of deactivation, it gives a rough estimation of the deactivation trend which may be correct in terms of the comparison of the relative behavior of the samples with respect to the amount of carbon formed during the reaction (Fig. 4).

Data reported in Fig. 4 show that there is no definite relationship between the initial change in productivity to phenol and amount of carbon formed in 3 h of time on stream. This indicates that, the deactivation behavior of Fe/zeolite catalysts is probably determined by the stability of iron-species during the catalytic reaction. A change in their nature was noted in Fe-silicalite samples [13] and reasonably also occurs in these Fe-BEA and Fe-MFI samples.

A second interesting information shown by the data reported in Fig. 4 is that the amount of carbon in the MFI samples ranges from 5 to 8 wt.% in 3 h of reaction, and between 10 and 15 wt.% for the Fe-BEA samples. Therefore, probably due to the larger dimensions of the cavities, Fe-BEA catalysts form a higher amount of carbon during the reaction than Fe-MFI catalysts, although this does not have a considerable influence on the phenol productivity, as shown in Figs. 1–3, at least during the first 3 h of reaction.

Fig. 4 also shows that there is no apparent relationship between the amount of iron in the catalyst and the formation of carbon during the reaction.

Reported in Fig. 5 are the derivative weights of the TPO curves for carbon formed during the catalytic reaction in the Fe-MFI and Fe-BEA samples prepared by ion-exchange (using iron-nitrate, Fig. 5a and iron ammonium sulfate, Fig. 5b). Three peaks for carbon species could be identified: (1) centered at about 410 °C; (2) centered at about 510 °C; (3) centered at about 550 °C. Higher temperatures of oxidation of the carbon indicate the formation of products with a higher degree of condensation. By comparing the TPO derivative weight it is evident that Fe-BEA samples give rise to bulkier carbon types than the corresponding Fe-MFI samples, again reasonably due to the larger dimensions of the cavities (especially at the intersections of the channels along the [1 0 0] and [0 0 1] directions).

4. Conclusions

The objective of the study presented here was to explore the possibility to prepare active Fe/zeolite catalysts having the BEA framework structure, due to the larger dimensions of the cavities with respect to the MFI structure (such as ZSM-5 and silicalite) which allow these catalysts to be used in the selective hydroxylation of molecules having larger kinetic diameters than benzene, such as substituted aromatics (for example, *p*-substituted alkylaromatics) which are of relevant interest in the synthesis of intermediates for fine chemicals.

The results evidence that Fe-BEA catalysts have comparable catalytic performances in selective benzene hydroxylation to phenol to Fe-MFI catalysts. Different types of preparations were examined: (a) the classical hydrothermal synthesis (introduction of iron in the framework and controlled framework to extra-framework migration by thermal treatment) and (b) two different ion-exchange procedures. In all cases, apart from minor differences, the catalytic behavior of Fe-BEA samples can be considered well comparable with that of the analogous Fe-MFI samples, at least on the time scale studied in the present experiments.

However, all the Fe-BEA samples show a higher formation of carbon than the corresponding Fe-MFI samples as well as the formation of carbon having a higher degree of condensation. This is connected to the larger cavities in the BEA framework, especially at the intersections of the channels, with respect to the MFI framework. Therefore, the development of catalysts for the selective hydroxylation of larger molecules than benzene requires the development of Fe/zeolites having larger dimensions of the channels, but not a three-dimensional structure of the channels leading to larger voids at the intersection between the channels.

Another interesting observation in this work regards the high activity of samples obtained by ion-exchange at 80 °C with the iron ammonium sulfate solution. The phenol productivity in both Fe-MFI and Fe-BEA samples is about 60–70% higher than that of comparable samples prepared by hydrothermal synthesis. The ion-exchange method of preparation, which leads to samples having comparable behavior independent of the framework structure (Fig. 3), is therefore promising for the development of new active catalysts for the selective hydroxylation of benzene with N_2O.

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