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Innovations in the synthesis of Fe-(exchanged)-zeolites☆

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Abstract

Several aspects on the preparation of Fe-zeolites are discussed. In contrast to the many studies highlighting the characterisation of the active sites, new approaches for incorporation of Fe are presented.

Full utilization of exchange capacity of zeolites has been achieved by a controlled alkaline treatment of the parent sample. With this method, iron can be fully exchanged by liquid phase ion-exchange on ZSM5 without the formation of inactive Fe-oxides.

The second topic is the use of a mild oxidant (H_2O_2, and peroxides in general) to break down strong complexating equilibria during ion-exchange by controlled redox titration of the ligands. Hydrogen peroxide oxidizes effectively chelating groups releasing Fe species at a controlled rate. The method is demonstrated for the preparation of Fe-FER through Ferric-citrate.

The final concept discussed is the detemplating of the zeolite with the simultaneous incorporation of the iron (combined detemplation and ion-exchange). This *one-pot* preparation minimizes the number of steps considerably. To realize this, a strong oxidant is necessary to remove the organic template, and Fe-cations for exchange. Both requirements are met with the Fenton's-chemistry ($Fe^{3+/2+}/H_2O_2$ mixtures) involving radical chemistry.

Keywords: Zeolite; ZSM-5; BEA; FER; Fe-zeolites; Liquid ion-exchange; Post-synthesis modification; Alkali treatment; Mesopore formation; Decomplexation; H_2O_2 titration; Detemplation; Fenton's chemistry

1. Introduction

The use of Fe-MFI systems is described in several publications in the 1990s [1–4]. Fe-ZSM5 catalysts attracted a lot of attention due to their extraordinary activity for hydrocarbon-assisted reduction of N_2O [5,6], N_2O reduction by NH_3 [7], oxidation of benzene to phenol [8] and selective catalytic reduction (SCR) of NO_x with hydrocarbons [9–12]. Recently, they were reported active for N_2O-assisted oxidation of alkanes to oxygenates products [13].

Different variants on Feng and Hall's approach [9,10,14] have been developed, including sublimation of $FeCl_3$ [15–21], high-temperature sublimation [22], and solid ion-exchange [11,12,23]. Alternatively, a method based on post-steamed isomorphously substituted Fe-ZSM5 zeolite was reported [24]. A major area of activity is, nowadays, focused on the characterisation of the active sites [15–21,25–31]. The subject is still controversial. Binuclear and isolated Fe species as well as Fe nanoparticles containing Al have been proposed as active sites for the various reactions mentioned. However, available data are not yet sufficient to discriminate between other active form(s) of Fe. The current publishing trends (Fig. 1) indicate that the characterisation of the active sites is the most popular topic, while new preparation and sustainable routes to incorporate Fe have received less attention in the last years. Indeed, most of the new input on preparations has been focused on the effect of the calcination-steaming cycles.

Differences in the incorporation methods for Fe can affect the activity and selectivity for a particular reaction. This is related to the different structure of the active sites. In addition to this, the nature of the starting material influences the final performance as well. Most of the preparations reported are based on commercial zeolites that are very heterogeneous. For industrial reactors, such heterogeneity is irrelevant but for few grams of catalyst it is critical.

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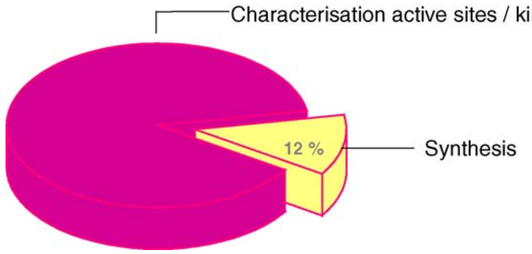

Fig. 1. Current publishing trends on Fe-zeolites during the 2001–2005 period. *Source*: ISI, Web of Knowledge (Thomson Corporation).

Assuming that the starting zeolite is rather homogeneous, another question remains unsolved. Will knowledge of the exact structure of the active sites enable us to design an improved catalyst? This is difficult to predict since we normally manipulate macroscopic variables like concentration, temperature, pH, drying rate, etc. Therefore, a detailed description of the active sites is not always mandatory to improve existing formulations.

Reviewing the most applied methods, they frequently lack of fully industrial perspective. CVD is based on $FeCl_3$, which yields corrosive HCl. In addition, the gas–solid contact is difficult to achieve, because $FeCl_3$ is mostly deposited at the beginning of the bed (heterogeneity). Formation of FeO_x has been observed upon calcination, which leads to pore blocking [32]. Framework substitution and steaming has been previously reported to give an active catalyst in our research group [24], but it lacks flexibility for the Fe-loading. The amount of Fe that can be incorporated is limited. For wet ion-exchange (WIE) this can be tuned with the Si/Al ratio.

To our understanding, the most simple-to-apply method for industrial practice is wet ion-exchange. However, the method still has several challenges: (i) understanding (via thermodynamics and practice) the Fe(III) hydrolysis and obtaining the optimal pH conditions to perform the exchange, (ii) utilization of the full exchange capacity of the zeolites, (iii) minimization of waste by using organometallic salts instead of nitrate and sulphate, and (iv) reducing steps during the synthesis. This will make the process faster and easier involving less equipment and manpower. All these aspects will be discussed below by introducing three new approaches on the synthesis of Fe-zeolites.

2. Materials and methods

2.1. Parent zeolites

The zeolites used were commercially acquired. ZSM-5 from Alsi Penta (AP-SM27), FER from TOSOH Corp. (720 KOA) and BEA from Zeolyst (CP-814E). They consist of an ammonium form with a Si/Al ratio around 8–12 to achieve high loading of Fe. In the case of FER, the starting form was Na/K, which was exchanged twice with NH_4NO_3 to get the NH_4-form. Chemical analysis for all the samples revealed some iron present as a trace (100–500 ppm).

2.2. Fe-incorporation

Both the *decomplexation* and the *one-pot* method will be thoroughly explained Section 3. The alkaline method will be explained below in detail as it involves more steps.

2.2.1. Alkali-treatment of the samples using NaOH solutions

The NH_4-ZSM5 zeolite was treated with an alkali solution at different conditions, followed by exchange with a NH_4NO_3 solution to recover the NH_4^+ form. Finally, iron was introduced by wet ion-exchange under controlled conditions.

For the alkaline treatment, the sample was subjected to a 0.2 M NaOH solution (75 ml/g). The slurry mixture was heated at 353 K under reflux for two durations (leaching time): 30 and 120 min. These values were selected after a preliminary screening over a wider window, and being representative for mild and severe conditions. The samples were then filtered, washed, dried, and finally exchanged twice with 0.5 M NH_4NO_3 at 353 K for 1 h.

The incorporation of Fe was done by wet ion-exchange (WIE), both on the as-received (reference) and alkaline-modified zeolite. WIE was carried out at pH 2.5 for a targeted Fe loading of 2.0 wt.% (ca. full exchange for Fe(III)). Finally, once filtered, washed and dried, the catalysts were calcined at 773 K for 4 h. Both the catalyst precursors (treated zeolites) and catalysts (containing Fe) are further referred to as AT-time (30 or 120 min) and Fe-AT-time, respectively.

2.3. Physical–chemical characterisation

Elemental analyses of the catalysts were done by ICP-OES (Perkin-Elmer Optima 3000DV (axial)).

Thermogravimetric analyses were performed in a Thermal Science STA 1500H apparatus, using a heating rate of 10 K/min in air.

Temperature-programmed reduction with H_2 was done in a Micromeritics TPD/TPR 2900 apparatus, using a high purity mixture of 10 vol.% H_2 in Ar to reduce samples. Cupric oxide (Aldrich) was used for calibration. The following procedure was applied: (i) heating samples in He at 423 K for 1 h, (ii) cooling down to room temperature in the same gas, (iii) flush with He during 0.5 h at room temperature to get the baseline stabilized, and (iv) switch to the reductive H_2/Ar mixture and start the temperature program (heating rate 10 K/min). The gas at the reactor outlet was passed through a cold trap to remove the water coming from the reduction before entering the detector (TCD).

The morphology of the samples was visually studied by scanning electron microscopy (SEM). Images were recorded with a Philips XL 20 microscope at 10 kV. Samples were coated with gold to improve contrast.

High-resolution low-pressure Ar physisorption was carried out in a QuantaChrome Autosorb-6B apparatus. Samples were previously evacuated at 573 K for 16 h. The pore-size distribution was calculated according to the Saito–Foley model applied to the adsorption branch of the isotherm [33].

2.4. Activity tests

N_2O decomposition was used as a model reaction. This allows an easy comparison between the new preparation methods with the conventional ones.

Activity tests were carried out in a six-flow reactor system [34]. In every run, 50 mg of catalyst particles (125–250 μm) was used. The catalysts were tested in pure N_2O/He conditions (4.5 mbar N_2O) at a total pressure of 3 bar-a. The term bar-a refers to absolute pressure. The space time, $W/F^0(N_2O)$, was 900 kg s mol^{-1} (W is the catalyst mass and $F^0(N_2O)$ is the molar flow of N_2O at the reactor inlet). The products were discontinuously analyzed by gas chromatography (Chrompack CP 9001) and continuously analyzed with a chemiluminescence NO-NO_2 analyzer (Ecophysics CLD 700 EL). If not otherwise stated, prior to reaction the catalysts were pretreated in He at 673 K for 1 h, and cooled down in the same gas to the starting reaction temperature. After 1 h on stream, the concentration of the different gases was constant and then considered steady state.

3. Results

3.1. Utilization of full exchange capacity of zeolites

We have observed systematically a low degree of Fe-exchange on ZSM5, well below the full exchange capacity. Visualizing the zeolite's crystals in Fig. 2A (>2 μm), the poor exchange is presumably related to crystal size. Big crystals imply large diffusional lengths for the Fe-species to reach the Brønsted sites inside the channels during ion-exchange. Therefore, the amount of iron that can be introduced is limited.

This problem can be circumvented by shortening the diffusional lengths. Acid treatment of zeolites is a well-known method to modify the Si/Al ratio by Al removal and creating mesoporosity [35,36]. In contrast, treatments using alkaline solutions remove preferentially silicon [37–44]. This will maintain the exchange capacity of the zeolite (Brønsted sites). We present a new approach based on fracturing the crystals-agglomerates by desilication. This implies treating the parent zeolite in a NaOH solution at different conditions. Two particular conditions were chosen representative of mild (AT-30) and severe (AT-120) leaching.

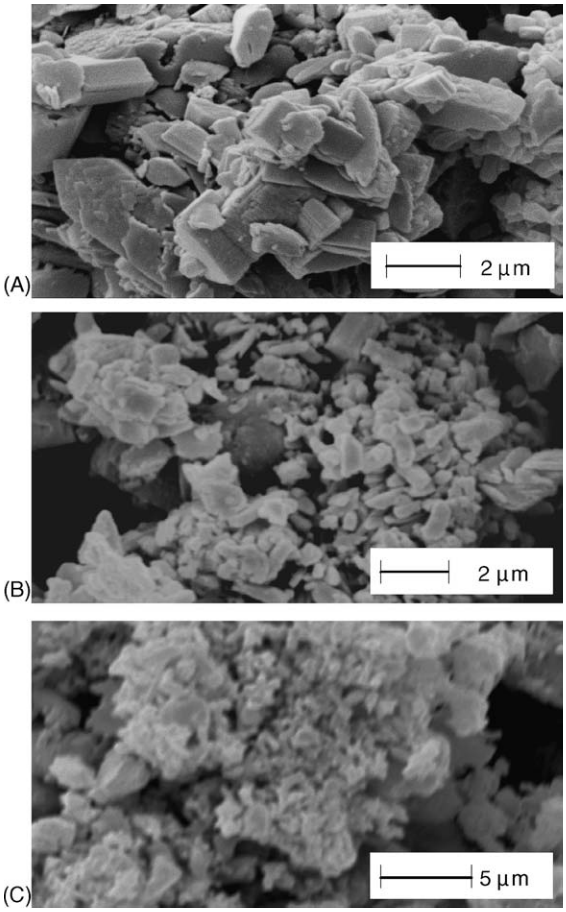

Fig. 2. SEM pictures of: (A) the parent ZSM-5 sample, (B) alkaline treated for 30 min (AT-30) and (C) 120 min (AT-120).

Visual inspection of the leaching effect on the sample morphology is given in Fig. 2. The as-received material (Fig. 2A) presents agglomerates of large crystals between 2 and

Table 1
Summary of data derived from ICP-OES and TPR analyses

Sample	Method	Fe target (%)	Fe-ICP (wt.%)	Si/Al (mol)	FeO_x/Fe_{total} (mol%)[e]
ZSM5[a]	–	–	468[d]	12.7	
Fe-ZSM5	Wet ion-exchange, pH 2.5	5.00	0.86	13.1	30
Fe-AT-30	Alkaline leaching, wet ion-exchange, pH 2.5	2.00	1.93	13.0	2
Fe-AT-120	Alkaline leaching, wet ion-exchange, pH =2.5	2.00	1.98	10.9	2
FER[b]	–	–	102[d]	9.2	–
Fe-FER nitrate	Wet ion-exchange, pH 2.5	0.50	0.44	9.7	0
Fe-FER citrate	H_2O_2-citrate	0.50	0.49	9.3	0
BEA[c]	–	–	58[d]	12.7	–
Fe-BEA nitrate	Wet ion-exchange, pH 2.5	1.70	1.74	14.0	13
Fe-BEA *one-pot*	Detemplating ion-exchange	1.70	1.60	12.8	0

[a] Alsi-Penta SM27.
[b] TOSOH HSZ-720 KOA.
[c] TOSOH HSZ-930 NHA.
[d] Concentration of Fe (ppm) found in the parent zeolites.
[e] Relative (mol) percentage of the total Fe. Rough calculation from TPR data.

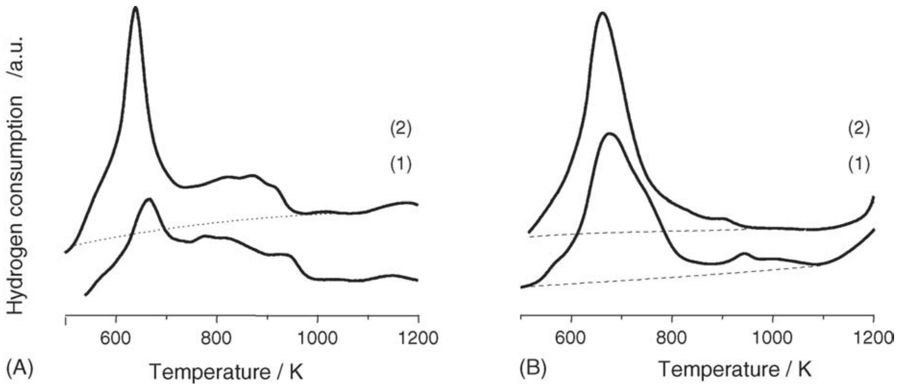

Fig. 3. H_2-TPR profiles of: (A) the untreated Fe-ZSM5 catalysts, (1) 0.5 wt.% Fe and (2) 5.0 wt.% Fe, both targeted and (B) profiles for the alkaline modified catalysts, (1) Fe-AT-30 and (2) Fe-AT-120. Conditions: 5% H_2/Ar; ramp. 10 K/min.

4 μm. A significant change is observed upon alkaline-treatment (Fig. 2B). Large crystals were broken down into smaller ones with sizes <1 μm. Similar results were obtained for both treatments (Fig. 2B and C). This anticipates that diffusional limitations during Fe ion-exchange has been sufficiently minimized or eliminated to allow full exchange.

This was confirmed by elemental analyses (Table 1). Two major conclusions can be drawn from ICP: (i) a fully exchanged ZSM5 zeolite can be prepared upon alkaline pre-treatment and (ii) the Si/Al decreases only after prolonged treatment. N_2-physisorption data (not shown) revealed that mesoporosity is developed only for 120 min-treatment. However, it is irrelevant for the exchange process, since shortening the crystal size allows full exchange (AT-30).

TPR measurements gave additional evidence for the full exchange. The alkaline-modified Fe-catalysts only contain Fe-exchange species (Fig. 3B) with a peak at ca. 700 K, while large proportions of FeO_x clusters (between 800 and 1000 K) are detected for the unmodified Fe-ZSM5 (Fig. 3A). Therefore, all the Fe is incorporated in the Brønsted sites.

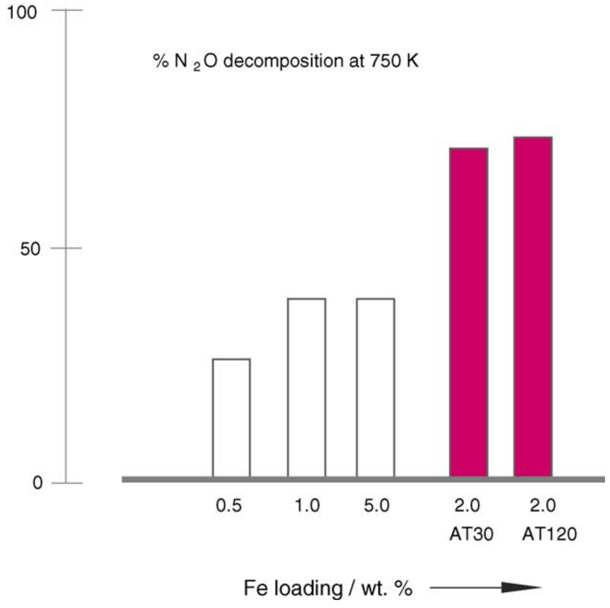

Fig. 4. Effect of the targeted iron loading on N_2O decomposition activity for the ZSM5 system. Hollow bars correspond to the untreated Fe-ZSM5 catalysts, while the filled ones are the Fe-AT catalysts. Reaction conditions: 4.5 mbar N_2O, He balance at 3 bar-a total pressure and $W/F^0(N_2O) = 900$ kg s mol^{-1}.

Based on this, an improvement in the N_2O-decomposition performance is envisaged for the modified samples. The tests were carried out in N_2O/He and showed the anticipated enhancement (Fig. 4). Such effect is due to the larger proportion of Fe exchanged in the zeolite matrix. For the Fe-AT-120 sample a slightly higher activity was observed, which is ascribed to the presence of the mesoporosity. This implies better diffusional transport through the created mesochannels.

Summarizing, Fe-ZSM5 is fully exchanged without the formation of FeO_x upon calcination, leading to an enhancement of the N_2O decomposition activity. This is achieved by controlling the size of the primary crystals of the zeolite, and thus enhancing its accessibility. Alkaline leaching is applied to achieve this.

3.2. Decomplexation for Fe ion-exchange of zeolites

According to WO 99/349017 [45] catalysts are prepared via ion-exchange using ferric nitrate and NH_4-Ferrierite, yielding the most active state-of-the-art Fe-catalyst for N_2O decomposition. However, one important issue that remains unresolved is the waste generated during manufacturing (NO_3^- and NO_x). Nitrates in waste water lead to eutrophication in the emitted water. Denitrification is expensive since facultative heterotrophic bacteria are conventionally used for that.

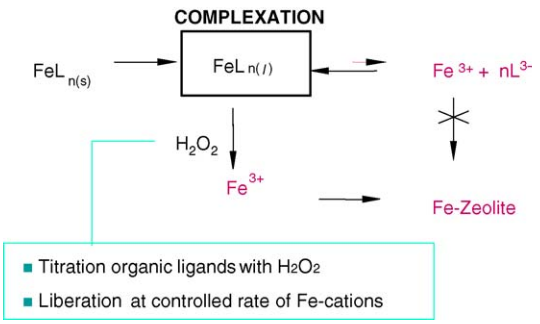

Fig. 5. Complexation of Fe with carboxylic ligands hinders the exchange process. Not all the Fe is exchanged. By using H_2O_2, the ligands can be oxidized and Fe is released at a controlled rate.

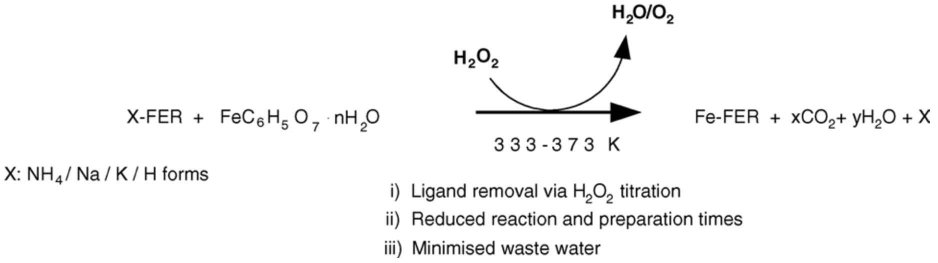

Fig. 6. Fe-FER was prepared by liquid ion-exchange by titrating the citrate groups with H_2O_2. The procedure only yields CO_2 and H_2O.

Alternatively, the use of organic Fe precursors, which yield CO_2 (instead of NO_x) and water during calcination will minimize the waste generated. Studies using Fe citrate, acetate and oxalate revealed that the performance of these catalysts was inferior to the conventionally exchanged ferric nitrate (data not shown), indicating that not all the Fe was exchanged. Organic salts form stable complexes with Fe cations, which hinder the exchange process. This is illustrated in Fig. 5. Such problem has already been reported by Marturano et al. on Fe(II)-oxalate over ZSM-5 [46]. Uncharged species $[Fe(C_2O_4)(H_2O)_4]$ were accounting close to 30% of the total iron in solution.

Our second concept presented is to break down complexation equilibria by titrating the chelates with H_2O_2. The removal of ligands liberates Fe^{3+} cations and/or partially charged Fe(III) hydroxocomplexes, and the exchange is expected to be improved (Fig. 5).

This approach was demonstrated for Fe-FER via the citrate route (Fig. 6). A set of catalysts was prepared using iron citrate ($FeC_6H_5O_7$, Sigma) as a precursor with 0.5 wt.% iron loading. The choice of this salt was based on the solubility in water and costs. The complexation of Fe(III)-citrate is very strong, log $K_{ML/M \cdot L}$ = 11.5, against 3.05 for Fe(II)-oxalate [47]. The strong complexation of Fe-citrate in combination with the larger molecular size makes its use for ion-exchange very difficult and challenging.

The Fe-citrate solution was added to the zeolite (NH_4-FER, TOSOH Si/Al=9). Then, the appropriate amount of H_2O_2 (30 wt.% in water, Merck) was added to the slurry. The total volume of the liquid added corresponded with ca. 150% of the pore volume of the zeolite. This approach is already known for impregnation as incipient wetness, but it is not applied in ion-exchange, where usually a large excess of liquid is used. Typically, ion-exchange is carried out for a much longer time (12–24 h). The reaction time could be reduced here to ca. 1 h since the N_2O-decomposition performance did not improve for longer times (not shown). After titration, the sample was dried at 373 K in the synthesis vessel for 2 h, and no washing was carried out. The sample was calcined at 823 K for 6 h, and tested in the decomposition of N_2O.

Temperature is very critical for the H_2O_2 oxidation potential. Fine-tuning experiments were performed at different temperatures: 333, 353 and 373 K. Fig. 7A shows the N_2O conversion level at 673 K for different titration temperatures. The optimal temperature was around 353 K. The activity level was even higher than the reference catalyst (Fe-FER prepared by conventional ion-exchange, according to [45]. An intermediate temperature (ca. 353 K) is optimal to break down the complexation equilibria efficiently.

It can be assumed that at lower temperatures the titration is slow and, therefore, not all the citrate complexes have been

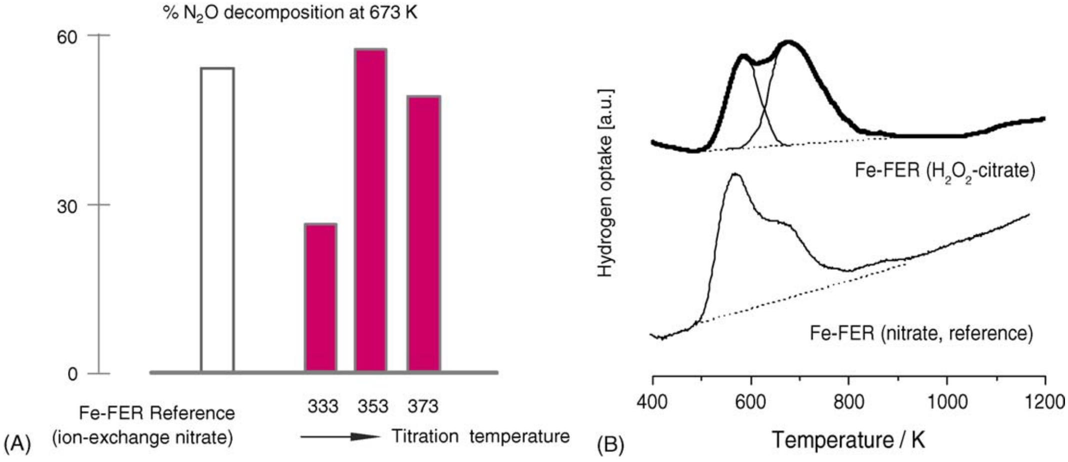

Fig. 7. (A) N_2O decomposition activity at 673 K for the Fe-FER at different H_2O_2-titration temperatures. Comparison is made with a reference catalyst prepared using Fe(III)-nitrate. Reaction conditions: 4.5 mbar N_2O, He balance at 3 bar-a total pressure and $W/F^0(N_2O)$ = 900 kg s mol^{-1}. (B) Temperature-programmed reduction of the citrate (top) and nitrate (bottom) Fe-FER catalysts. Conditions: 10% H_2/Ar mixture at 10 K/min heating rate.

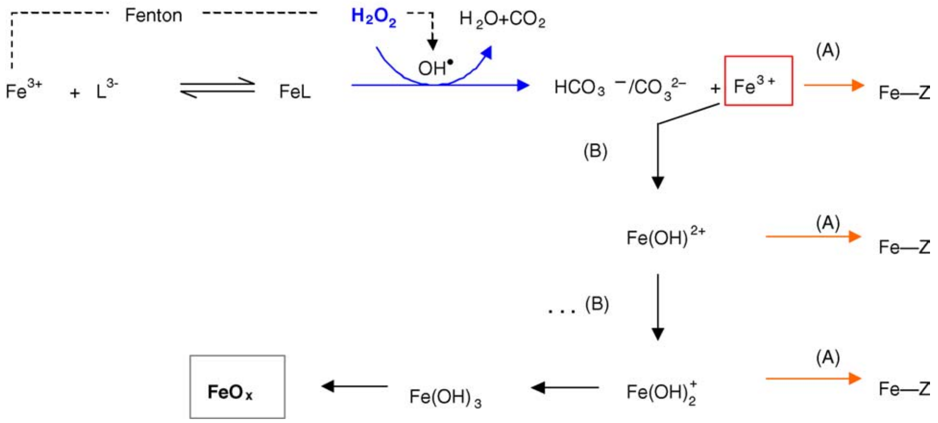

Fig. 8. Proposed titration mechanism when H_2O_2 is added to a Fe-citrate solution containing the zeolite (Z). Fe-exchange (route A) and precipitation to FeO_x (route B) can take place depending on the conditions of the titrations. Formation of weaker bicarbonate-Fe complexes can also takes places as compensating charge anion.

decomposed. At the highest temperature, the kinetics of the titration is that fast that the Fe-exchange with the zeolite is too slow and the excess Fe^{3+} is hydrolysed to $Fe(OH)_3$, which yields inactive species for N_2O decomposition. An intermediate temperature, where a balance between these competing processes is obtained, allows an optimal synthesis.

However, the results are not straightforward. Many phenomena occur during the removal of the ligands. For instance, the hydrolysis of metal cations [48]. Once the ligands are being removed, the metal cation starts to hydrolyse (Fe(III) to $FeO(OH)_x$), which in the end gives inactive hydroxide species (route B in Fig. 8). Based on the TPR results, the species in the optimal catalyst were similar to those typically encountered in the ion-exchanged catalysts using Fe-nitrates: Fe-hydr(oxo) complexes stabilized in the zeolites cavities [49,50]. The relative intensity of the peaks is different but it is clear that exchanged species are formed. No large FeO_x clusters that reduce at higher temperatures were detected. Formation of small-sized FeO_x clusters deposited on the external zeolite's surface cannot be ruled out from the characterisation carried out. Currently, research is ongoing to further clarify the possible (micro)precipitation.

The situation is even more complex since Fenton-like oxidation involving hydroxyl radicals occur as well. Ferric salts in presence of H_2O_2 generate $OH^\bullet$ radicals (Eqs. (1) and (2)) which are strongly oxidizing (Fenton's chemistry).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + OH^\bullet \quad (2)$$

The rate of oxidation depends on the initial concentration of ferric ions, which is not negligible according to thermodynamic calculations of ferric citrate solutions. Therefore, both direct H_2O_2 and hydroxyl radicals can both be involved on the oxidation.

In terms of performance, there is no doubt that the system is as good as that obtained with the conventional Fe-nitrate. The stability of the optimized catalyst (Fe-FER, H_2O_2-citrate-353) was evaluated as well. Simulated conditions of a nitric acid plant for 45 h on-stream, including the presence of NO, O_2 and H_2O together with N_2O, were employed. The results obtained were excellent. It shows high stability (no deactivation, activity loss $<2\%$) under such conditions.

So far, the use of an oxidant to remove organic ligands in solution has been claimed. Strong complexating equilibria can be overcome during ion-exchange by controlled redox titration of the ligands. Hydrogen peroxide oxidizes effectively citrate groups releasing Fe species at a controlled rate. This opens new ways to use organic salts of the metals in catalyst synthesis, which only renders water and carbon dioxide during titration. Additionally, hydrogen peroxide is a very clean solvent, as being decomposed in water and oxygen, which makes the preparation environmentally very attractive. As catalysts are specialty products, the market price of H_2O_2 (150 \$/mT, 100% basis [51]) is less critical than is usually the case in the chemical industry.

Concluding, we have developed a new synthesis route involving less waste water, much shorter synthesis time and less undesired gas emissions than calcination. The H_2O_2-citrate Fe-FER is a greener synthesis route and an example of Process Intensification [52]. An intensified process involves for instance less energy consumption, shorter time-to-market, but it does also require less waste emissions. Both aspects of the current study, the preparation and application of the catalyst in N_2O abatement, contribute to an intensified technology.

3.3. Combined detemplating and Fe ion-exchange

The preparation of Fe-zeolite involves multiple steps: (i) hydrothermal synthesis of the zeolite using organic templates, (ii) detemplation by thermal treatment, (iii) accommodation of the zeolite to the desired form (usually NH_4-form), (iv) incorporation of the Fe (ion-exchange), (v) drying, and (vi) calcination. Reducing the number of steps will contribute to an improved and faster synthesis process.

The last idea presented is the combination of the detemplation of the zeolite with the incorporation of the iron. This *one-pot*

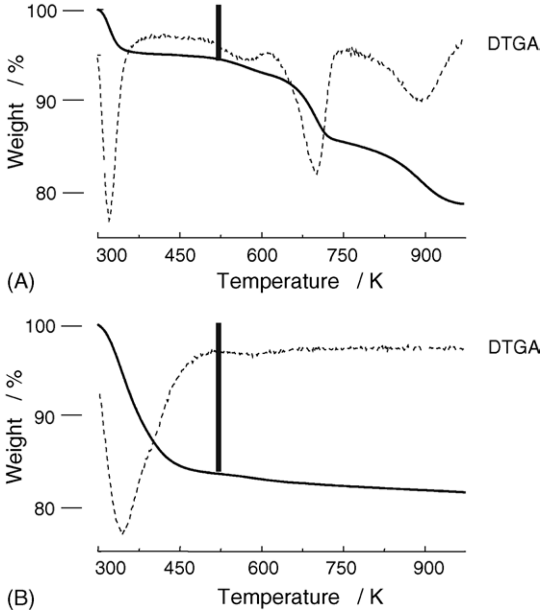

Fig. 9. Thermogravimetric analyses of: (A) BEA zeolite containing the template and (B) *one-pot* catalyst. Conditions: air atmosphere (100 ml/min) at 10 K/min heating rate.

process will simplify the abovementioned steps. To realize this: (i) a strong oxidant is necessary to remove the organic template molecules and (ii) Fe-cations for exchange. Both requirements are met with the so-called Fenton's reagent [53], a Fe^{2+} solution of H_2O_2 (diluted). Fe(III)-salts can also be used (Fenton's-like chemistry). The mixture is strongly oxidizing by the formation of $OH^{\bullet}$ radicals. Contacting the synthesized zeolite with this reagent leads to a *ready-to-use catalyst*.

The experiments were performed with a commercial BEA zeolite from TOSOH containing the template (HSZ-930NHA, Si/Al = 9.2 measured). Thermogravimetric analysis (TGA) shows three major weight losses around 350, 700 and 900 K (Fig. 9A). The first is due to physisorbed water, while the other two exothermal processes come from the template. Temperatures as high as 900 K are needed to completely remove the template.

The method differs slightly from the already reported in Ref. [54]. Adjustments were made to avoid possible run-away upon heating of the Fenton's mixture. An aqueous solution of Fe^{3+} and a 30%-H_2O_2 solution were simultaneously added dropwise to a slurry containing the zeolite at 333 K. The reaction was ended after 2 h after addition of all H_2O_2. The suspension was filtered off and the solid dried at 373 K overnight. The catalyst is referred to as *one-pot* Fe-BEA.

The effectiveness of the detemplation was studied by TGA (Fig. 9B). The sample presents one weight loss due to physisorbed water, while the template decomposition is missing (two steps). Additionally, the water content in the sample is significantly larger than for the original zeolite (see vertical lines in Fig. 9, 17 wt.% versus 5 wt.% respectively). This indirectly proofs that microporosity has been developed (more surface area) and water enters into the channels. The evolution of microporosity was studied by high-resolution low-pressure Ar physisorption. The pore-size distribution confirms the presence of microporosity in the *one-pot* catalyst. A pronounced development of a pore-size distribution between 5 and 8 Å with a maximum at 6 Å, characteristic of BEA channels ($\langle 1\,0\,0\rangle$ 12 $6.6 \times 6.7^{**} \leftrightarrow [0\,0\,1]$ 12 $5.6 \times 5.6^{*}$) is observed (Fig. 10).

Parallel to detemplation, Fe is incorporated into the zeolite. ICP analyses (Table 1) confirm that all the targeted Fe is incorporated into the sample, and it is close to its full exchange capacity. The Si/Al ratio stays close to the original value (no dealumination or desilication), which indicates that the sample is stable against such an oxidizing treatment. XRD analysis (not shown) indicates that the topology and crystallinity of the zeolite remains unchanged.

The Fe species were preliminary characterised by TPR (Fig. 11A). A Fe-BEA reference catalyst was prepared by the conventional ion-exchange method at pH of 2.5 with the previously calcined zeolite. This sample presents a main peak around 700 K due to Fe-exchanged into the zeolite, while a contribution at 850 K accounting for ca. 13% corresponds to clustered FeO_x. The *one-pot* sample presents different aspects. No FeO_x species were detected, and the Fe-species reduce at lower temperature than the reference one.

N_2O-decomposition results are given in Fig. 11B. The reference sample was calcined at 823 K for 4 h prior to the reaction as usually done in order to remove nitrate groups left in

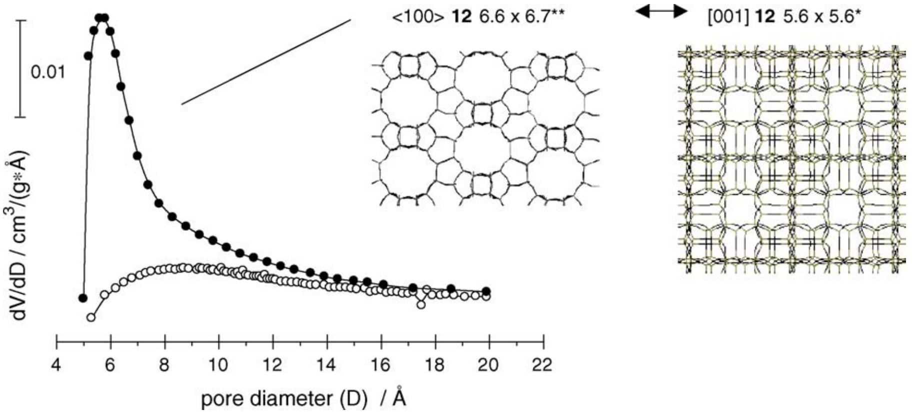

Fig. 10. Micropore size distribution (Ar physisorption) based on the Saito–Foley adsorption model [33]: (○) BEA zeolite containing the template, (●) *one-pot* catalyst.

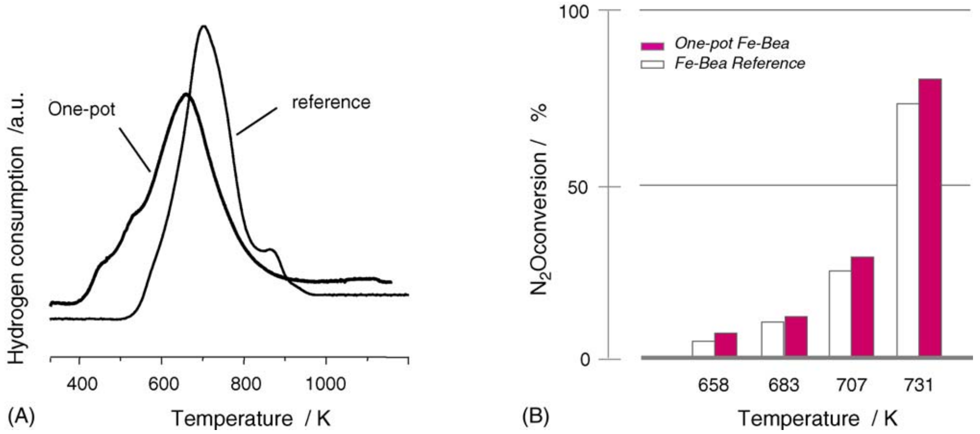

Fig. 11. (A) Temperature-programmed reduction of the *one-pot* and reference catalyst (based on conventional wet ion-exchange) Fe-BEA catalysts. Conditions: 10% H_2/Ar mixture at 10 K/min heating rate. (B) N_2O decomposition activity at different temperatures for both catalysts. Reaction conditions: 4.5 mbar N_2O, He balance at 3 bar-a total pressure and $W/F^0(N_2O) = 900$ kg s mol^{-1}.

the catalyst, while the *one-pot* was directly tested. The performance of the *one-pot* sample was superior at all temperatures to the reference catalyst. This correlates with the TPR data: (i) higher reducibility and (ii) the sample does not contain FeO_x.

Summarizing, application of Fenton's-chemistry to a templated BEA zeolite proves to be efficient for the combined detemplating and full Fe-exchange. $OH^\bullet$ radicals are able to oxidize the template at low temperature whereas Fe-cations are simultaneously exchanged into the Brønsted sites. The benefits of the approach are the reduction in time (manpower) and steps required in the preparation route (equipment). Additionally, the method avoids high-temperature calcination of the zeolite—both for detemplation and catalyst activation prior to the reaction—which minimizes the cracks in the structure.

4. Conclusions

Several unconventional aspects on the synthesis of Fe-zeolites have been discussed. First, utilization of full exchange capacity of zeolites is achieved by shortening diffusional lengths upon a *mild alkaline leaching treatment*. Iron was fully exchanged by wet ion-exchange on ZSM5 without the formation of Fe-oxides.

Decomplexation of organic ligands through H_2O_2 redox titration was described as a tool for catalyst synthesis. With this concept an improved preparation method for Fe-Ferrierite (Fe-FER) is developed. The catalyst shows excellent performance and durability for N_2O decomposition under realistic conditions of nitric acid plants. Further characterisation is needed to describe better the active sites generated through this new route.

Finally, Fenton's chemistry was successfully employed to the synthesis of Fe-zeolites by introducing the concept of *combined detemplation and Fe ion-exchange*. BEA zeolite has been simultaneously detemplated and Fe-exchanged by treating the parent zeolite with a Fenton's-type reagent (Fe^{3+}/H_2O_2) at low temperature. This *one-pot* process simplifies and speeds up considerably the preparation route. The catalyst shows excellent performance on N_2O decomposition compared to conventionally prepared Fe-BEA.

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