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Ben-Younes, N.; Martinez-Ortigosa, J.; Marie, O.; Blasco Lanzuela, T.; Mhamdi, M. (2021). Effect of zeolite structure on the selective catalytic reduction of NO with ammonia over Mn-Fe supported on ZSM-5, BEA, MOR and FER. *Research on Chemical Intermediates*. 47(5):2003-2028. <https://doi.org/10.1007/s11164-020-04382-7>



The final publication is available at

<https://doi.org/10.1007/s11164-020-04382-7>

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# Effect of zeolite structure on the Selective Catalytic Reduction of NO with ammonia over Mn-Fe supported on ZSM-5, BEA, MOR and FER

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**Abstract:** A series of catalysts based on Mn-Fe loaded zeolites was prepared by impregnation and their activity in the selective catalytic reduction of NO with ammonia (NH<sub>3</sub>-SCR) was investigated. The highest catalytic conversion was recorded for MnFe-ZSM-5 (MnFe-Z) followed by MnFe-BEA (MnFe-B) and MnFe-MOR (MnFe-M) while MnFe-FER (MnFe-F) showed a very poor activity over the entire temperature range. In order to evidence a correlation between the structure and acidity of the zeolites and NO conversion, the prepared samples were characterized by various techniques (ICP-AES, N<sub>2</sub> physisorption at 77K, XRD, <sup>27</sup>NMR, Raman, FTIR spectroscopy of adsorbed ammonia, H<sub>2</sub>-TPR, DRS UV-Vis, EPR and XPS). The superior catalytic activity of MnFe-Z at low temperature is attributed to the abundance of Mn<sup>4+</sup> concentration as revealed by XPS, the highest NH<sub>3</sub>-L/NH<sub>4</sub><sup>+</sup> ratio indicative of the contribution of metals in generating Lewis acidic centers as evidenced by IR-NH<sub>3</sub>, and the better reducibility of manganese and iron on ZSM-5 which increases the kinetics for red-ox cycles as confirmed in TPR analysis. Fe<sub>3</sub>Mn<sub>3</sub>O<sub>8</sub> mixed oxide phase is also detected by XRD and XPS and can be associated with the high reducibility of MnFe-Z which generates a high oxidation ability favoring NO to NO<sub>2</sub> oxidation. Raman spectroscopy was also used to confirm the existence of a strong synergy between metals and ZSM-5 support revealed by the shift in the signal position and the decrease in band intensities. The results showed that the zeolite framework and acidity generate catalysts with different textural and structural properties which influence the metal dispersion and speciation and hence influence the catalytic performances.

**Keywords:** Zeolites; Iron; Manganese; NO; NH<sub>3</sub>-SCR

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## 1. Introduction

The control of NO<sub>x</sub> emission has become one of the major environmental concerns that has attracted more attention for the past years. Abatement of nitrogen oxides has been forced through the introduction of regulation standards by environmental management authorities for both stationary and mobile sources. Among the commonly used technologies, Selective Catalytic Reduction of NO<sub>x</sub> by ammonia (NH<sub>3</sub>-SCR) was proved to be one of the best-established and efficient processes applied for the abatement of nitrogen oxides in the presence of oxygen excess. The catalyst is the key element in the SCR denitrification (de-NO<sub>x</sub>) system. The catalysts available for the SCR process cover a wide range of metal oxides and zeolites exchanged or impregnated with transition metal ions [1] and many others are under development. Since the late 1980's, studies have been amplified to replace common commercial SCR catalysts based on V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> promoted with WO<sub>3</sub> or MoO<sub>3</sub> and initially developed for stationary sources [2]. In this perspective, various transition metals (e.g. Ni, Co, Cr, Mn, Fe, Ce, Cu) have been studied with various formulations on different supports and showed good SCR activities. Among the studied supports, zeolites attracted great attention and research have been devoted to the study of the transition metal-based zeolite catalysts for NH<sub>3</sub>-SCR reaction. Redox properties of zeolites modified by transition metals are crucial to ensure good catalytic performances, as shown by various studies on different catalytic systems such as Fe/ZSM-5 [3], Fe/BEA [4], Cu/ZSM-5 [5], Cu/BEA [4], Cu/CHA [6], Cu/MOR [7], Co/ZSM-5 [8], Co/BEA, Co/MOR [7], Mn/ZSM-5 [8], Mn/MOR and Ni/MOR[7]. Among these studied catalysts, a lot of interest was given to manganese and iron as a consequence of their excellent catalytic properties. Long et al. [9] revealed that Fe-ZSM-5 exhibits better performances in SCR of NO by NH<sub>3</sub> at stationary sources compared to the classical vanadia based catalyst. Manganese are of interest because they contain diversiform oxidation states (Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup>) and generate different types of labile oxygen, which are necessary to complete the catalytic cycle [10]. Kapteijn et al. [11] reported that the highest SCR activity per unit of surface area is recorded for MnO<sub>2</sub> species followed by Mn<sub>5</sub>O<sub>8</sub>, Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>, while Mn<sub>2</sub>O<sub>3</sub> oxide presents the highest N<sub>2</sub> selectivity. Besides, compared to Cu, V, Ni and Co, Mn is generally recognized to be the least toxic and most abundant metallic component in the nature [12]. On the other side, the chosen zeolitic system has a considerable effect on the speciation of the loaded metals and leads to different catalytic behaviors. Several types of Si-rich zeolites with narrow pores showed excellent performances for the reduction of nitrogen oxides due to the low Al concentration in the framework (Si/Al>8) generating a strong Brønsted acidity [13]. Rahkamaa-Tolonen et al. [14] studied hydrogen, copper, iron and silver ion exchanged ZSM-5, mordenite, beta, ferrierite, and Y-zeolites. They affirmed that zeolites-based catalysts are very promising for the ammonia SCR reaction since the activity at low and high temperatures was higher than the activity of commercial vanadia-based catalysts. Sultana et al [15] made a correlation between the NO reduction ability of Pt/zeolite catalysts (ZSM-5, FER, MOR, BEA) and the zeolite structure and acidity. They proposed that the structure of the zeolite plays a key role in the NO conversion rather than Pt crystallite size and zeolite acidity. Some other studies reported also that the zeolite topology affects the catalytic performances of Mn- and Fe-zeolites. Qi et al [16] claimed that zeolites with medium and narrow channel-pore structures are suitable for NH<sub>3</sub>-SCR and SCO catalytic reaction. They found that the catalytic activity decreased as follow Fe-ZSM-5 > Fe-MOR > Fe-FER > Fe-Beta > Fe-Y. In their study, Chen et al [17] revealed that the catalytic activity in HC-SCR reaction with iso-butane and propane over different Fe/zeolites decreased as follow: Fe/BEA > Fe/MFI >> Fe/FER > Fe/MOR ≈ Fe/Y. According to Putluru et al [18], both metal and support influence the catalytic activity. They claimed that, at 300°C, the catalytic activity follows the next sequence for iron: Fe/ZSM-5 > Fe/BEA > Fe/SSZ-13 while for manganese it follows this order: Mn/BEA > Mn/SSZ-13 > Mn/ZSM-5.

In the last decade, trends were directed to the development and study of bimetallic catalysts and it has been shown that the addition of a second metal to both zeolitic and non-zeolitic catalytic systems can significantly improve their activity. One of the most studied systems during the last five years is the Fe-Cu/ZSM-5 catalyst which combines the good low temperature activity of Cu and the high temperature activity of Fe, resulting in the expansion of the temperature range[19]. Saeidi and Hamidzadeh [20] reported that Fe, Co and Cu co-doping in Mn/ZSM-5 enhanced the catalytic performance in the SCR of NO by ammonia reaching approximately 100 % of NO<sub>x</sub> conversion in the low temperature range. Jouini et al. [21] studied SCR reaction over Fe-Cu modified highly silicated zeolites (BEA, MOR and FER). They claimed that the amount, environment and distribution of metal species is controlled by the zeolite framework. Carja et al. [22] indicated that Ce addition to Fe/ZSM-5 increased considerably the NO conversion (>75%) in a wide temperature range due to a specific interaction of both metals within the zeolite framework. In another work, Carja et al [23] demonstrated that a complex porous structure combining both micro and mesoporous features is formed on Mn-Ce/ZSM-5 upon Mn and Ce over exchange leading to high activities in a broad temperature range (>75%). Within this large variety of catalysts, manganese-based formulations have once again attracted attention for their good conversion at low temperature whereas iron appeared to be one of the most adequate co-loaded metal due to its high level of activity. For instance, Krivoruchenko et al. [24] developed a Mn-Fe/Beta bifunctional catalyst and found that the formation of MnO<sub>x</sub>

clusters favors NO oxidation, while Fe cations facilitate the “fast-SCR” reaction. Iron is also used as promoter for Mn/zeolites catalysts. Indeed, Wang et al [25] studied the effect of iron modification on Mn-Fe/ZSM-5 system. XRD and XPS analysis showed that the addition of an appropriate amount of iron on Mn/ZSM-5, promotes the dispersion of active components and increases Mn<sup>4+</sup> ratio which would enhance the “fast-SCR reaction”. In the same context, Lin et al [26] found that Fe addition enhances the dispersion of both manganese and iron and improves the surface acidity of 10%Mn-8%Fe/USY catalyst which increases the concentration of adsorbed ammonia and thus enhances the catalytic activity. To the best of our knowledge, most of the reports dealing with zeolites co-exchanged with iron and manganese focus on ZSM-5 and BEA systems. Therefore, it is of interest to extend these studies by comparing the catalytic activity of previously studied supports such as ZSM-5 and BEA to other zeolites such as MOR and FER in order to highlight the difference between their catalytic performances. Thus, this study aims at obtaining knowledge on the influence of the zeolite structure (ZSM-5, BEA, MOR and FER) in the NH<sub>3</sub>-SCR reaction with excess of oxygen. The catalysts properties were studied using several physicochemical techniques (ICP-AES, N<sub>2</sub>-physisorption, XRD, <sup>27</sup>Al-NMR, Raman, FTIR-ammonia, H<sub>2</sub>-TPR, UV-Vis, EPR and XPS) in order to determine a relationship between the zeolites topology and catalytic performance for SCR of NO with NH<sub>3</sub>.

## 2. Experimental

### 2.1. Catalysts preparation

The catalysts were prepared by incipient wetness impregnation of commercial zeolites provided by Zeolyst International (NH<sub>4</sub><sup>+</sup>-ZSM-5 (Si/Al=15), NH<sub>4</sub><sup>+</sup>-BEA (Si/Al=12.5), NH<sub>4</sub><sup>+</sup>-MOR (Si/Al=10) and NH<sub>4</sub><sup>+</sup>-FER (Si/Al=10)) with two precursor salts: manganese chloride (Sigma-Aldrich) and ferric chloride (Sigma-Aldrich) in a two steps method. In the first step, the commercial zeolite and MnCl<sub>2</sub>.4H<sub>2</sub>O precursor (with a target of 4% wt of Mn) are dissolved in a sufficient quantity of water in order to obtain a homogeneous paste. The mixture is stirred for 4 hours and then dried in the oven at 100°C overnight. The obtained sample is then heated in argon flow (25 cm<sup>3</sup>.min<sup>-1</sup>) for 4 hours at 500°C (5°C per minute). The powder obtained in the first step is finely grounded, mixed with iron chloride FeCl<sub>2</sub> (with a target of 2% wt of Fe) and water, dried and heated again under argon at 290°C in order to avoid iron sublimation during the heat treatment.

The prepared samples were denoted as MnFe-Z, MnFe-B, MnFe-M and MnFe-F.

### 2.2. Catalytic activity measurements

The catalytic activity of MnFe-zeolites was tested in a fixed bed quartz reactor at atmospheric pressure. The sieved catalysts (0.4–0.6 mm) were introduced (about 500 mg) and heated up to 550°C under an inert atmosphere (nitrogen) and further maintained at this temperature for 1h. The experiments were carried out by decreasing the temperature stepwise between 550 and 200°C. The composition of the feed gas mixture was 800 ppm NO, 800 ppm NH<sub>3</sub> and 5% O<sub>2</sub> using N<sub>2</sub> as the balance gas using a total flow of 700 mL/min. The conversion of NO was measured under steady state conversion at each temperature by a Thermo Electron Corporation Model 42C chemiluminescence gas analyzer.

The NO conversion was calculated according to the following equation:

$$NO_{conversion} = \frac{NO_{in} - NO_{out}}{NO_{in}} \times 100$$

$$S_{N_2} = \frac{NO_{in} + NH_{3in} - NO_{out} - NH_{3out} - 2N_2O_{out}}{NO_{in} + NH_{3in} - NO_{out} - NH_{3out}} \times 100$$

where NO<sub>in</sub>, NH<sub>3in</sub> are the inlet NO and NH<sub>3</sub> concentrations and NO<sub>out</sub>, NH<sub>3out</sub>, N<sub>2</sub>O<sub>out</sub> are the outlet NO, NH<sub>3</sub> and N<sub>2</sub>O concentrations.

### 2.3. Catalysts characterization

In order to determine the amount of metals in the synthesized catalysts, inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out in a Varian 715-ES equipment.

N<sub>2</sub> Adsorption–desorption measurements at 77 K were performed with a Micromeritics ASAP 2020 apparatus. The samples were preliminary outgassed at 200 °C for 4h under vacuum. The specific surface area and total pore volume were determined by BET and BJH methods, respectively.

The XRD pattern of the fresh samples were collected using a PANalyticaCubix diffractometer, with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a graphite monochromator, in the  $2\theta$  angle range of 5–50°. The phase composition of the samples was determined using the software PANalyticalX'PertHighScore. The diffractograms were compared to the references provided by the International Centre for Diffraction Data (ICDD).

<sup>27</sup>Al MAS NMR spectra were recorded at room temperature on a Bruker WB spectrometer with a frequency of 104.21 MHz and using Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as a reference material. For the measurements, an excitation pulse of 1.0 microsecond corresponding to a flip angle of the magnetization of  $\pi/12$  and a recycle time of 6 ms and 60 ms respectively, were used accumulating 4096 free induction decays.

Raman spectra were collected with a Horiba Jobin Yvon-Labram HR UV–vis-NIR (200–1600 nm) Raman Microscope Spectrophotometer, using a 512 nm laser as the excitation source. The spectra were recorded by averaging 10 scans at a resolution of 2 cm<sup>-1</sup>.

In situ IR adsorption of ammonia as probe molecule was performed in order to quantify Lewis and Brønsted acid sites of metal exchanged-zeolites. Previous to experiments, pellets of the samples (2 cm<sup>2</sup>, 12-17 mg) were first heated under vacuum ( $< 10^{-6}$  Torr) at 500 °C during 1h. Small doses of ammonia were injected at room temperature. The concentrations of both Brønsted (NH<sub>4</sub><sup>+</sup>) and Lewis (NH<sub>3</sub>-L) acid sites were calculated, after mass correction on the bases of the areas of the bands after saturation with ammonia, using extinction coefficient values from the literature ( $\epsilon_{\text{NH}_4^+} = 12 \text{ cm}^2 \mu\text{mol}^{-1}$  [27] ;  $\epsilon_{\text{NH}_3\text{-L}} = 2.6 \text{ cm}^2 \mu\text{mol}^{-1}$  adapted from [28]). The IR spectra were recorded at room temperature with a Nicolet 6700 FTIR spectrometer equipped with a DTGS detector at a spectral resolution of 4 cm<sup>-1</sup> by accumulating 128 scans.

H<sub>2</sub>-TPR analysis were performed using a Micromeritics AutoChem 2920 analyzer. The samples were pretreated in a U-shaped quartz cell under 5vol% O<sub>2</sub> in He at 500 °C (10 °C/min) with a total flow of 30 cm<sup>3</sup> min<sup>-1</sup> for 30 min and then cooled down to 30°C under helium. The samples were then reduced in a stream of 5 vol% H<sub>2</sub> in Ar at a flow rate of 15 mL min<sup>-1</sup> up to 700°C using a temperature ramp of 10°C/min.

DRS UV–vis spectra were collected in the wavelength range of 200-800 nm using BaSO<sub>4</sub> as reference material. Perkin Elmer Lambda 45 spectrophotometer apparatus equipped with a diffuse reflectance attachment was used for the measurements.

EPR spectra were recorded at 105 K on a Bruker EMX-12 spectrometer operating in the X band with a frequency and an amplitude modulation of 100 kHz and 1.0 Gauss respectively.

SPECS spectrometer equipped with an MCD-9 detector with Al-K $\alpha$  X-ray ( $h\nu = 1486.6 \text{ eV}$ ) was used to perform the X-ray photoelectron spectroscopy (XPS) analysis. The binding energy values obtained in the XPS analysis were corrected by the C<sub>1s</sub> peak at 284.6 eV.

## 3. Results

### 3.1. NH<sub>3</sub>-SCR performance

**Fig. 1** NO conversion and N<sub>2</sub> selectivity over MnFe-Z, MnFe-B, MnFe-M and MnFe-F catalysts

Figure 1 compares the DeNO<sub>x</sub> performances N<sub>2</sub> selectivity of the MnFe-loaded catalysts in the 250-500°C temperature window. The catalytic activity increases as a function of temperature up to 400°C. Among the different samples, MnFe-Z reveals a better activity in the whole temperature range compared to MnFe-B, MnFe-M and MnFe-F. All the catalysts exhibit their maximum NO conversion at high temperature (~400°C). The maximum conversion is around 64% for MnFe-Z, 60% for MnFe-BEA, 59% for MnFe-M and 56% for MnFe-F. In the high temperature range (above 400°C), a clear similarity in the catalytic activity of MnFe-B and MnFe-M can be noticed. In the low temperature range, the differences in NO conversion between the catalysts are more pronounced. MnFe-Z exhibits significantly higher activities with a conversion (at 250°C) of 45%, being only 19% for MnFe-F. MnFe-B and MnFe-M show 33 and 23% respectively, at the same temperature. Thus, below 400°C, the activity of the different MnFe-Zeolites is found to be in the following order: MnFe-Z > MnFe-B > MnFe-M > MnFe-F. It is worth noting that the catalysts present different behaviors for samples possessing a similar composition pointing out that the zeolite topology has a considerable effect on the catalytic activity. Indeed, the studied zeolites possess different pore structure, pore size and surface acidities which influence their catalytic behavior. ZSM-5 zeolite has a 3-dimensional pore structure which results from the interconnection of straight and sinusoidal channels linked perpendicularly and delimited by a 10-membered ring (0.52-0.57 nm in diameter). BEA zeolite is formed by the stacking of two very open zeolitic phases revealing two pore subsystems formed by cycles

with 12-membered rings (or tetrahedra). The first phase is described by two identical linear channel systems which are mutually orthogonal and parallel to c-axis (0.66 - 0.67 nm in diameter). The intersection of these channels creates a second subsystem elucidated as a one-dimensional channel parallel to a-axis with a pore opening diameter of about 0.55 -0.56 nm. Both ZSM-5 and BEA with a 3-dimensional pore structure may ensure better diffusion of the reaction molecules allowing better interaction with the active sites. The MOR pore structure has a two channels system consisting in an elliptical and noninterconnected channels parallel to the c-axis formed by 12-membered rings (0.6 -0.7 nm) and perpendicular 8-membered ring channels. These channels are connected together by pores called “side pockets”, that only allow the diffusion of small molecules. Thus, the mordenite microporous system can be described essentially by a two-dimensional network with elliptical channels with 12 rings along the c direction and a limited diffusion in the b direction (side pockets), explaining the poor conversion specially at low temperature. FER pore structure is composed of perpendicular 10- and 8-ring channels. Parallel to the 10-membered ring channels, stand up channels with 6-membered ring whose intersection with the 8-membered ring channels form cavities. These cavities are only accessible through 8-ring channels. With its smaller channels aperture and the related difficulty of accessing the cavities, FER support may limit the access of reaction molecules to the sites inside the pores. On the other side, regarding the low catalytic performances of these catalysts compared to the literature, it is worth noting that the use of chloride precursors may also be involved in the drop of the catalytic activity. In our case, the maximum of NO conversion reaches only 64% at 400°C for MnFe-Z catalyst. In previous work, Kim et al. [29] reported that iron addition in Mn/ZSM5 catalyst enhanced the NO conversion performance in the low temperature region (80% of NO conversion at 160°C). Wang et al. [25] also reported that a reasonable amount of iron facilitates the catalytic activities (96% of NO<sub>x</sub> conversion at 100°C). Both studies used nitrate precursors for the introduction of the metals. Indeed, in addition to the fact that metals impact the catalytic performance, the nature of the precursors used may also play an important role in determining their catalytic efficiency. This may be correlated to a low degree of MnCl<sub>2</sub> decomposition as reported by Vankova et al. [30]. These results were also observed by Xu et al. [31] study, who suggested that acetate and nitrate precursors reach better performances than chloride precursors on Mn/ZSM-5 and Mn/BEA catalysts. Yet, other studies [16][32] reported that in the case of iron, chloride precursor is more suitable for DeNO<sub>x</sub> application at high temperature when introduced by Chemical vapor ion exchange (CVD) or Solid state ion exchange (SSIE) methods. The presence of iron may explain the rise in the activity at around 400°C but its effect may still be limited the presence of MnCl<sub>2</sub>.

N<sub>2</sub> selectivity was above 80% over the tested Mn-Fe based catalysts as shown in Fig. 1. The formation of N<sub>2</sub> is slightly more rapid for MnFe-Z, MnFe-B and MnFe-M in the low temperature range; starting at 250°C, then increasing to reach a maximum at around 400°C and shows no exhaustion up to 500°C.

### 3.2. Physicochemical Characterization

#### 3.2.1. ICP-AES and N<sub>2</sub> physisorption at 77K results

**Table 1** Results of ICP-AES and N<sub>2</sub> physisorption at 77 K

Catalysts	Mn (wt %)	Fe (wt %)	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>mic</sub> (m <sup>2</sup> )	Pore volume (cm <sup>3</sup> /g)
NH <sub>4</sub> -ZSM-5	-	-	367	291	0.22
MnFe-Z	3.36	2.04	273	185	0.16
NH <sub>4</sub> -BEA	-	-	556	398	0.88
MnFe-B	4.49	2.51	444	272	0.76
NH <sub>4</sub> -MOR	-	-	336	274	0.82
MnFe-M	3.79	2.06	312	265	0.11
NH <sub>4</sub> -FER	-	-	337	275	0.21
MnFe-F	4.27	2.30	234	196	0.08

Table 1 shows the chemical composition of the synthesized manganese and iron supported zeolites. The values obtained are close to the theoretical content expected from the preparation method (4 and 2 wt% for Mn and Fe respectively), which confirms that, as expected, the impregnation or the heat treatment did not affect the samples. The metals are loaded either on the external surface of the zeolites or inside its channels. A slight increase in the mass percentage may be noticed for MnFe-B and MnFe-F catalysts that can be attributed to experimental errors. The textural properties obtained from the N<sub>2</sub>-adsorption/desorption isotherms of the different catalysts and their parent zeolites are also gathered in Table 1. As expected, the impregnation process is accompanied with a decrease in the initial specific surface area for all the samples. This extent of decrease suggests the presence of oxide aggregates sufficiently bulky to partially block the pores either inside or at the entrance of the zeolites channels. It

is well known that a large specific area provides more reactant gases adsorption sites on the surface, promoting the SCR reaction at low temperature [33]. Xu et al. [31] found that, to a certain extent, changes in textural properties of Mn/ZSM-5 and Mn/BEA catalysts can be correlated to SCR performances. They reported that catalysts prepared using manganese chloride as precursor exhibit a low NO conversion and present a great loss of the specific area of the parent zeolite compared to those prepared from nitrate and acetate precursors. In our case, the specific area cannot be correlated with the catalytic activity as the BET area follows the sequence: MnFe-B > MnFe-M > MnFe-Z > MnFe-F. Thus, although MnFe-Z and MnFe-F present the lowest surface area, the first exhibit the highest catalytic activity and the second the lowest activity suggesting that the specific area itself may not be a decisive factor influencing MnFe-zeolite SCR activity, as reported for Mn-Ce [33] and V<sub>2</sub>O<sub>5</sub>-MnO<sub>x</sub> based catalyst[30].

### 3.2.2. XRD results

**Fig. 2** XRD patterns of parent zeolites and MnFe-zeolite

Fig. displays the XRD patterns of pure and exchanged zeolites. The X-ray diffraction analysis shows that the crystal structure of the zeolites was preserved during the impregnation and the heat treatment. Nevertheless, the diffractograms reveal a slight decrease in the intensity of the peaks compared to the parent zeolite indicative of potential interaction between metals and the zeolites[25]. This decrease may also be the consequence of the higher X-ray absorption coefficient of Fe and Mn compounds [35]. MnFe-B, MnFe-M and MnFe-F samples show no additional obvious characteristic peaks besides the standard diffraction patterns of the pure zeolites. The absence of peaks attributed to iron and/or manganese oxides indicates that the species are quite poorly crystallized and well dispersed. They may also be amorphous or present in a nanocrystalline state or as small crystallites with a size less than 4 nm in diameter undetectable by XRD. In the case of MnFe-Z, new peaks at 12.7°, 21.9°, 27.1°, 33.5° and 35.2° appeared. The first two peaks correspond to MnO<sub>2</sub> phase (ICDD PDF card # 82-2169). The peak observed at 27.1° can be attributed to Mn<sub>2</sub>O<sub>3</sub> species (ICDD PDF card # 78-0390). Hematite Fe<sub>2</sub>O<sub>3</sub> appears at 2θ=33.5° (ICDD PDF card # 33-0664). The peak at 35.2° may be related to the formation of a new phase such as Fe<sub>3</sub>Mn<sub>3</sub>O<sub>8</sub> (ICDD PDF card # 89-4837). The presence of these peaks with a relatively low intensity indicates that manganese and iron oxides are present to a low extent.

### 3.2.3. <sup>27</sup>Al-NMR MAS results

**Fig. 3** <sup>27</sup>Al MAS NMR spectra of pure and exchanged zeolites

<sup>27</sup>Al magic-angle spinning (MAS) NMR spectroscopy was performed to understand the chemical environment of this nucleus after impregnation (Fig. ). NMR spectra of the parent zeolites show a strong signal at around 54 ppm and a weak pic at 0 ppm, corresponding to tetrahedrally coordinated Al species in the framework and extra-framework octahedrally coordinated Al species respectively [36]. The overall intensity of the spectra, and especially that of tetrahedral Al, decreases and the signals appear broadened upon manganese and iron loading, due to the interaction with paramagnetic cations (Fe<sup>3+</sup>, Mn<sup>2+</sup>) which may prevent the observation of all aluminum. Anyhow, the spectra strongly suggest that zeolite dealumination does not occur after heat treatment, testifying of i) the stability of the different zeolite structures as suggested by XRD analysis and ii) the absence of extra-framework aluminum species (EFAL).

### 3.2.4. Raman results

**Fig. 4** Raman spectra of (a) MnFe-Z, (b) MnFe-B, (c) MnFe-M and (d) MnFe-F

Raman spectra of MnFe-B, MnFe-M and MnFe-F (Fig. ) display the same bands located at 222, 290, 403, 490, 605 and 640 cm<sup>-1</sup>. These bands are commonly attributed to hematite species (α-Fe<sub>2</sub>O<sub>3</sub>) [37]. However, the band at 640 cm<sup>-1</sup> usually appears with a weak intensity as reported by Léon et al [38]. Moreover, it was reported that this band can also be assigned to MnO<sub>2</sub> species [39]. Thus, regarding the intensity of this band and based on XPS results on these samples (see paragraph 3.2.9), the band at 640 cm<sup>-1</sup> is ascribed to MnO<sub>2</sub> species. Another broad band located at around 1300 cm<sup>-1</sup> for the same samples can be assigned to a two-magnon scattering which arises from the interaction of two magnons created on antiparallel close spin sites in antiferromagnetic hematite [40]. MnFe-Z catalyst shows bands at 185, 251 and 338 cm<sup>-1</sup>. The first band is ascribed to MnO<sub>2</sub> species [41] and the two second bands are assigned to hematite (α-Fe<sub>2</sub>O<sub>3</sub>). It can however be noticed that only one large band with a

sharp peak appears at around  $610\text{ cm}^{-1}$  replacing the two bands at  $605$  and  $640\text{ cm}^{-1}$  observed for the other catalysts. The band broadening reflects contributions arising from single oxide phases, along with those due to the presence of amorphous Fe-Mn mixed oxide phases as reported by Herranz et al. [42]. On the other hand, the shift of the bands of MnFe-Z to lower wavenumbers reveals a strong interaction between the ZSM-5 support and the metals showing a better dispersion of manganese and iron within the zeolitic structure. We can also note that the intensity of the bands changes depending on the support in the following order: FER > MOR > BEA > ZSM-5. The decrease in the intensity also reveals a better dispersion of the metals within the ZSM-5 structure ensuring better synergy between the metals and the support, thus probably enhancing the catalytic activity.

### 3.2.5. IR-NH<sub>3</sub> adsorption results

**Fig. 5** FTIR spectra of ammonia adsorbed on MnFe-zeolite

The FTIR-spectroscopic investigation of ammonia adsorption is a common method used for the quantification of both Brønsted and Lewis acidic sites [43]. Figure 5 presents IR spectra of adsorbed ammonia on MnFe-zeolite. The catalysts present four distinguished bands at around  $3370$ ,  $3280$ ,  $3214$  and  $3182\text{ cm}^{-1}$  and two others at  $1614$  and  $1470\text{ cm}^{-1}$  after ammonia small doses adsorption. The bands at  $3370$  and  $3280\text{ cm}^{-1}$  can be assigned to  $\nu(\text{NH})$  stretching modes for ammonium ions, while the bands at  $3214$  and  $3182\text{ cm}^{-1}$  can be attributed to coordinated ammonia. The bands at around  $1470\text{ cm}^{-1}$  are associated to the  $\delta(\text{NH})$  bending mode for  $\text{NH}_4^+$  (Brønsted acidic sites), while the bands at  $1614\text{ cm}^{-1}$  can be assigned to bending vibrations of the N–H bonds in the  $\text{NH}_3$  coordinated to the Lewis acidic sites  $\text{NH}_3\text{-L}$  [44]. Small doses of ammonia were introduced in the cell in order to follow the evolution of Lewis and Brønsted acid sites. Evaluation of the total acidity was performed based on the area of the bands in the  $\delta(\text{NH})$  region for both Lewis and Brønsted acid sites for each sample. Above each IR spectra is plotted the area of these bands as a function of the number of moles of introduced ammonia. The extinctions coefficients associated to the Lewis and Brønsted acid sites are different, yet these graphs show linearity in the evolution of the bands associated with both sites. This indicates that ammonia does not have any particular interaction with one site. Therefore, the spectrum corresponding to the last small dose of introduced ammonia (before saturation with  $\text{NH}_3$  equilibrium pressure) was used to determine the ratio between Lewis and acid Brønsted sites. Table 2 gathers the theoretical and experimental acidity of the samples as well as the ratio between Lewis and Brønsted acid sites determined by IR quantitative measurements of ammonia sorption in MnFe-zeolite.

**Table 2** Quantification of Lewis and Brønsted bands from Infrared spectra of chemisorbed ammonia

	Theoretical acidity calculations ( $\mu\text{mol.g}^{-1}$ )				Experimental acidity calculations ( $\mu\text{mol.g}^{-1}$ ) <sup>c</sup>	$\text{NH}_3\text{-L}/$ $\text{NH}_4^+$ <sup>d</sup>
	Zeolite <sup>a</sup>	Mn <sup>b</sup>	Fe <sup>b</sup>	Total		
<b>MnFe-Z</b>	1040	612	366	2020	3138	7.8
<b>MnFe-B</b>	1230	818	450	2500	2750	3.95
<b>MnFe-M</b>	1520	690	369	2570	2418	1.48
<b>MnFe-F</b>	1520	778	412	2710	2428	1.73

<sup>a</sup> Calculated from Si/Al values of each zeolite

<sup>b</sup> Calculated from %wt given by ICP analysis

<sup>c</sup> Calculated based on the area in presence of  $\text{NH}_3$  equilibrium pressure

<sup>d</sup> Calculated via  $\epsilon$  from the literature using individual peak area (Lewis or Brønsted) after the last small  $\text{NH}_3$  dose

It is clearly shown that the acidity of the different catalysts depends on the zeolite type being loaded with the same content of Mn and Fe. More precisely, the comparison between theoretical calculations of acidity and those based on spectrum at  $\text{NH}_3$  saturation (under  $\text{NH}_3$  equilibrium pressure) clearly reveals an overestimation especially for the MnFe-Z catalyst. Indeed, the theoretical maximum total value for acid sites is evaluated from the hypothesis that the whole metal loaded through impregnation is highly dispersed at the external area of the zeolites crystallites. As a consequence, the total acidity is considered as the sum of the sites arising from the zeolite and each of the metal assuming a 1:1 stoichiometry. These hypotheses thus lead to a maximum limit value for the total amount of acid sites. The higher value measured from the amount of  $\text{NH}_3$  adsorbed at saturation (at room temperature) most probably arises from physisorbed  $\text{NH}_3$  and soft interaction leading to oligomeric H-bonded species such as  $\text{NH}_4^+ \dots \text{NH}_3$ . A semi quantitative approach was then preferred, applying  $\epsilon$  values from the literature for each single species, i.e  $\text{NH}_3\text{-L}$  or  $\text{NH}_4^+$ . The spectra obtained just before the  $\text{NH}_3$  equilibrium pressure were submitted to integration of bands area and the Table 2 reports the estimated  $\text{NH}_3\text{-L}$  to  $\text{NH}_4^+$  molar ratio.



Assuming from the NMR data that no or negligible amount of Lewis acidic sites is expected from the zeolite itself (no detected EFAL species), one must conclude that the  $\text{NH}_3\text{-L}$  IR signal comes essentially from the interaction between ammonia and Mn or Fe. As a consequence, the MnFe-Z sample showing the highest  $\text{NH}_3\text{-L}/\text{NH}_4^+$  ratio, suggests that the ZSM-5 structure would be the one favoring the ionic exchange leading to  $(\text{Mn}_x\text{O}_y)^{z+}$  or  $(\text{Fe}_x\text{O}_y)^{z+}$  as charged compensating species (possibly oxo species) within the structure at the expense of  $\text{NH}_4^+$  species.

### 3.2.6. EPR results

**Fig. 6** EPR spectra of (a) MnFe-Z, (b) MnFe-B, (c) MnFe-M and (d) MnFe-F

The EPR spectra of the various catalysts represented in Figure 6 show a strong and broad signal at  $g = 2.02$  and another weaker at  $g \approx 4.27$  but the interpretation of the spectra is complicated because the occurrence of various paramagnetic oxidation states of the metal cations properties. The signal at  $g \approx 4.27$  has been attributed in Fe-zeolites to  $\text{Fe}^{3+}$  sites in tetrahedral coordination and appears frequently with two more signals at  $g \approx 6$  and  $g \approx 2.0$  [45]. The signal at  $g \approx 6$  is not distinguished in the spectra of figure 6, and that at  $g \approx 2.0$ , usually assigned to iron oxide clusters, is probably contributing to the broad signal present in the spectra of the MnFe-zeolites. Regarding manganese, EPR is able to detect  $\text{Mn}^{2+}$  ( $g$  values slightly above 2.0) and  $\text{Mn}^{4+}$  ( $g$  values slightly below 2.0) while  $\text{Mn}^{3+}$ , although undetectable owing to its large zero field splitting, reduces the EPR signal [46]. According with XPS measurements (see below) all these oxidation states co-exist in the MnFe-zeolites making difficult the proper interpretation of the spectra. The absence of a well resolved hyperfine structure of  $\text{Mn}^{2+}$  indicates the occurrence of extra-framework clusters or oxidic phase in agreement with previous works reporting that high quality EPR signal can be attained only for samples with low Mn loadings, although the existence of well dispersed species cannot be ruled out.

### 3.2.7. DRS UV-vis results

**Fig. 7** DRS UV-vis spectra of (a) MnFe-Z, (b) MnFe-B, (c) MnFe-M and (d) MnFe-F

A classification of three types of Fe-oxo units was proposed in the literature [47]:  $\text{Fe}^{3+}$  in its isolated form or as small clustered species may appear at  $\lambda < 300$  nm, oligomeric  $\text{Fe}_x^{3+}\text{O}_y$  clusters present in the zeolite channels fall at  $300 < \lambda < 400$  nm and  $\text{Fe}_2\text{O}_3$  aggregates at the external surface of the zeolite crystal may appear for  $\lambda > 400$  nm. Considering manganese species, according to previous studies [48], charge transfer transition of  $\text{O}^{2-} \rightarrow \text{Mn}^{3+}$  in zeolite lattice can be detected around 270 nm, extra-framework species may appear at  $300 < \lambda < 500$  nm, and the crystal field transitions of  $\text{Mn}^{2+}$  in  $\text{Mn}_2\text{O}_3$  or MnO show a band at 500 nm. It was also suggested that a  $\text{Mn}^{2+}$  contribution may appear at around 245 nm [49]. On the bases of the above data from literature, the bands observed (Figure 7) at 238 nm for MnFe-Z and MnFe-M may arise from  $\text{O}^{2-} \rightarrow \text{Mn}^{2+}$  charge transfer and/or  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  transition in tetrahedral coordination. MnFe-B and MnFe-M show typical bands at 283 and 277 nm ascribed to  $\text{O}^{2-} \rightarrow \text{Mn}^{3+}$  charge transfer in a tetrahedral coordination in the zeolite framework and/or  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  transition in octahedral coordination (five or six oxygen ligands)[50]. In general the bands between  $300 < \lambda < 500$  nm are assigned to extra-framework manganese species as reported by Khatamian et al. [48]. Other studies suggest that these bands arise from  $\text{O}^{2-} \rightarrow \text{Mn}^{3+}$ [51] or  $\text{O}^{2-} \rightarrow \text{Mn}^{4+}$  [52] charge transfer. These bands may also indicate the presence of a mixed  $\text{Mn}^{4+}\text{-Mn}^{3+}$  amorphous oxide as reported by Lamaita et al. [53]. Also, according to the literature, octahedral  $\text{Fe}^{3+}$  in small oligomeric  $\text{Fe}_x\text{O}_y$  clusters charge transfer can rise in this region. Finally, the bands above 500 nm for MnFe-Z, MnFe-B and MnFe-F are usually attributed to large  $\text{Fe}_2\text{O}_3$  clusters probably existing on the surface. As a conclusion, the MnFe-Z catalyst presenting the higher relative intensity for band at 360 nm would possess the higher relative amount of oligomeric  $\text{Fe}_x^{3+}\text{O}_y$  clusters and/or extra-framework  $\text{Mn}^{3+}/\text{Mn}^{4+}$  species. This result is consistent with  $\text{NH}_3$  adsorption followed by IR that evidenced a higher relative amount of Lewis acid sites.

### 3.2.8. $\text{H}_2$ -TPR results

**Fig. 8** Experimental and de-convoluted  $\text{H}_2$ -TPR profiles of mono- and bi-metallic impregnated zeolites

In the last decade some authors showed that the catalytic performances were governed by redox properties, which can affect the  $\text{NH}_3\text{-SCR}$  reaction. The oxidation states of the active compounds contained in various MnFe-zeolites were thus investigated by  $\text{H}_2$ -TPR. Figure 8 shows the experimental  $\text{H}_2$  consumption curves together with their fit using Gaussian functions aiming at identifying the distinct  $\text{Mn}^{n+}$  and  $\text{Fe}^{n+}$  species loaded in zeolites. The parent

zeolites used as supports did not display any reduction peaks within the tested temperature range (not shown) suggesting that all H<sub>2</sub> consumption could be attributed to the reduction process of MnO<sub>x</sub> and FeO<sub>x</sub> species. According to the literature reports [54], iron containing catalysts presents three peaks in three distinct regions; I: < 400°C, II: > 400°C and III: > 500°C. The lowest temperature is attributed to Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> reduction. The second band is usually associated to the formation of small FeO clusters. The temperatures above 500°C are finally assigned to the reduction of Fe<sup>2+</sup> into Fe<sup>0</sup>. Regarding the manganese oxides, the reduction takes place in successive steps often described as follows: MnO<sub>2</sub>→Mn<sub>2</sub>O<sub>3</sub>→Mn<sub>3</sub>O<sub>4</sub>→MnO. However, the direct identification of manganese oxides appears to be more difficult. This is attributed to the fact that MnO<sub>x</sub> present on the catalysts are usually non-stoichiometric systems allowing them to easily change their properties [55]. In addition, depending on the MnO<sub>x</sub>-support interaction, different manganese oxide species can coexist on the surface [56]. Furthermore, both metals share the same temperature zone for reduction and mixed oxide formation between manganese and iron on the surface cannot be excluded [57]. In order to better distinguish iron and manganese peaks and thus to facilitate the MnFe-support H<sub>2</sub> consumption peak de-convolution, monometallic catalysts were also analyzed (Figure 8). All Mn- and Fe-zeolites show three peaks related to the reduction sequences of iron and manganese as proposed in the literature. For the bimetallic catalysts, MnFe-B, MnFe-M and MnFe-F exhibit five reduction peaks. The first is associated with the reduction of MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub> and the second is attributed to Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> reduction. The third peak can be related to the co-reduction of Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. The two last peaks ranging from 518 to 628°C can be ascribed to complete reduction of MnO<sub>x</sub> to MnO and Fe<sub>x</sub>O<sub>y</sub> to Fe respectively. In the case of MnFe-Z catalyst, only four peaks at 310, 406, 505 and 600°C can be detected. The peak located at 310°C can be ascribed to the simultaneous reduction of MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> species. Clearly, the zeolitic support system has a considerable effect on the interaction and the nature of the species present on the surfaces given the difference in both the intensity and the position of the bands. In the literature, it was suggested that the high catalytic performance ability at low temperatures was correlated to the reduction peaks arising in the lower temperature regions [58]. Thus, the redox ability of samples could be established from the initial reduction temperature: the lower the initial temperature, the higher the redox ability. In the frame of our study, the redox ability then exhibits the following order: MnFe-Z > MnFe-M > MnFe-B > MnFe-F.

Regarding the theoretical amount of loaded metal, one simple calculation leads to about 730 μmol/g for Mn (based on a 4 wt% values) and to about 365 μmol/g for Fe (based on a 2 wt% values) respectively.

**Table 3** H<sub>2</sub> consumption over mono- and bi-metallic impregnated zeolites (μmol/g)

<b>Support Metal</b>	<b>ZSM-5</b>	<b>BEA</b>	<b>MOR</b>	<b>FER</b>
<b>Fe</b>	43.67	53.14	52.18	66
<b>Mn</b>	25.82	19.13	14.95	19.91
<b>MnFe</b>	60.62	35.24	59.43	58

The values for measured total H<sub>2</sub> consumption of the different catalysts are listed in Table 3. Obviously, the amount of consumed H<sub>2</sub> is more than one order of magnitude lower than the theoretical one, thus indicating that whatever the global stoichiometry considered to get the metal amount from the total amount of consumed H<sub>2</sub> (1 for Mn and 2/3 for Fe), less than 10 % of loaded metal is involved in a red-ox process.

In more details, it can be seen that H<sub>2</sub> consumption over Mn monometallic systems is higher on ZSM-5 support than that on the other catalysts. This indicates that the manganese species are more reducible over ZSM-5 than on the other catalysts, probably due to the synergy between manganese and ZSM-5. Moreover, H<sub>2</sub> consumption over monometallic Fe-zeolites is way higher than that over Mn-zeolites despite its lower loading. This can be attributed to a lower degree of decomposition of MnCl<sub>2</sub> salt compared to FeCl<sub>2</sub>. On the other hand, it can be noticed that in the bimetallic catalysts, the total H<sub>2</sub> consumption only increased (compared to monometallic Fe) in the case of MnFe-Z and MnFe-M samples. This finding indicates that iron introduction improves the redox properties of these catalysts. Besides, a shift to the lower reduction temperature is recorded for MnFe-Z compared to Mn-Z. This indicates that iron addition enhances the reducibility of Mn-Z, probably due to the interaction between the two metals and ZSM-5, which, as a consequence, also enhances the catalytic activity at low temperature.

To further study the oxidation states of manganese and iron in MnFe-Zeolite catalysts, XPS spectra were thus complementary recorded.

### 3.2.9. XPS results

**Fig. 9** Mn 2p, Fe 2p and O 1s XPS spectra of MnFe-Zeolite

**Table 4** XPS quantitative analysis

Sample	Binding Energy (eV) / Atomic Composition (%)							Mn <sup>4+</sup> / Mn <sup>3+</sup>	Fe <sup>2+</sup> / Fe <sup>3+</sup>	Mn/Si	Fe/Si
	Mn		Fe			O					
	Mn <sup>2+</sup>	Mn <sup>3+</sup>	Mn <sup>4+</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	O <sub>α</sub>	O <sub>β</sub>				
<b>MnFe-Z</b>	640,2/ 19.7	641,8/ 49	644,2/ 31.28	710,9/ 58,15	713,8/ 41,85	530/ 30,07	532,7/ 69,93	0.63	1.34	9.72E-3	6.33E-3
<b>MnFe-B</b>	640,3/ 20.34	641,7/ 49.8	644,6/ 29.87	710,9/ 55,31	713,8/ 44,69	530,9/ 23,36	533,1/ 76,64	0.60	1.24	9.24E-3	2.54E-3
<b>MnFe-M</b>	640,9/ 40.55	641,9/ 40.61	644,4/ 18.84	710,9/ 47,1	713,8/ 52,9	529,8/ 23,07	532,6/ 76,93	0.46	0.90	9.69E-3	5.89E-3
<b>MnFe-F</b>	640,3/ 28.72	641,9/ 49.45	644,1/ 21.83	710,9/ 31,17	713,8/ 68,83	530,2/ 22,97	532,9/ 77,03	0.44	0.45	9.11E-3	4.02E-3

Figure 9 shows the results obtained from XPS analysis performed in order to identify the chemical states and atomic concentrations of active species at Mn-Fe/catalysts surface. The XPS spectra of Mn 2p, Fe 2p and O 1s were numerically fitted using Gaussian curves, while the binding energies and surface atomic concentration of different metal species are compiled in Table 4.

Mn 2p spectra of the investigated catalysts show two main peaks due to Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> at around 642 and 653.5 eV respectively. The Mn 2p<sub>1/2</sub> peak corresponds to a Mn<sup>2+</sup> satellite peak. The asymmetric Mn 2p<sub>3/2</sub> peak confirmed the coexistence of manganese in a mixed valence state. Mn 2p<sub>3/2</sub> spectra can be fitted into three characteristic peaks that could be ascribed to Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> at around 640, 641 and 644 eV respectively. The proportion of each manganese species was calculated from the Mn 2p<sub>3/2</sub> spectra based on area for each single peak, and the results are summarized in Table 4. Generally, in the literature it is agreed that high valence Mn oxide species enhances the catalytic activity, so the MnO<sub>x</sub> catalytic ability is ranked as: Mn<sup>4+</sup> > Mn<sup>3+</sup> > Mn<sup>2+</sup> [59]. It can be noticed that the MnFe-B, MnFe-M and MnFe-F samples have the highest Mn<sup>2+</sup> concentration suggesting that these catalysts may present a low SCR efficiency at low temperature. In contrast, a good catalytic activity at low temperature is often attributed to Mn<sup>4+</sup> species that would play a key role in promoting the oxidation of NO to NO<sub>2</sub>, then favoring the “fast SCR” reaction [60]. These suggestions are confirmed from the data in Table 4, which shows that the most SCR efficient catalyst, i.e. MnFe-Z, presents the highest Mn<sup>4+</sup> relative amount. Regarding the red-ox efficiency, the Mn<sup>3+</sup>/Mn<sup>4+</sup> couple should also be considered as impacting the catalytic activity. As a consequence, the MnFe-Z catalyst that also possesses the highest amount of (Mn<sup>3+</sup> & Mn<sup>4+</sup>) species would be again the most active. It can be concluded from XPS, that manganese species exist mainly in Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> form, which is in good agreement with Raman and UV-Vis results. Comparing with the results of the catalytic test, it can be however assumed that the concentration of Mn<sup>4+</sup> and Mn<sup>3+</sup> may not be sufficient enough to achieve the best NO conversion. This may arise from the use of the MnCl<sub>2</sub> precursor since it was reported that catalysts prepared by manganese acetate and manganese nitrate precursors may form more Mn<sup>4+</sup> dispersed species in the catalyst surface ensuring better NO conversion [60].

Fe 2p<sub>3/2</sub> peak for these catalysts was located at around 712.2eV and was subdivided into two distinct peaks at around 710.9 and 713.8 eV, ascribed to Fe<sup>2+</sup> and Fe<sup>3+</sup> respectively [37]. It was proposed that the Fe<sup>2+</sup>/Fe<sup>3+</sup> couple is beneficial for the formation of oxygen vacancies and electron transfer in the redox cycle between manganese and iron: Mn<sup>3+</sup> + Fe<sup>3+</sup> = Mn<sup>4+</sup> + Fe<sup>2+</sup>. The abundance of Fe<sup>2+</sup> thus contributes to the easy formation of oxygen vacancies which are more favorable to the adsorption of oxygen on the catalyst surface, producing chemisorbed active oxygen [61]. The Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio presented in Table 4 is higher for MnFe-Z catalyst, which is again in agreement with its expected higher catalytic performances.

The XPS spectra of O<sub>1s</sub> is divided into two distinct peaks at around 530 and 533 eV corresponding to zeolite lattice oxygen (denoted as O<sub>α</sub>) and chemisorbed oxygen (denoted as O<sub>β</sub>) respectively [25], the later O species being most probably coordinated to superficial Mn<sup>x+</sup> or Fe<sup>x+</sup> species. As evidenced from table 4, the amount of chemisorbed O<sub>β</sub> is always at least twice the amount of lattice O<sub>α</sub>. Since XPS is a surface sensitive technique, this is a clear proof that an enrichment in oligomeric Mn<sub>x</sub>O<sub>y</sub> and/or Fe<sub>x</sub>O<sub>y</sub> at the external area of the zeolite crystals occurred during the metal loading step. The lower contribution of O<sub>β</sub> with the MnFe-Z catalyst suggests that i) either a higher proportion of metal has diffused within the zeolite channels to replace H<sup>+</sup> as compensating cations (in agreement with NH<sub>3</sub> adsorption data) or that ii) under the ultra-low pressure required for XPS analysis, part of chemisorbed O<sub>β</sub> has been removed thanks to a higher reducibility of Mn<sub>x</sub>O<sub>y</sub> and/or Fe<sub>x</sub>O<sub>y</sub> species. Therefore, it might be inferred that the catalyst possessing the highest iron reducibility, thus allowing the stabilization of the highest valence for manganese according to: Mn<sup>3+</sup> + Fe<sup>3+</sup> = Mn<sup>4+</sup> + Fe<sup>2+</sup>, here MnFe-Z, would exhibit the best catalytic performances. The surface atomic ratios were quantified based on the ratio of the corresponding peak intensities, corrected with theoretical sensitivity factors of Scofield’s photoionization cross-sections [62]. It can be seen in table 4, that the Mn/Si ratio on the external surface of the zeolites is similar for the different supports. On the other hand, iron appears to become enriched on the surface of the catalysts, especially for the ZSM-5 support. Indeed, Fe/Mn ratio of the MnFe-Z catalyst appears to be closest to the stoichiometry of the Fe<sub>3</sub>Mn<sub>3</sub>O<sub>8</sub> phase identified in XRD. Thus,

one can conclude that i)  $\text{Fe}_3\text{Mn}_3\text{O}_8$  mixed oxide phase would be associated with the high reducibility of MnFe-Z which generates a high oxidation ability favoring NO to  $\text{NO}_2$  oxidation, ii) ZSM-5 structure, favoring the ionic exchange leading to  $(\text{Mn}_x\text{O}_y)^{2+}$  or  $(\text{Fe}_x\text{O}_y)^{2+}$  as charged compensating species (as viewed by  $\text{NH}_3$ -IR and XPS of O 1s), provides a high adsorption capacity of ammonia in the microporosity (Lewis sites) with limited pore obstruction.

## 4. Discussion

In this study, ZSM-5, BEA, MOR and FER zeolites were impregnated with Mn (about 4 wt%) and Fe (about 2 wt%) and their catalytic activity in  $\text{NH}_3$ -SCR was investigated. In order to get more insights on the relationships between the zeolite structure, physicochemical properties and catalytic activity, several techniques were explored. XRD proved that no significant damage of the zeolite host structure occurs after impregnation and thermal treatment. No dealumination was detected by  $^{27}\text{Al}$ -NMR evidencing the stability of the different zeolite structures and the absence of Lewis acidic sites associated with extra-framework Al species. The studied MnFe-zeolites differ from each other in Si/Al ratio, acidity, pore diameter and structure. In the low temperature range, the catalytic performances can be ranked as follow:  $\text{MnFe-Z} > \text{MnFe-B} > \text{MnFe-M} > \text{MnFe-FER}$ . XRD and Raman revealed the presence of  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  oxides on the surface of MnFe-Z in addition to the development of a new  $\text{Fe}_3\text{Mn}_3\text{O}_8$  mixed oxide phase. The presence of these species either in an amorphous state or as small crystalline particles may be one of the key factors for the enhancement of the catalytic activity of MnFe-Z at low temperature compared to MnFe-B, MnFe-M and MnFe-F.

In this study, it was clearly exposed that the zeolite structure has a considerable effect on the textural features and induces distinct metal properties, which influence the catalytic performances. In fact, ZSM-5 and BEA possessing a three-dimensional pore structure, may ensure better diffusion and dispersion of the loaded metals (Mn and Fe) during the preparation step. The higher proportion of metal loaded within the microporous system of the ZSM-5 structure, suggested by  $\text{NH}_3$  adsorption followed by IR, would ensure a closer interaction between reacting molecules with both the redox and acidic active sites. Moreover, the 10-membered rings defining the three-dimensional network of channels of ZSM-5 is large enough to allow the accessibility of ammonia through the structure and its interaction with the acid sites [63]. For BEA zeolite, the intersection of the perpendicular channels defining the 12-membered rings creates cavities giving also free access for ammonia to the zeolite system. In the case of MOR, the limited diffusion in the b direction (side pockets) may explain the poor conversion specially at low temperature. As for FER, its small channels aperture may limit the access of reaction molecules to the sites inside the pores, as soon as oligomeric metal oxides may block pore mouths.

Considering the textural properties, it was revealed, in this study, that the specific area may not be the key factor to increase SCR activity:  $S_{\text{BET}}$  of MnFe-Z (most active in SCR) is lower than those of MnFe-M and MnFe-B. A specific area of about  $270 \text{ m}^2/\text{g}$  is thus largely sufficient to ensure good diffusion and dispersion of the metals. The zeolite structure and the catalyst active metal phase are thus, the main factors that influence SCR activity as advanced by Li et al. [33].

The surface acidity of the catalysts appears to play also an important role in NO reduction. A classification of the zeolites acidity was carried out using IR by adsorption of ammonia and showed that a direct correlation between the  $\text{NH}_3\text{-L}/\text{NH}_4^+$  ratio and the catalytic activity can be established. Indeed, the catalysts with the highest  $\text{NH}_3\text{-L}/\text{NH}_4^+$  ratio exhibit the best catalytic performances which is probably related to a higher amount of  $(\text{Mn}_x\text{O}_y)^{2+}$  or  $(\text{Fe}_x\text{O}_y)^{2+}$  as framework compensating charged species within the zeolitic channels. MnFe-M and MnFe-F with the lowest  $\text{NH}_3\text{-L}/\text{NH}_4^+$  ratios show a low activity especially at low temperature. As a consequence, one can conclude that ZSM-5 structure is more adapted to favor metal dispersion within the microporous channels and generates Lewis acidic centers which might promote the absorption of  $\text{NH}_3$  and increase the catalytic performance at low temperature [26].

Since, according to the IR results, the best NO conversion observed with MnFe-Z could be due to the presence of manganese and iron, it was important to study their speciation. XPS, EPR and UV-Vis spectroscopy were used for the determination of the different metal species. These analysis revealed that manganese species are present mainly in  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  state while iron exists as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species. EPR evidenced that  $\text{Fe}^{3+}$  species in strongly distorted tetrahedral coordination would be favored by the ZSM-5 structure.

It was reported in the literature that Mn supported catalysts exhibit good NO conversion due to the presence of different types of labile oxygen and different oxidation states, which enhance the catalytic cycle [10]. XPS results show that the highest amount of  $\text{Mn}^{4+} + \text{Mn}^{3+}$  leads to the enhancement of the catalytic activity. Indeed, the abundance of  $\text{Mn}^{4+}$  at the surface of MnFe-Z catalyst would enhance the NO to  $\text{NO}_2$  oxidation and hence favors the "fast-SCR" reaction [25]. However, it is noticed that the catalytic activity of MnFe-M is better than MnFe-F, while the former shows a higher  $\text{Mn}^{2+}$  and lower  $\text{Mn}^{4+}$  concentration. Hence, even though the speciation of Mn on the surface of the catalyst influences the catalytic activity, the zeolite topology determines the accessibility to the remaining active sites. Besides, under the ultra-high XPS vacuum, MnFe-Z presents the highest amount of  $\text{Fe}^{2+}$

and thus the easiest iron reducibility. Iron-based zeolites (mostly Fe/ZSM-5 and Fe/BEA) give usually very high NO reduction efficiencies for SCR at high temperature ( $>400^{\circ}\text{C}$ ). However, Fe can also be used as a promoter in order to enhance catalytic activities at low temperature. The abundance of  $\text{Mn}^{4+}$  on the surface of MnFe-Z catalyst is indicative of the transformation of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  probably due to the strong interaction between amorphous Mn and Fe oxides upon Fe addition through the redox equilibrium of  $\text{Mn}^{3+} + \text{Fe}^{3+} \leftrightarrow \text{Mn}^{4+} + \text{Fe}^{2+}$  [25]. In addition, MnFe-Z catalyst presents the lowest proportion of superficial labile oxygen  $\text{O}_{\beta}$  probed by XPS, which is consistent with the hypothesis of  $(\text{Mn}_x\text{O}_y)^{z+}$  or  $(\text{Fe}_x\text{O}_y)^{z+}$  oxo species within the microporous system.

It was also reported that for exchanged zeolite catalysts, the easy reduction of the metals on the surface favors the low temperature activity. This is explained by the high oxidation capacity of easily reducible metallic species which generates  $\text{NO}_2$  and nitrates [64]. MnFe-Z show a better reducibility of the metals as it can be seen in TPR analysis where the reduction temperatures are lower than that in the other catalysts. In addition, the reduction temperatures of MnFe-Z were shifted to lower values compared to Mn-Z. This indicates that iron enhances the redox ability of both manganese and iron over ZSM-5 support which is confirmed by  $\text{H}_2$  total consumption values and is consistent with the high  $\text{Fe}^{2+}$  amount detected by XPS. Although TPR profiles of MnFe-Z and MnFe-F are similar, the former exhibit only four reduction peaks and has excellent catalytic properties at low temperature, unlike MnFe-F where activity is relatively poor and does not exceed 20%. In fact, ZSM-5 has better accessibility to the acid sites located in the pores allowing better reactivity and better synergy with the loaded metals. Likewise, MnFe-B and MnFe-M have almost the same appearance of thermograms which would perhaps explain the similar catalytic activity at high temperature. One can conclude that the better reducibility of manganese and iron on ZSM-5 increases the kinetics for red-ox cycles, which ensure a better catalytic activity especially at low temperature. Raman spectroscopy also confirms the existence of a strong synergy between metals and ZSM-5 support regarding the shift in the signals position and the decrease on the bands intensities.

However, taking into account the relatively low NO conversion of the catalysts in the present study, the precursor, can be presented as an important factor influencing NO reduction efficiency as reported by Wang et al. [60] and Xu et al. [31]. They suggested that acetate and nitrate precursors favor metal dispersion, oxygen mobility and high active species concentrations which enhance the redox ability of the catalysts. The rather low conversion presented in the current work may then be associated to the fact that  $\text{MnCl}_2$  is only partially decomposed in  $\text{MnCl}_2$ -modified zeolites when calcined between  $310\text{--}600^{\circ}\text{C}$  [65]. Besides the concentration of  $\text{Mn}^{4+}$ , even for the MnFe-Z catalyst, may be not sufficient to enhance the catalytic performances at low temperature. Indeed, some studies also claimed that the use of chloride as a manganese precursor can inhibit the formation of  $\text{Mn}^{4+}$  species on the surface of the catalyst [60] due to the weak decomposition of  $\text{MnCl}_2$  [66].

## 5. Conclusions

In this work, the activity of zeolite-based catalysts in the  $\text{NH}_3$ -SCR reaction with excess oxygen was studied. In the low temperature range, the activity of the different MnFe-Zeolites was found to decrease along the series:  $\text{MnFe-Z} > \text{MnFe-B} > \text{MnFe-M} > \text{MnFe-F}$ . This difference in NO conversion is mainly attributed to the difference in manganese speciation and the preferential location of metallic species inside the microporous system for the 3D ZSM-5 and BEA structures. From the results above, a direct correlation between the structure and the acidity of the host zeolites and the catalytic performance was established. Considering these parameters, ZSM-5 zeolite ensures better catalytic performances in the whole temperature range compared to BEA, MOR and FER supports. However, its catalytic activity remains limited and does not exceed 64%. This low NO conversion may be attributed to the low degree of  $\text{MnCl}_2$  decomposition. MnFe-F was substantially less active due to its narrow pore system that causes geometric constraints and partial pore blocking after metal loading, making the active species inaccessible to reactants.

## 6. Declarations

### Acknowledgements

Financial support by the MINECO of Spain through the Severo Ochoa (SEV-2016-0683) and RTI2018-101784-B-I00 projects is gratefully acknowledged. J.M.-O. (SEV-2012-0267-02) is grateful to the Severo Ochoa Program for a predoctoral fellowship.

### Conflicts of Interest / Competing interests

The authors declare no conflict of interest.

**Ethics approval**

Not applicable.

**Consent to participate**

Not applicable.

**Consent for publication**

Not applicable.

**Availability of data and material**

Not applicable.

**Code availability**

Not applicable.

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