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# Selective Catalytic Reduction of NO<sub>x</sub> over Cu- and Fe-exchanged zeolites and their mechanical mixture

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## **Abstract**

SCR-NH<sub>3</sub> activities of Cu-SAPO-34 (Cu-CZC) and Fe-Mordenite (Fe-MOR) and their mechanical mixture (50:50) were investigated in the temperature range 150-450 °C using *operando* FTIR spectroscopy. Structural and textural studies assessed the quality of the material synthesis, while *in situ* IR characterisation allowed the quantification of the acidic sites at the surface of the zeolites, as well as the cationic distribution inside the pores. As expected, Cu-CZC showed high NO<sub>x</sub> activity at lower temperatures (75 % of NO<sub>x</sub> conversion at T < 300 °C), while Fe-MOR was more active (> 85 %) at higher temperatures (300-450 °C). The co-presence of Cu and Fe in the mechanical mixture catalyzes the undesirable oxidation of ammonia and leads to the formation of NO, especially at high temperatures. However, the mechanical mixture of Cu-CZC and Fe-MOR has been found to efficiently operate in the presence of excess ammonia (NH<sub>3</sub>/NO<sub>x</sub> = 1.3) in a much broader temperature range comparing to the catalysts modified with only one transition metal (Fe or Cu) and also respect to a sample containing both cations in a single zeolitic framework, thus opening new opportunities in the catalytic reduction of NO<sub>x</sub>.

**Keywords:** NH<sub>3</sub>-SCR, metal exchanged zeolites, Mordenite, SAPO-34, composite catalysts.

## 1. Introduction

Owing to their fuel efficiency and durability, the number of diesel engines has greatly increased worldwide [1]. However, the emission of  $\text{NO}_x$  and particulate matter (PM) from diesel propelled vehicles remains a major constraint for their use. Nitrogen oxides ( $\text{NO}_x$ ) are amongst the most serious world ecological problems since they cause irreversible changes in the terrestrial and aquatic ecosystems such as acid rain and photochemical smog [2], as well as health diseases [3,4]. In recent years, great efforts have been applied to limit the emission of  $\text{NO}_x$ . The Selective Catalytic Reduction (SCR) of  $\text{NO}_x$  with  $\text{NH}_3$  is one of the most promising technologies due to their low cost and high efficiency [5,6,7]. Among the  $\text{NH}_3$ -SCR catalysts, metal oxides and zeolite-based catalysts promoted by transition metals are the materials of choice for this reaction [5,8]. The latter one has attracted much attention due to their superior activity, thermal stability and relatively low cost [8]. In general, Fe-containing zeolites were found to be highly active at higher temperatures ( $> 350\text{ }^\circ\text{C}$ ), while Cu-zeolites are more active at lower temperatures ( $< 300\text{ }^\circ\text{C}$ ) [9]. Given the difference in activities of Fe- and Cu-zeolites, it seems plausible that a combination of the two catalysts might achieve higher  $\text{NO}_x$  conversions over a broader temperature range. Such combined Fe- and Cu-zeolite systems were thoroughly investigated in the literature [10,11,12,13,14]. Mektar *et al.* [10] showed that the Fe-ZSM-5 and Cu-Chabazite dual layer catalyst exhibited excellent  $\text{NO}_x$  reduction efficiency over the entire temperature range of  $250\text{--}550\text{ }^\circ\text{C}$ . Various configurations (copper-zeolite layer on top or at the bottom of iron-zeolite layer) and thicknesses of the dual layer were investigated in order to obtain maximum  $\text{NO}_x$  conversion for fast SCR reaction. Other studies showed improvements in NO conversion over zeolites containing simultaneously copper and iron cations [11,12,13,14]. These catalysts were prepared by different methods such as one-pot aqueous ion-exchanged method (AIE) [12,13], solid state ion-exchange method (SSIE) [14], two-step post synthesis and conventional wet

impregnation procedure [11]. These methods, however, present several drawbacks. For example, the steric hindrance caused by the formation of solvation shells of multivalent metal ions cannot be controlled during the one-pot AIE method. On the other hand, the use of two-step post synthesis needs numerous steps and raises difficulties to overcome the metal leaching during the second ion-exchange step. In the case of conventional SSIE, which requires high temperatures ( $> 700\text{ }^{\circ}\text{C}$ ), the partial destruction of zeolite framework could take place. Even though the previous studies showed a superior performance of Cu-Fe-zeolites for the SCR reaction, the NO conversion over these catalysts did not exceed 30 % at  $T = 150\text{ }^{\circ}\text{C}$ , a temperature currently reached by the exhaust gases at the cold-start or during low speed driving, as downtown. However, a facile route to prepare catalytic formulations, in which both copper and iron are co-present, is required in order to understand the synergistic effects between the two metals and to control the catalytic performance at low-high temperatures. Thus, in contrast to the previous studies in which complex systems with dual layer catalysts and Cu-Fe-zeolites were thoroughly investigated, our approach is alternatively based on the complementarity of single copper- and iron-containing zeolites used to prepare mixed catalysts that are expected to cover efficiently a broad temperature range, especially at low temperatures, in the so-called cold-start domain.

In this study, the SCR-NH<sub>3</sub> activities of Cu-SAPO-34 (Cu-CZC) and Fe-Mordenite (Fe-MOR) and their mechanical mixture (50:50) were investigated in the temperature range of 150-450  $^{\circ}\text{C}$  using *operando* FTIR spectroscopy. The impact of mechanical mixing of the two catalysts on the catalytic performance will be discussed and compared with the literature results. *In situ* IR studies will support the critical discussion on the role of each cation in the reaction pathway and the modification of the porous host properties upon their introduction.

## 2. Experimental part

### 2.1. Materials

Two commercial CHA-type zeolites, as protonated (H-CZC) and copper exchanged (Cu-CZC) silicoaluminophosphates (SAPO-34) were directly used as received from Clariant. It should be noted that the incorporation of iron in SAPO-34 catalyst using ion exchange process was very difficult due to the small pore openings in the SAPO chabazite structure.

The parent Mordenite ( $\text{Si/Al} = 6.2$ ,  $\text{Na}^+$ -form, abbreviated as MOR) was supplied by Zeolyst. The Cu or Fe-containing mordenite were prepared by conventional ion exchange procedure and labeled Cu-MOR and Fe-MOR, respectively. In the first step, 1 g of parent zeolite was mixed with 40 mL of aqueous solutions containing 0.05 M of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and stirred at  $T = 60^\circ\text{C}$  for 4 h. The obtained suspensions were centrifuged, washed thoroughly with deionized water, freeze-dried for 2 nights and then calcined at  $500^\circ\text{C}$  for 4 h. The ion-exchange procedure was repeated three times. The parent Na-MOR was also calcined under the same conditions and used as a reference.

### 2.2. Techniques

X-Ray Diffraction (XRD) analyses of the parent and metal exchanged catalysts were carried out with a PANalytical X'Pert Pro diffractometer using  $\text{CuK}\alpha$  radiation ( $1.5418 \text{ \AA}$ ) and a graphite monochromator at room temperature. Diffraction patterns were recorded between  $5$  and  $50^\circ$  ( $2\theta$ ) using increments of  $0.02^\circ$ . The relative crystallinity (%) was calculated by comparing the peak intensities of the metal exchanged-zeolites to that of the parent materials, which were considered to be 100 % crystalline.

Nitrogen adsorption/desorption measurements were performed with an ASAP 2020 MP instrument. The specific surface area was calculated with the BET equation while the

microporous volumes were determined by the t-plot method. Prior to the measurements, samples were outgassed *in situ* at 350 °C for 3 h.

The actual contents of Si, Al, Cu, Fe and P in the samples were analyzed using a Varian ICP-OES 720-ES inductively coupled plasma spectrometry (ICP).

The MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer with rotor diameter of 4 mm. For  $^{29}\text{Si}$  (79.5 MHz), a 10  $\mu\text{s}$  pulse was used with a repetition time of 15 s and 2 s for ion-exchanged zeolites. For  $^{27}\text{Al}$  (104.3 MHz), a 10  $\mu\text{s}$  pulse was used with a repetition time of 1 s. For  $^{31}\text{P}$  (162.0 MHz), a 4  $\mu\text{s}$  pulse was used with a repetition time of 20 s. A mass correction is done for each sample. The ratio of tetrahedral silicon and aluminium in the zeolite framework can be directly calculated from the line intensities in a  $^{29}\text{Si}$  MAS NMR spectrum by the following equation [15]:

$$\text{Si/Al} = \sum I_{\text{Si}(n\text{Al})} / \sum n/4 I_{\text{Si}(n\text{Al})} \text{ with } n = \{0;4\} \quad (1)$$

DR-UV-Vis measurements relevant to the oxidation state of iron and copper were carried using a Cary 4000 UV-Vis spectrophotometer and a HARRICK praying Mantis diffuse reflectance accessory. All spectra were recorded between 200-800 nm using an average time of 0.2 s and a scan rate of 300 nm/min.

Hydrogen temperature-programmed reduction (TPR) was carried out in a flow of 5% of  $\text{H}_2$  in Ar (40  $\text{mLmin}^{-1}$ ). The sample was placed in a quartz microreactor and the quantitative consumption of  $\text{H}_2$  from 25 to 800 °C (10  $\text{degree.min}^{-1}$ ) was monitored by a TCD detector. No peaks were observed in the  $\text{H}_2$ -TPR spectrum of Cu-CZC (not shown here) since the loading amount of Cu in the zeolite structure is below the detection limit.

*In situ* IR adsorption tests were performed in order to study the quantity and the strength of acid sites (Lewis and Brønsted) of parent and metal exchanged-zeolites. The samples were first heated under vacuum ( $<10^{-6}$  mbar) at 450 °C during 2 h. Then, one equilibrium dose of pyridine (1 mbar) was put in contact with each sample at room temperature. Quantification

was performed, after mass correction, by multiplying the area of the peaks corresponding to Lewis (L.A.S:  $1450\text{ cm}^{-1}$ ) and Brønsted (B.A.S:  $1545\text{ cm}^{-1}$ ) acid sites by the molar extinction coefficient values cited in the literature ( $\epsilon_{\text{L.A.S}} = 2.22\text{ cm.mol}^{-1}$ ;  $\epsilon_{\text{B.A.S}} = 1.67\text{ cm.mol}^{-1}$ ) [16]. It should be noted that the quantification was based on spectra recorded after pyridine evacuation at increasing temperatures to exclude an overlap of the bands of Py-L and hydrogen physisorbed pyridine. The adsorption step was followed by a Temperature Programmed Desorption study (TPD) between 25 and 450 °C was carried out to study the strength of acid sites. The IR spectra were recorded with a Nicolet 6700 FTIR spectrometer equipped with a DTGS detector at a spectral resolution of  $4\text{ cm}^{-1}$  by accumulating 128 scans.

The interaction of redox sites (Cu or Fe) with carbon monoxide (CO) or nitric oxide (NO) was also studied. Catalysts were always pre-heated under vacuum at 450 °C during 2 h. Small doses of CO or NO (between 2 and 145  $\mu\text{mol/g}$  catalyst) were then put in contact with each sample until saturation. The analysis was followed by a TPD study. For quantification, the integrated areas of characteristic bands were plotted against the adsorption amount of gas ( $\mu\text{mol/g}$ ). The slope of the initial linear part of the correlation curve and the value at saturation provide the molar extinction coefficient and the amount of Lewis acid sites, respectively.

### 2.3. *Catalytic test*

The SCR-NH<sub>3</sub> activity was tested in an Aabspec CXX 800 °C IR reactor-cell. Prior to the experiment, the catalyst (casted in a disc of ~13.50 mg) was pretreated at 500 °C for 2 h with a raising temperature speed of 5 °C/min under 10 % of O<sub>2</sub> in Ar. Then, the reaction was studied in the 450 °C and 150 °C temperature range using a model feed gas composition, which reflects the conditions measured at the exhaust of a diesel car [17] (see details in Table 1). The gas flow rate in all experiments was controlled at 31 cc.min<sup>-1</sup>, to obtain a space velocity of 143 076 h<sup>-1</sup>.

All the reactants of the Reaction Flow were analysed by Mass Spectrometry (Quadrupole Pfeiffer Omnistar GSD 301) and stabilized before being sent to the cell. Finally, the composition of the output gas from the IR reactor cell was analyzed simultaneously as follows: NO and NO<sub>2</sub> by Chemiluminescence (Thermo-Scientific, model 42 i-HL); CO and NH<sub>3</sub> by an IR spectrometer equipped with a gas cell (ThermoNicolet NEXUS 670 FTIR) and MCT with a spectral resolution of 4 cm<sup>-1</sup> and accumulating 64 scans. The NO<sub>x</sub> and NH<sub>3</sub> conversions were respectively calculated from the equations (2) and (3).

$$\text{NO}_x \text{ conversion [\%]} = \frac{\text{NO}_{x,\text{inlet}} - \text{NO}_{x,\text{outlet}}}{\text{NO}_{x,\text{inlet}}} * 100 \text{ [\%]} \quad (2)$$

$$\text{NH}_3 \text{ conversion [\%]} = \frac{\text{NH}_{3,\text{inlet}} - \text{NH}_{3,\text{outlet}}}{\text{NH}_{3,\text{inlet}}} * 100 \text{ [\%]} \quad (3)$$

### 3. Results and discussion

The main idea of the present paper is to show how the complementary properties of copper and iron cations hosted in specific zeolitic structure can cover efficiently a broad range of temperatures in relevant conditions for the NH<sub>3</sub>-SCR reaction. Therefore, we will present below the properties of two different families of zeolites (with and without Cu/Fe cations), then we will compare their catalytic performances when both cations will be inserted in the same porous structure, or when the two zeolites will be simply mixed mechanically. The results will be discussed relatively to the chemical-physic properties of each sample, as well as on their supposed influence on the reaction pathway.

#### 3.1. Study of H-CZC and Cu-CZC catalysts

Along with the continuous research work on NO<sub>x</sub> removal by zeolitic catalysts, it was recently reported that extremely high deNO<sub>x</sub> activities (> 80%) and N<sub>2</sub> selectivities (> 90%) across a broad temperature range of 200–400 °C were achieved by introducing Cu in a small



pore CHA-type zeolite, as both silicoaluminophosphate (SAPO-34) and aluminosilicate (chabazite or SSZ-13) were employed [18]. The excellent catalytic behavior and hydrothermal stability of Cu-CHA-type zeolites were attributed to their particular structure combining narrow pore openings of ca. 3.8 Å (8 member ring) with large cavities [19]. Therefore, two commercial SAPO-34-type zeolites: H-CZC and Cu-CZC are here employed in the fast SCR-NH<sub>3</sub> reaction and studied by different techniques, notably spectroscopic, in order to establish a structure-activity relationship.

### ***3.1.1. Catalytic activity for the SCR-NH<sub>3</sub> reaction***

The SCR activities of H-CZC and Cu-CZC samples were measured in the range of 150-450 °C (Fig. 1(A)). Compared with parent zeolite, Cu-CZC shows superior catalytic activity in the whole temperature range. The NO<sub>x</sub> conversion exceeds 75 % at 150 °C and it reaches a maximum of 93 % at 350 °C. Meanwhile, the NO<sub>x</sub> conversion drops from 93 % to 70 % as the reaction temperature increases from 350 to 450 °C. By comparing the NO<sub>x</sub> and NH<sub>3</sub> conversions over Cu-CZC, it is clear that NO<sub>x</sub> and NH<sub>3</sub> conversions are essentially stoichiometric below 350 °C, while 10 % NH<sub>3</sub> over consumption is evident for T > 350 °C. This result confirms the non-selective oxidation of ammonia at high temperature. Therefore the decline of SCR activity at high temperature is caused by two reasons: first, part of inlet NO<sub>x</sub> cannot react due to the insufficient amount of NH<sub>3</sub>, which is partially consumed in NH<sub>3</sub> oxidation. Second, NO is produced during NH<sub>3</sub> oxidation reaction, directly decreasing the NO<sub>x</sub> conversion at high temperature, as shown by chemiluminescence data. Similar trends were observed by Leistner et al. [20] during SCR-NH<sub>3</sub> reaction over 1.6 wt% Cu-SAPO-34, with however, lower NO<sub>x</sub> conversion (40 %) at 150 °C compared to our catalyst. Importantly, it should be noted that during the SCR experiments, no side products as N<sub>2</sub>O were detected in the outlet, witnessing for a 100 % of selectivity for both H-CZC and Cu-CZC samples during the NO<sub>x</sub> to N<sub>2</sub> conversion.

Conversions of CO and hydrocarbons during the SCR-NH<sub>3</sub> reaction were also investigated (Fig. S8), being currently present in a typical automotive exhaust. Both conversions increase with increasing the temperature from 150 to 450 °C. This result can be explained by the oxidation of CO and HC in the presence of NO<sub>2</sub>, as it will be discussed later. It should be noted that a part of CO was adsorbed on Cu-CZC (band at 2153 cm<sup>-1</sup>, not shown here) and rapidly consumed at low temperatures (200-250 °C).

### **3.1.2. Characterization of catalysts**

#### *Structural and textural properties*

Table 2 summarizes the main structural and textural properties of the samples. Both H-CZC and Cu-CZC show the typical chabazite (CHA) structure for SAPO-34, with a loss of crystallinity after copper exchange (diffraction patterns and further details can be found in Supplementary Information, SI). Cu<sub>2</sub>O and CuO phases are absent, suggesting that the copper species exist in highly dispersed states or they are beyond the detection limit of XRD [21]. The Cu content of Cu-CZC is 1.56 wt. % with a low copper exchange level (Cu/Al = 0.08). By comparing the Si/Al and Si/P molar ratios of H-CZC and Cu-CZC, it can be seen that the amount of Al and P gradually decreases after ion exchange, indicating a possible dealumination of the zeolite framework [22]. The Cu-CZC catalyst exhibits a significantly decreased specific surface area (568 m<sup>2</sup>.g<sup>-1</sup>) and micropore volume (0.19 cm<sup>3</sup>.g<sup>-1</sup>) as compared with the parent H-CZC catalyst ( $S_{BET} = 731 \text{ m}^2\text{.g}^{-1}$ ;  $V_{mic} = 0.25 \text{ cm}^3\text{.g}^{-1}$ ). This decrease can be attributed to the partial pores blockage by copper species and/or the partial dissolution of the chabazite framework due to the acid attack coming from copper precursor [23,24]. These results are in agreement with the partial loss in crystallinity shown by XRD.

MAS NMR was used to investigate the coordination of framework Al, Si and P of the parent H-CZC and Cu-CZC samples. Results are reported in SI (Fig. S2). They indicate that

after copper exchange some Si–O–Al bonds have been broken, causing the migration of tetrahedral Al atoms outside their framework positions to form octahedrally coordinated or extraframework Al species [25]. After copper exchange, also the signal corresponding to the tetrahedral silicon becomes broader and less intense, suggesting the formation of amorphous silicon complexes after breakage of Si–O–Al bonds [25]. The  $^{31}\text{P}$  MAS NMR signal confirms the formation of extraframework aluminum and suggests that free phosphorous atoms could be coordinated to water molecules to form  $\text{P}(\text{OAl})_x(\text{H}_2\text{O})_y$  clusters.

The DR-UV-vis spectra of the chabazite samples are reported and discussed in SI. They show the typical features of tetrahedral Al species and isolated  $\text{Cu}^{2+}$  species.

#### *In situ IR analysis*

The FTIR-spectroscopic investigation of pyridine adsorption is a widely used method for the characterization of both Brønsted and Lewis acidic sites [26]. For the sake of brevity, the FTIR spectra of pyridine adsorbed on H-CZC and Cu-CZC samples are not shown here. The resulting quantitative data are summarized in Table 2, where the amounts of Brønsted and Lewis acid sites are referred to the mass of catalyst.

A low amount of B.A.S has been detected in H-CZC samples (0.77  $\mu\text{mol/g}$ ), possibly resulting from Si-OH-Al groups. The respective Cu-CZC sample shows a relative decrease of B.A.S amount, so that only a marginal Brønsted acidity remained in this sample (0.11  $\mu\text{mol/g}$ ). These data point to the replacement of protons by copper during ion exchange. The concentration of Lewis acid sites resulting from  $\text{Al}^{3+}$  of H-CZC sample is 15.8  $\mu\text{mol/g}$ . The quantification data confirms that copper induces additional Lewis acidity for the Cu-CZC sample (17.8  $\mu\text{mol/g}$ ). The same behavior was observed by Dang *et al.* [21] during the adsorption of pyridine on Cu/SAPO-5 catalyst. The adsorption step was followed by a Temperature Programmed Desorption study (TPD) between 25 and 200  $^{\circ}\text{C}$  in order to reveal

the strength of Lewis acid sites on both H-CZC and Cu-CZC (Fig. 1(A)). The increase of temperature from 25 to 150 °C results in a gradual decrease of L.A.S. by 73 % and 58 % for H-CZC and Cu-CZC, respectively. The amount of L.A.S. remains accountable on Cu-CZC after desorption beyond 150 °C, indicating the presence of strong acidic sites in this sample. It should be noted that the determination of strength of Brønsted acidity was difficult due to the low initial amount of B.A.S. in both samples (in fact the small size of the CZC cavities limits the site accessibility to pyridine). However, a complete desorption of pyridine on B.A.S. is observed at 150 °C for the Cu-CZC sample.

CO and NO *in-situ* chemisorption experiments were conducted to determine the nature and the relative amount of copper sites (Fig. 2(A and B)). The H-CZC support does not chemisorb any CO or NO molecules (results not shown here). The IR spectra of CO adsorption on the Cu-CZC samples are shown on Fig. 2(A). A main band appears at 2154 cm<sup>-1</sup> and it is due to C–O stretching vibrations for the (Cu<sup>+</sup>-CO) species [27]. As the equilibrium pressure increases, two other weak bands appear at 2184 and 2109 cm<sup>-1</sup>. These bands could be attributed to Cu<sup>2+</sup>-CO and Cu<sup>0</sup>-CO carbonyl species, respectively. The molar extinction coefficient of the Cu<sup>+</sup>-CO complex, calculated from the band at 2154 cm<sup>-1</sup> by introducing increasing probe molecule aliquots on the sample, is 10.81 cm.μmol<sup>-1</sup>. This value is in agreement with the literature [27]. The total estimated amount of Cu<sup>+</sup> sites is thus 71.9 μmol.g<sup>-1</sup> with 25 % of cationic dispersion. It is worth noting that this amount is overestimated compared to the L.A.S. number calculated from pyridine-adsorption experiment (Table 2). This difference is mainly due to the pore diameter of the 8-MR of SAPO-34 (CHA structure,  $d = 3.8 \text{ \AA}$ ), which is accessible to CO ( $d = 3.72 \text{ \AA}$ ), but not to pyridine molecules ( $d = 4.92 \text{ \AA}$ ).

Small doses of NO were progressively added in contact to Cu-CZC (Fig. 2(B)), leading to the development of two strong absorption bands at 1911-1900 and 1800 cm<sup>-1</sup> characteristic of

$\text{Cu}^{2+}$ -NO and  $\text{Cu}^+$ -NO cations, respectively [27]. At the higher equilibrium pressures, an additional weak band develops at  $1943\text{ cm}^{-1}$ . This band has been assigned to  $(\text{Cu}^{2+})_n$  slightly associated sites [27]. Therefore, we can conclude that in the conditions of the probe molecule adsorption, both  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  sites are accessible in the substituted zeolite.

At the light of these results, we can propose that the observed SCR-activity of Cu-CZC catalyst can be related to the nature of copper species, that predominantly exhibit two types of states:  $\text{Cu}^{2+}/\text{Cu}^+$  and CuO clusters, as shown by DR-UV-VIS and FTIR *in situ* analyses. The presence of  $\text{Cu}_x\text{O}_y$  clusters in Cu-CZC sample can catalyze the low-temperature de $\text{NO}_x$  reaction, while isolated  $\text{Cu}^+/\text{Cu}^{2+}$  are responsible for the  $\text{NO}_x$  conversion observed at high temperature [8].

### **3.2. Study of MOR, Cu-MOR and Fe-MOR catalysts**

Among different framework types, the zeolites with large-micropore, such as Mordenite (MOR), show a good catalytic activity in  $\text{NH}_3$ -SCR. Mordenite is a large-pore zeolite with 12-MR windows, that impose less steric hindrance during the metal exchange. For small- and medium-pore zeolites, cations exchanged during the first exchange step may block the pores and thus limit the level of exchange [28]. In this part, Cu- and Fe-Mordenites, labeled respectively Cu-MOR and Fe-MOR, were prepared by ion exchanged method, characterized using different techniques, and then evaluated during  $\text{NH}_3$ -SCR process in the range of 150-450 °C.

#### **3.2.1. Catalytic activity in SCR- $\text{NH}_3$ reaction**

$\text{NO}_x$  and  $\text{NH}_3$  conversion profiles during  $\text{NH}_3$ -SCR over Na-MOR, Cu-MOR and Fe-MOR are shown in Figure 3(B). As it can be seen, the catalytic activity of parent zeolite (Na-MOR) is rather good, but only at low temperatures, while ammonia is mainly oxidized at high temperatures. The  $\text{NO}_x$  conversion exceeds 60 % at temperatures between 150 and

350°C. The modification of MOR with copper (4.3 wt% Cu) significantly increases its catalytic activity in the high-temperature SCR-NH<sub>3</sub> reaction, without improving the low-temperature activity of MOR. By the consequence, these evidences clearly show that the presence of copper moieties alone is not a guarantee for obtaining high activity at low temperatures, but the zeolitic structure play a role. These results can be explained by the presence of isolated Cu<sup>+</sup>/Cu<sup>2+</sup> ions as predominant species in Cu-MOR, which are responsible for the high-temperature SCR activity. The Fe-MOR sample shows lower activity than the other catalysts at low temperatures (150-200°C), while it is the most active catalyst in the 300-450°C temperature range.

CO and HC conversions during NH<sub>3</sub>-SCR reaction were also investigated (Fig. S8), being species typically present in an automotive exhaust and potentially having an effect on the conversion rates and selectivities [17,29]. The Cu-MOR sample shows higher CO and HC conversions than Fe-MOR sample, especially at high temperatures ( $T > 350\text{ }^{\circ}\text{C}$ ).

### ***3.2.2. Characterization of catalysts***

#### *Structural and textural properties*

The X-ray diffraction patterns of the parent and metal exchanged Mordenite show a preserved structure (with a limited loss of cristallinity) and the absence of extra-framework oxidic species. The main structural and textural properties are resumed in Table 2 and detailed in SI. We can remark that the Si/Al content is similar for all samples, as well as the metal weight percentage. Metal substitution slightly increases the specific surface area and the porosity of the parent compound, due to the replacement of cations with species having a smaller ionic radius, as well as thanks to the removal of residual impurities. MAS NMR spectra show a limited amount of extra-framework aluminum, mainly due to the cation exchange of Na-MOR and namely concerning the Si(1Al) groups. DR-UV-Vis spectra

witnesses for the presence of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  in the related compounds, also confirming a majority of isolated tetrahedral  $\text{Fe}^{3+}$  ions in Fe-MOR, i.e. small oligonuclear  $\text{Fe}_x\text{O}_y$  clusters.

### *In situ IR analysis*

IR data recorded after exposure of parent and metal-exchanged mordenite to pyridine are shown on Table 2. In particular, the acidity was studied after evacuation at 100 °C, i.e. after the removal of physically adsorbed pyridine. The IR spectrum obtained with the Na-MOR sample (not shown here) evidences mainly adsorbed pyridine on sodium cations. IR data (Table 2) show, as expected, that surface acidity is very low in the Na-MOR sample. Cu-MOR and Fe-MOR possess a significant amount of both Brønsted and Lewis acid sites. The latter is evidenced by the interaction between pyridine and copper/iron species. The increase of Brønsted acidity can be explained by the consequent increase of hydroxyls for cationic and defect compensation [30].

The concentration of Lewis acid sites is 41.4 and 64.7  $\mu\text{mol/g}$  for Cu-MOR and Fe-MOR, respectively. About 42 % of initial L.A.S. of Cu-MOR is still in interaction with pyridine after thermodesorption at 400 °C, indicating the presence of very strong Lewis acidic sites (Fig. 1(B)). The pyridine strongly adsorbed on B.A.S. of Cu-MOR completely disappears after evacuation at 400 °C. A different behavior can be observed for the iron-exchanged MOR sample (Fig. 1(C)). An increase in the Lewis acidity takes place when the temperature increases from 100 to 350 °C, suggesting that some Lewis acid sites of medium-high strength can be recovered during the thermo-decomposition of pyridine.

Infrared investigation by CO and NO probe molecule adsorption was performed as well, to have a clearer view of the cationic states. The *in situ* IR spectra of CO adsorbed on Cu-

MOR and Fe-MOR samples at different equilibrium CO pressures are shown in Figure 2(C and E). At low CO pressures, the IR spectra mainly consist of a single band at 2159  $\text{cm}^{-1}$  for Cu-MOR due to  $\text{Cu}^+$ -CO monocarbonyl species and at 2191  $\text{cm}^{-1}$  for Fe-MOR attributed to  $\text{Fe}^{2+}$ -CO monocarbonyl species [31,32]. The intensity of these bands is progressively increased with increasing the CO pressure accompanied by the formation of one new band at 2220  $\text{cm}^{-1}$  assigned to the  $\text{Al}^{3+}$ -CO species [31]. At high CO pressure, the band at 2187  $\text{cm}^{-1}$  in the Cu-MOR spectrum can be attributed to the symmetric stretching vibration of  $\text{Cu}^+$ -(CO)<sub>2</sub> dicarbonyls. For Fe-MOR, some authors assigned the band at 2158  $\text{cm}^{-1}$  to CO adsorbed on Si-OH groups [27]. On the other hand, it has been claimed that CO does not form complexes with  $\text{Fe}^{3+}$ , but in some cases bands at 2223 and 2158  $\text{cm}^{-1}$  were attributed to  $\text{Fe}^{3+}$ -CO species [33]. The assignment of these bands to  $\text{Fe}^{3+}$ -CO species usually lacks from evidence. It should be noted that no changes were observed in the hydroxyl region of zeolites during CO exposure (not shown here). In agreement with the literature [27], the molar extinction coefficients of Cu(I)-CO and  $\text{Fe}^{2+}$ -CO species are 11.29  $\text{cm} \cdot \mu\text{mol}^{-1}$  and 2.46  $\text{cm} \cdot \mu\text{mol}^{-1}$ , respectively. Consequently, the concentration of  $\text{Cu}^+$  and  $\text{Fe}^{2+}$  sites is 219  $\mu\text{mol/g}$  (32 % of dispersion) and 51  $\mu\text{mol/g}$ , respectively, with a very low dispersion (4 %).

Fig. 2(D) shows the IR spectra formed upon NO adsorption. An increase in NO amount results in the formation of distinctly resolved two bands at 1910 and 1812  $\text{cm}^{-1}$  assigned to  $\text{Cu}^{2+}$ -NO and  $\text{Cu}^+$ -NO nitrosyl complexes, respectively. A less intense feature appears at 1952  $\text{cm}^{-1}$  after exposure of 1 mbar equilibrium dose of NO, which was assigned to slightly associated ( $\text{Cu}^{2+}$ )<sub>n</sub> sites [34].

The FTIR spectra of NO adsorption on Fe-MOR (Fig. 2(F)) are comparable with those presented by Decyk *et al.* [35] or by Ivanova *et al.* [32]. The broad band at 1886  $\text{cm}^{-1}$  is assigned to mononitrosyl complex [ $\text{Fe}^{2+}$ -NO]. It seems to cover another species at lower wavenumber (1813  $\text{cm}^{-1}$ ) suggesting the presence of other type of nitrosyl complexes. The



exposure to 1 mbar NO at equilibrium results in the formation of one band at  $1765\text{ cm}^{-1}$  assigned to the  $\text{Fe}^{2+}\text{-(NO)}_2$  complex [32].

### 3.3. Study of Cu-CZC and Fe-MOR mechanical mixture

As we have seen from the previous results, Cu-CZC catalyst shows the best SCR activity at low temperatures (150-350 °C), while Fe-exchanged mordenite is the most active catalyst above 300 °C. In order to increase the  $\text{NO}_x$  conversion temperature window, a mechanical mixture of Cu-CZC (50 %) and Fe-MOR (50 %) was prepared at room temperature and tested in SCR- $\text{NH}_3$  reaction from 150 to 450 °C. The SCR activity results for this sample are shown in Figure 3(C). Under stoichiometric conditions ( $\text{NH}_3/\text{NO}_x$  molar ratio = 1), the mechanical mixture shows lower SCR activity than the individual Cu-CZC and Fe-MOR zeolites in the whole temperature range. About 50-60 %  $\text{NO}_x$  conversion is achieved in the range of 150-450 °C. Comparing with  $\text{NO}_x$  conversion, 30 % overconsumption of ammonia is observed at high temperatures, which is due to the undesired ammonia oxidation reaction. To compensate the overconsumption of ammonia, an additional SCR test was carried out in the presence of 30 % excess  $\text{NH}_3$  ( $\text{NH}_3/\text{NO}_x$  molar ratio = 1.3). The results (Fig. 3(C)) clearly show an enhancement in the SCR activity of the mechanical mixture in the whole temperature range. The  $\text{NO}_x$  conversion reaches 60 % at 150 °C, and it exceeds 80 % in the temperature range of 200-450 °C. Comparing with the activities of mono-component catalysts (Cu-CZC in Fig. 3(A) and Fe-MOR in Fig. 3(B)), it can be found that the mechanical mixture exhibits high SCR- $\text{NH}_3$  activities in a wide temperature range (150-450 °C), with 100 % of selectivity (no traces of  $\text{N}_2\text{O}$  could be detected).

The IR surface spectra of the mechanical mixture recorded during the SCR- $\text{NH}_3$  reaction ( $\text{NH}_3/\text{NO}_x = 1.3$ ) at different temperatures are shown in Figure 4. Two significant bands at

1442 and 1626  $\text{cm}^{-1}$  were observed during the low-temperature SCR (150-350  $^{\circ}\text{C}$ ). The band at 1442  $\text{cm}^{-1}$  belongs to the asymmetric vibration of  $\text{NH}_4^+$  on the Brønsted acidic sites, while that at 1626  $\text{cm}^{-1}$  is assigned to the  $\text{NH}_3$  coordinated to Lewis acid sites (copper or iron sites). The latter can be also overlapped by water adsorption. The bands corresponding to the adsorption of  $\text{NO}_x$  species are located at 1319  $\text{cm}^{-1}$  and 1343  $\text{cm}^{-1}$ . The first band is only observed at 150  $^{\circ}\text{C}$  and it can be assigned to  $\text{N}_2\text{O}_3$  species. The latter can be associated to the nitro compound species ( $\text{M-NO}_2$ ) that are rapidly formed (in the first 3 min, spectrum not shown here) and decomposed with increasing the temperature. In the 2800-3400  $\text{cm}^{-1}$  region, the observed bands can be assigned to the N–H stretching vibration of ammonium ions and coordinated ammonia. Differently from the former positive N–H bands, the negative peaks detected at 3607  $\text{cm}^{-1}$  should be generated from the occupation of  $\text{NH}_3$  on structural Si–OH–Al groups. The intensities of all the bands decreased when increasing the temperature from 150 to 450  $^{\circ}\text{C}$ , indicating the desorption of ammonia. The IR bands of the coordinated  $\text{NH}_3$  (1626  $\text{cm}^{-1}$ ) and  $\text{NH}_4^+$  ions (1442  $\text{cm}^{-1}$ ) almost disappear at 400  $^{\circ}\text{C}$ , although the SCR reaction still persists.

#### 4. Discussion

The set of experimental data revealed that the Cu-CZC (1.5 wt %) exhibits high SCR activity at lower temperatures, while Fe-MOR sample demonstrated a superior de- $\text{NO}_x$  activity at high temperatures, with a clear role of the zeolitic structure into promoting the catalytic efficiency. The mechanical mixing of 50 % Cu-CZC and 50 % Fe-MOR shows lower SCR activity than the individual zeolites in the whole temperature range due to the ammonia oxidation under stoichiometric conditions ( $\text{NH}_3/\text{NO}_x = 1$ ). In the presence of excess ammonia ( $\text{NH}_3/\text{NO}_x = 1.3$ ), the mechanical mixture results in highly active catalytic formulation for SCR- $\text{NH}_3$  at an extended temperature range (150- 450  $^{\circ}\text{C}$ ). The question now

arises on the role of copper and iron species as well as their co-presence in the mechanical mixture in the SCR-NH<sub>3</sub> reaction at 150-450 °C. To clarify the role of these species influencing the catalytic activity, we have correlated the characterization results with the catalytic behavior for NH<sub>3</sub>-SCR.

It is proposed in the literature that the adsorption of NH<sub>3</sub>-surface species or NH<sub>3</sub>-intermediates is the key step in the SCR process [36]. Thus, the areas of NH<sub>3</sub> adsorbed on both L.A.S. (1626 cm<sup>-1</sup>) and B.A.S. (1442 cm<sup>-1</sup>) are calculated for Cu-CZC, Fe-MOR and their mechanical mixture at different temperatures and summarized in Figure 5. By comparing the three catalysts, the smallest amounts of coordinated NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> were obtained in the presence of Cu-CZC sample, which results from the low concentrations of both Lewis and Brønsted acid sites (Table 2). Therefore, the concentration of adsorbed NH<sub>3</sub> species cannot be the only parameter to justify the high de-NO<sub>x</sub> activity of Cu-CZC at low temperatures (Fig. 3(A)). So that, the reactivity of Cu-CZC can be attributed to the predominance of dispersed (32 % of dispersion) Cu<sup>+</sup>/Cu<sup>2+</sup> species that are considered as the main active sites for SCR [8]. However, the intensity of the NH<sub>4</sub><sup>+</sup> band declines noticeably with the increasing reaction temperature, in agreement with the acidity results reported in Figure 1. The difficulty to retain ammonia and transform it into ammonium can explain the low SCR activity of Cu-CZC at temperatures above 350 °C as it can be seen in Fig. 3(A). From Figure 5, we notice that Fe-MOR led to significantly higher amounts of coordinated NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> that remain adsorbed on catalyst surface even at high temperatures (> 350 °C). This is certainly correlated with the presence of high concentrations of Brønsted and Lewis acid sites, able to retain adsorbed NH<sub>3</sub> (Table 2 and Fig. 1(C)), which results in the high-temperature deNO<sub>x</sub> activity of Fe-MOR (Fig. 3(B)). In fact, we must remember that the reported concentrations for acid sites were calculated upon pyridine desorption, accounting for site strength too, as aforementioned.

Monitoring the NO<sub>x</sub> signals by chemiluminescence for Cu-CZC sample (see SI, Fig. S9), we observe that the initial amount of NO<sub>2</sub> (75 ppm) can be completely suppressed at low temperatures (150-200 °C). This is related to the principal pathway of NO<sub>2</sub> transformation into NO. However, a part of NO<sub>2</sub> can also be consumed during the oxidation of HC. Considering the amount of converted HC at 200 °C (Fig. S8 in SI): 25 ppm × 5.4% = 1.3 ppm of C<sub>3</sub>H<sub>6</sub> and 25 ppm × 2.6% = 0.65 ppm of C<sub>3</sub>H<sub>8</sub>, this would lead to the consumption of 18.2 ppm of NO<sub>2</sub> (C<sub>3</sub>H<sub>6</sub>/NO<sub>2</sub> = 1/9 and C<sub>3</sub>H<sub>8</sub>/NO<sub>2</sub> = 1/10). This hypothesis seems to be consistent with the NO<sub>2</sub> conversion at 200 °C (Fig. S9) : 75 ppm × 93% = 69.7 ppm, where 51.7 ppm participate to the SCR reaction according to the widely described fast SCR path and 17.9 ppm remaining for HC oxidation. Finally, it can be seen that pure NO<sub>2</sub> also contributes to the CO oxidation: the CO conversion is over 10% at 200 °C (Fig. S8). In the region of 300 and 350 °C, an equilibrium can be established between NO and NO<sub>2</sub> and followed by NO<sub>x</sub> consumption (especially NO<sub>2</sub>). This phenomenon is promoted by the oxidizing power of copper and the temperature. At 400-450°C, we can see a consumption of NO<sub>x</sub>, especially of NO<sub>2</sub>. However, a part of NO can be produced at these temperatures during the oxidation of NH<sub>3</sub>. The same trends were observed over Fe-MOR (not shown here for sake of brevity) and the mechanical mixture (see SI, Fig. S10). However, the transformation of NO<sub>2</sub> into NO is enhanced (in time and intensity) in the presence of the mechanical mixture.

The time-evolution of NH<sub>4</sub><sup>+</sup> (1442 cm<sup>-1</sup>) and NH<sub>3</sub> (1626 cm<sup>-1</sup>) band areas during SCR-NH<sub>3</sub> reaction at 150-250 °C is shown in Figure 6. Two different phases are observed on this figure. The first one is prominently rapid (in the first 2 minutes), and it is due to the adsorption of NH<sub>3</sub> gas molecules on catalyst surface (Fig. 6(B, D and F)). The second phase is ascribed to the consumption of coordinated NH<sub>3</sub> to L.A.S. simultaneously accompanied by the formation of NH<sub>4</sub><sup>+</sup> ions. This result proves that the Lewis acid sites play the role of storing and supplying the NH<sub>3</sub> species to the active sites where ammonium is formed during

the  $\text{NH}_3$ -SCR process [36,37]. Compared to other catalysts, the rapid adsorption of  $\text{NH}_4^+$  on Fe-MOR and its accumulation on catalyst surface until saturation can be observed at low temperatures, especially at 150 °C (Fig. 6(A)). Thus it appears that the de $\text{NO}_x$  activity of the Fe-MOR was hindered by excess ammonia, as already pointed out by other authors [38]. This behavior was attributed to an ammonia inhibition effect via direct blocking of the active sites, suggesting the presence of an optimal ammonia surface concentration in order to increase  $\text{NO}_x$  conversion. However, the co-presence of iron and copper in the mechanical mixture leads to the formation of an optimal concentrations of coordinated  $\text{NH}_3$  and  $\text{NH}_4^+$  ions, which is lower than the coverage established on Fe-MOR sample, but higher than that observed for Cu-CZC (Fig. 5 and 6). This suggests a synergistic effect between Cu and Fe metals in the mixed catalysts resulting in higher SCR- $\text{NH}_3$  (when  $\text{NO}_x/\text{NH}_3 = 1.3$ ) in a wider temperature range. In addition, it was recently shown that the copper of CuO species becomes mobile in the presence of  $\text{NH}_3$  and NO at medium temperatures (250-350 °C), resulting in the migration of Cu species [14,39]. Based on this feature, several composite (Cu+Fe)-zeolite catalysts were prepared starting from the physical mixture of CuO and Fe-exchanged zeolites under NO and  $\text{NH}_3$  [39]. Thus, a possible migration of copper from Cu-CZC into the Fe-MOR structure during SCR- $\text{NH}_3$  might be envisaged, especially in the range of 250-450 °C. However, further studies are needed, such as EXAFS/XANES analyses, in order to confirm or discard this hypothesis.

Despite different reaction conditions, the SCR- $\text{NH}_3$  performance of combined (2%)Cu-(2%)Fe-BEA catalyst prepared by solid ion-exchange method ( $[\text{NH}_3+\text{NO}]$  SSIE) [14] is similar to our results. Contrary to the results obtained by using the dual-layer samples [10], the activity of the studied mechanical mixture is not decreased by diffusion limitation. Thus, the mechanical mixture Cu- and Fe-containing catalysts is a strong alternative to the Cu-Fe-based zeolites reported earlier [10,12,14], thanks to lack of steric restrictions as well as its

simplicity and ease of preparation. For instance, varying the proportion of Cu- and Fe-zeolites in the mechanical mixture may result in even higher NH<sub>3</sub>-SCR activity.

## 5. Conclusions

In this study, commercial SAPO-34 (CZC) and mordenite (MOR) were exchanged with transition metals (Cu, Fe) and studied for SCR-NH<sub>3</sub> reaction in the 150-450 °C temperature range. The physicochemical properties of the prepared catalysts were investigated using XRD, N<sub>2</sub> physisorption at 77 K, MAS NMR, DR-UV-Vis and *in situ* FTIR spectroscopies. Copper exchanged CZC (1.5 wt %) exhibit the best low-temperature SCR activity, while Fe-MOR (7.4 wt. %) sample demonstrated a superior de-NO<sub>x</sub> activity at high-temperatures. Highly dispersed isolated lattice mononuclear Cu<sup>+</sup>/Cu<sup>2+</sup> species are predominant in Cu-CZC sample that are the most active species in the low-temperature SCR. The presence of high concentrations of Brønsted and Lewis acid sites in the Fe-MOR sample, as well as greater strength for NH<sub>3</sub> adsorption improves the SCR activity at high temperatures (> 350 °C). Under an excess of ammonia (NH<sub>3</sub>/NO<sub>x</sub> = 1.3), the mechanical mixture of (50 %) Cu-CZC and (50 %) Fe-MOR shows higher NH<sub>3</sub>-SCR activity over a broader temperature range as compared to the Cu-CZC and Fe-MOR counterparts. The synergistic effects between Cu and Fe metals, as well as their favorable redox properties in the mixture result in higher SCR-NH<sub>3</sub> activity. In addition, an optimal amount of coordinated NH<sub>3</sub> and surface ammonium was obtained in the presence of this mechanical mixture, which is favorable to the SCR activity. The mechanical mixing of Cu- and Fe-zeolites is a simple and viable route to prepare highly active catalytic formulations for SCR-NH<sub>3</sub> efficient at a wide temperature range.

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