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Preparation of zeolite type faujasite from glass waste and aluminum scraps for the selective catalytic reduction of NO with NH₃

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Abstract: The development of economic and environmental process for the synthesis of multifaceted functional zeolitic material received considerable attention. In this study, zeolite type faujasite was prepared from glass waste and aluminum scraps recovered from municipal solid wastes. The prepared zeolite was tested in the selective catalytic reduction of NO with NH₃ using simulated diesel exhaust consisted of NO 1000 ppm, NH₃ 1000 ppm in presence of oxygen (8%) and water vapor (3.5%). The alkaline fusion prior to hydrothermal synthesis technique was used for the preparation of the zeolite. XRD and SEM techniques showed that the main product after hydrothermal treatment at 60°C for 6 days is the zeolite type faujasite contaminated with small quantity of zeolite Na-P1. The ammonium form of the prepared zeolite and copper acetate precursor were used to prepare a series of three catalysts having different copper loadings (5%, 7% and 10%). Cu(10)-Z1 catalyst showed excellent NO conversion reaching 98 % in large temperature window 180 °C to 550 °C.

Keywords: Glass waste, aluminum scraps, zeolite, faujasite, NaP1, NH₃-SCR

1. Introduction

Zeolitic materials are microporous solids, with 3-dimensional framework of [SiO₄]⁴⁻ and [AlO₄]⁵⁻ tetrahedra linked at their corners. Those compounds are frequently used in heterogeneous catalysis [1,2]. Sodium silicate and sodium aluminate are the most widely used as silica and aluminum sources in zeolite preparations which are expensive and costly pure raw materials. Recently, the recovery of natural and waste solids containing silicon and

aluminum become a necessity to replace the use of high-priced raw materials. In fact, the preparation of zeolites from waste have been mentioned by many studies [1–8]. The nitrogen oxide NO has harmful effects on the nature and human health. Fossil fuels combustion and diesel mobiles are considered as the principal sources that produced NO gas [9]. To remove toxic NO_x (x=1 and 2) emitted from chemical plants and stationary power sources, the first developed technology was the Selective Catalytic Reduction with ammonia (NH₃-SCR) using mainly vanadium bases catalysts (V-catalysts) V₂O₅-WO₃/TiO₂ or V₂O₅-WO₃/TiO₂ [9–12]. Around 2005, NH₃-SCR technology using V-catalysts was introduced for heavy duty (HD) diesel vehicles in Europe [13]. Nevertheless, some disadvantages like the rapid decrease in activity and selectivity at temperatures above 550 °C [14–16] as well as the toxicity of vanadium species, which volatilize at temperatures above 650°C [17,18], prompted the development of new types of catalysts. Among them, zeolites exchanged with copper and iron [14–16] are active over a wider temperature range than catalysts based on vanadium oxide and are less selective for N₂O. Besides, they have very low NH₃ release and some sulfur tolerance. However, at this time, they exhibit poor stability in a hydrothermal environment above 650°C. The copper-exchanged zeolites have greater efficiency at low temperature and less activity depend on the NO₂/NO_x ratio compared to those exchanged with iron. Nevertheless, the copper-exchanged zeolites show greater selectivity towards N₂O and oxidize more ammonia than iron-exchanged ones [19,20]. The last decade has shown that Cu-CHA (CHA: Chabazite) zeolites offer excellent activity at low temperature and high hydrothermal stability compared to other conventional zeolite catalysts based on copper and iron [21]. Also, Cu/Fe-ZSM-5 and Fe/Cu-BEA zeolites are the most extensively investigated in the past 30 years [22-24]. Copper-based zeolites are usually more active in the low-temperature (<350°C) range while iron-based zeolites are more active at higher temperatures (>350°C). Small-pore zeolite Cu-SSZ-13 has received great attention due to its higher

activity and selectivity at low temperatures and improved hydrothermal stability for diesel vehicles [25-28].

NH₃-SCR is considered as the most efficient control technology for the removal of NO_x. For evident reasons it would not be desirable to use NH₃ for automotive applications since it is corrosive, toxic and difficult to handle. To overcome these difficulties, urea was used because it is safer and can generate NH₃ in situ and can be easily transported “on board” (known as AdBlue). NH₃/urea SCR technology has been adapted to heavy-duty (HD) and light-duty (LD) diesel vehicles with high NO_x reduction efficiency.

The current study aims to minimize the negative effects of waste production and management on human health and the environment, as well as to reduce the use of natural resources using a simple procedure to transform glass waste from fluorescent tubes and aluminum waste into zeolite (FAU). The prepared zeolite was evaluated in the NH₃-SCR of NO in an oxidizing atmosphere.

2. Experimental section

2.1 Starting materials

The silica source used for the preparation of the zeolites is glass of the end-of-life fluorescent tubes collected from the special containers established by the administration of the National Engineering School of Sfax-Tunisia for the collection of hazardous waste. The aluminum source is scraps (AS) collected from aluminum workshop and. Analytical grade NaOH pellets were purchased from Sigma Aldrich and 98%.

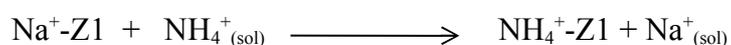
2.2. Preparation of the zeolite support

The zeolites were synthesized by alkaline fusion technique followed by a hydrothermal treatment using the same process reported by Sayehi et al. [5]. An aliquot of 10 g of glass

waste powder with particle <125 μm were ground with 10 g of NaOH pellets in porcelain mortar for 15 min. The mixture was then heated at 550 $^{\circ}\text{C}$ for 1h. After fusion, the fused product was cooled, ground again and mixed with aluminate solution, prepared by the dissolution of 0.5 g of A.S in 80 mL NaOH solution. The obtained mixture was stirred at room temperature for 2 h and then placed in an oven at 60 $^{\circ}\text{C}$ for 6 days. The zeolitic materials were separated by filtration and washed thoroughly several times with deionized water until pH 9 and dried at 80 $^{\circ}\text{C}$ for one night. The obtained solid was called Na-Z1.

2.3 Catalyst preparation

The parent zeolite used for the preparation of catalysts by the impregnation method was the ammonium form of Z1 zeolite, called (NH_4^+ -Z1). The experiment of ammonium ion exchange was carried out at room temperature (RT) using 2.5 g of Z1 zeolite added to 100 mL of a 0.5 M ammonium chloride solution. The suspension was stirred magnetically for 5 hours to exchange Na^+ ions with NH_4^+ ions according to the following reaction:



After centrifugation and drying at 100 $^{\circ}\text{C}$, NH_4^+ -Z1 solid was used as starting material to prepare a series of three catalysts having different copper loadings (5%, 7% and 10%). Thus, in a flask containing 50 mL of distilled water, the desired quantity of copper acetate $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ was added and after complete dissolution, a mass of 0.5 g of NH_4^+ -Z1 zeolite was added. The flask is then mounted on a rotary evaporator and the suspension is left under stirring for 4 hours at 80 $^{\circ}\text{C}$. The water was evaporated under pressure and the recovered solid was dried in an oven at 80 $^{\circ}\text{C}$ overnight and finally calcined at 550 $^{\circ}\text{C}$ under air flow (2 $^{\circ}\text{C}/\text{min}$) for 8 hours. The obtained catalysts were called $\text{Cu}(\text{x})\text{-Z1}$, with (x) referring to the amount of copper in wt.%.

2.4 NH_3 -TPD and NH_3 -SCR of NO catalytic activity measurements

The ammonia desorption programmed as a function of the temperature (NH₃-TPD) was carried out using an automated Micromeritics Autochem 2910 analyzer. An aliquot of 40 mg was first pretreated at 550 °C for 30 min under air flow (30 cm³/min) and cooled at room temperature, then saturated with NH₃/He (2500 ppm of NH₃, flow = 50 cm³ min⁻¹) at 100 °C and purged with helium for 45 min. . Following this adsorption, the physisorbed ammonia is removed by leaving the sample for 2 h at 100 °C, under a helium flow rate of 30 cm³/min. Finally, the temperature was raised to 550 °C (5 °C/min), under a helium flow rate of 50 cm³/min.

Catalytic performances of the Cu(x)-Z1 catalysts were evaluated in the NH₃-SCR of NO under atmospheric pressure using fixed-bed micro-reactor. An aliquot of 18 mg of each sample was activated in-situ at 180 °C under oxygen and helium mixture. The samples were tested from 180 °C to 550 °C, with a temperature ramp of 3.8°C, using simulated diesel exhaust gas: 1000 ppm of NO, 1000 ppm of NH₃, 3.5% of water vapor, 8% of oxygen and helium at a total flow rate of 100 cm³/min (VVH = 333,333 cm³/g. h). The composition of the outlet gas was continuously analyzed using a Pfeiffer quadruple mass spectrometer. The NOx conversion was calculated according to the following formula [22]: $X_{NO} = (NO)_0 - (NO)_T / (NO)_0$

3. Results and discussion

3.1. Characterization of zeolite product

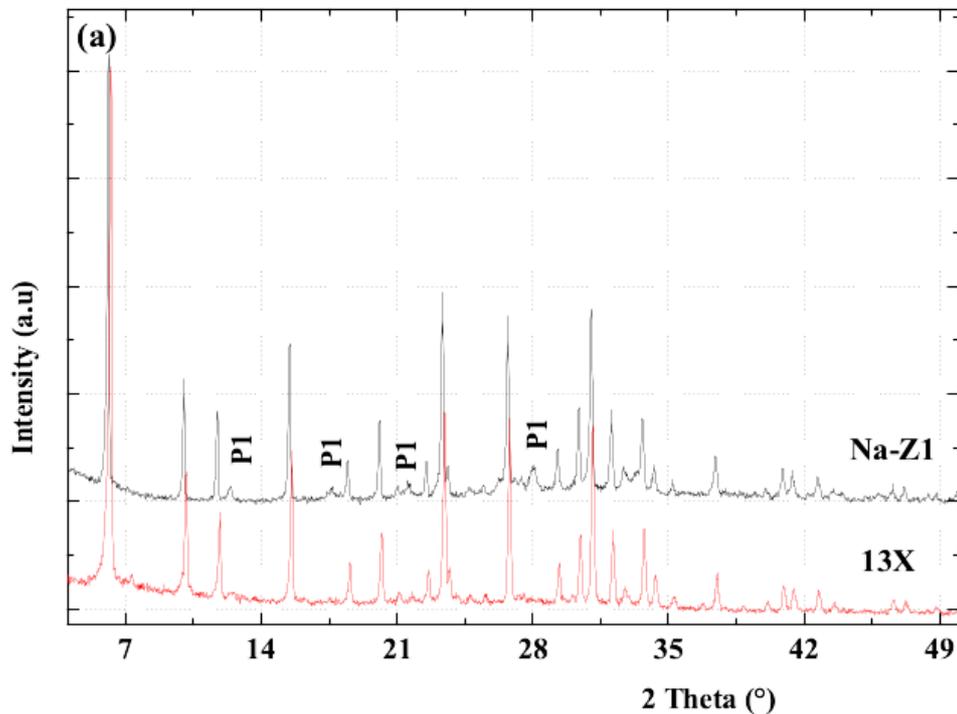
In **fig. 1** we reported the XRD patterns of Na-Z1 and 13X commercial zeolite (UOP), the SEM photomicrograph of Na-Z1 and ²⁹Si MAS-NMR of Na-Z1. **Fig. 1-a** reveals that XRD profile of Na-Z1 matches with that of 13X. The phase identification carried out using X'Pert High Score Plus software revealed that the main product is the zeolite type faujasite X (FAU X) ($[Na^+_{86}(H_2O)_{264}][Si_{106}Al_{86}O_{384}]$ (ICDD PDF No. 38-0237) contaminated with small quantity of Na-P1 zeolite ($[Na_6(H_2O)_{12}][Al_6Si_{10}O_{32}]$; (JCPDS N ° 01-071-096). The result of XRD analysis was supported by SEM technique (**Fig 1-b**). SEM photomicrograph exhibits

octahedral crystals which characterize the morphology of FAU zeolite and pseudo-spherical crystals attributed to zeolite Na-P1.

The ^{29}Si MAS-NMR spectrum of Na-Z1 sample illustrated in **Fig. 1-c**. showed five peaks centered at ca. -87, -92, -97, -102 and -107 related to the respective Q^4 Si coordination environments Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al) [5]. Assuming a random distribution of aluminum in the framework, it is possible to calculate the framework Si/Al ratio according to the equation:

$$\frac{Si}{Al} = \frac{\sum_{n=0}^4 I_{Si(nAl)}}{\sum_{n=0}^4 0.25 \times n \times I_{Si(nAl)}}$$

Where $I_{Si(nAl)}$ is the intensity of a ^{29}Si MAS NMR peak. The Si/Al molar ratio determined by ^{29}Si -NMR of Na-Z1 sample is about 1.67.



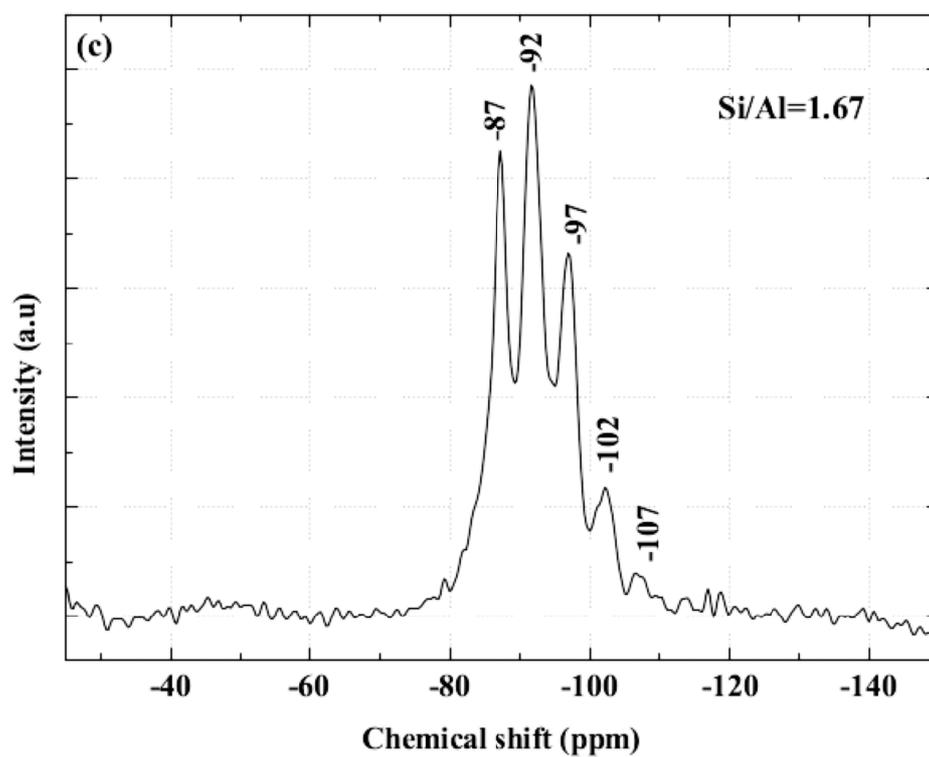
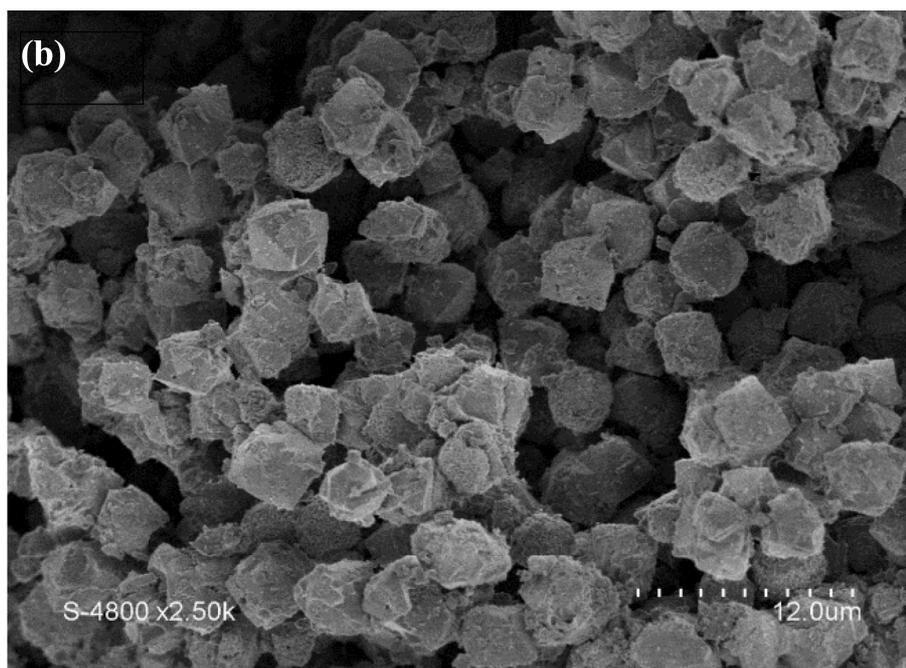


Figure 1: XRD patterns of Na-Z1 and 13X zeolites (a) SEM of Na-Z1 zeolite (b) and ²⁹Si MAS-NMR of Na-Z1 zeolite (c).

3.2. Characterization of Cu(x)Z1 catalysts

Fig.2 illustrated the XRD patterns of Na-Z1, NH₄-Z1 zeolites and Cu(x)-Z1 catalysts. One can see that the XRD patterns of Cu(x)-Z1 catalysts showed on the first hand, a slight decrease in the intensities of most peaks after copper exchange. This change in the crystallinity can be related to the removal of aluminum species from zeolite framework without complete destruction of the zeolite structure. The XRD profiles of catalysts with high copper contents (Cu(7)-Z1 and Cu (10)-Z1 catalysts) displayed the characteristic peaks of CuO (JCPDS, No. 80 – 0076) at the angles 35.48° and 38.7° in 2θ. On the other hand, we noted a slight rise of the background intensities in the region of 2θ region between 14 and 40° of the sample Cu(x)-Z1 catalysts. It is possible that, upon preparation and calcination of the catalysts some amorphous material was formed.

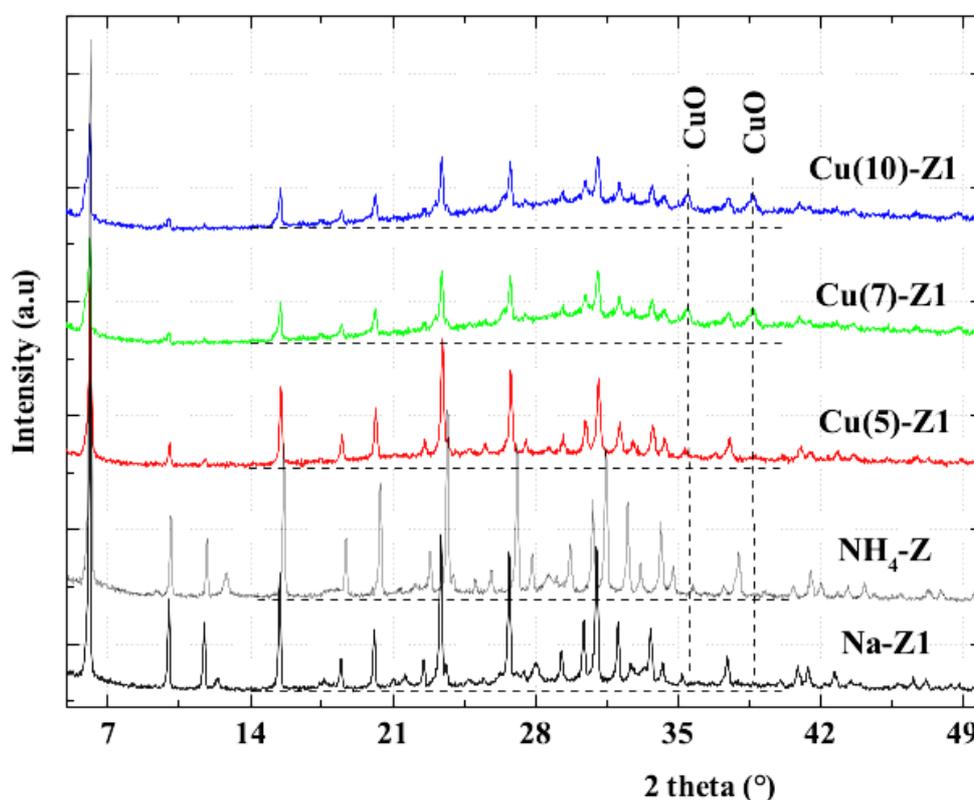


Figure 2: XRD patterns of Na-Z1, NH₄-Z1 zeolites and Cu(x)-Z1 catalysts.

Nitrogen adsorption-desorption of $\text{NH}_4\text{-Z1}$ zeolite and $\text{Cu}(x)\text{-Z1}$ catalysts revealed that the increase of copper content has small effects on the obtained isotherms (**Fig .3**). A typical type I adsorption-desorption isotherms were obtained in each case, indicating that the samples were microporous [29]. For relative pressures situated from 0.4 to 0.98 P/P^0 , we noticed the appearance of hysteresis loops which can be attributed to capillary condensation of nitrogen in inter-crystal mesopores arising from the packing of zeolite crystals. The textural properties reported in **Table 1** showed that there is a decrease of the S_{BET} with the increase of copper content. This result suggests that copper species, entrapped in the microporous matrix, obstruct the channel apertures of the parent zeolite $\text{NH}_4\text{-Z1}$. The increase of the amount of copper decreased the total surface area BET (S_{BET}) and the S_{ext} compared to zeolite $\text{NH}_4\text{-Z}$. For the decrease of S_{BET} , this is due to the existence of copper or extra-framework aluminum species entrapped in the cages or in the channels thus blocking the pores of the zeolite. The increase in the porous volume of both support and catalysts could be explained by the good dispersion of the copper. On the other hand, the increase in the copper content from 7% to 10%, decreases the external surface of the catalysts, this could be attributed to the presence of large CuO particles [30] or to the amorphization of zeolite structure. Our XRD also showed the appearance of peaks characteristic of CuO when copper was introduced at 7 wt% and their intensity and width increases when the copper content was at 10 wt% which goes hand in hand with the small reduction of the BET surface observed. Therefore, this small loss of surface area and porosity can be attributed with more certainty to some porosity blockage by CuO aggregates. Nevertheless, the BET surface area and porous volume of $\text{Cu}(10)\text{-FAU}$ are of $414 \text{ m}^2/\text{g}$ and of $0.175 \text{ cm}^3/\text{g}$, respectively.

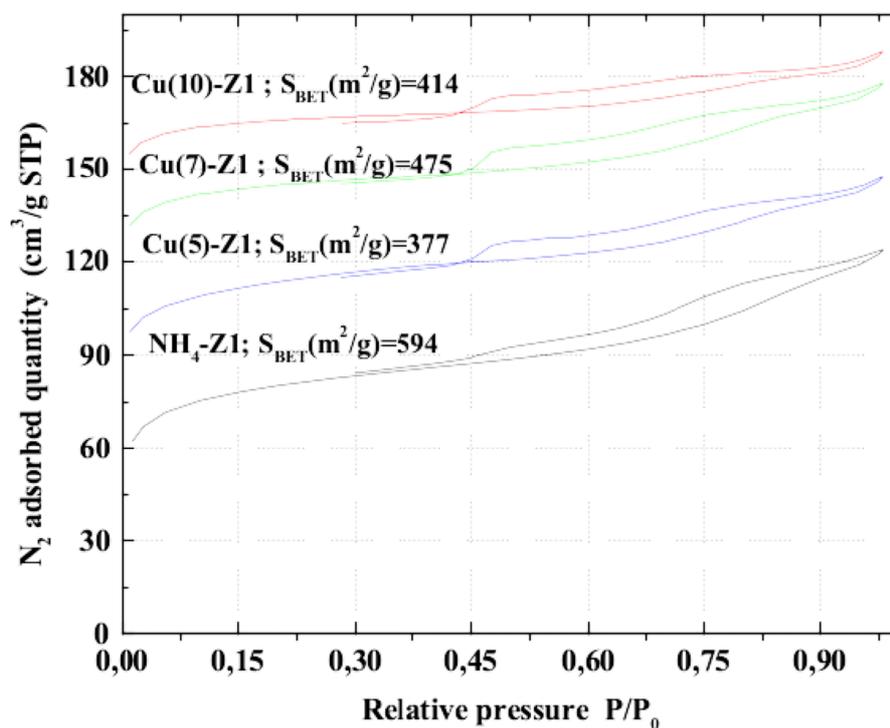


Figure 3: N₂ adsorption-desorption of NH₄-Z1 zeolite and Cu(x)-Z1 catalysts.

Table 1: Textural properties of Na-Z1, NH₄-Z1, Cu(5)-Z1, Cu(7)-Z1 and Cu(10)-Z1 samples.

Samples	S _{BET} (m ² /g)	S _{mic} (m ² /g)	S _{ext} (m ² /g)	V _{mic} (cm ³ /g)
Na-Z1	393	310	83	0.148
NH ₄ -Z1	593	498	95	0.237
Cu(5)-Z1	377	284	93	0.135
Cu(7)-Z1	475	316	59	0.198
Cu(10)-Z1	414	371	43	0.175

The evolution of acidity (Bronsted and Lewis) was studied by NH₃-TPD. **Fig. 4** illustrated the NH₃-TPD profiles of Na-Z1, NH₄-Z1, and Cu(x)-Z1 catalysts. NH₃-TPD profiles of Na-Z1, NH₄-Z1 and Cu(5)-Z1 samples reveal the presence of a broad ammonia desorption peak extending from 105°C to 477°C with a maximum around 200°C which can be attributed to the desorption of weakly chemisorbed ammonia on weak Lewis and/or Brønsted acid sites or

silanol groups [5, 6]. The increase of the copper content causes the appearance of new peaks around 330°C and 425°C for the two catalysts Cu(7)-Z1 and Cu(10)-Z1 which increase in intensity with the increase of the copper content. These two peaks are essentially related to desorption of ammonia from both strong Brønsted acid sites of the zeolite and the new Lewis acid sites created by the Cu species [7]. This is particularly clear for Cu(7)-Z1 and Cu(10)-Z1 with the ammonia desorption at 330 °C . We can then attribute this high peak to NH₃ desorbing from copper species.

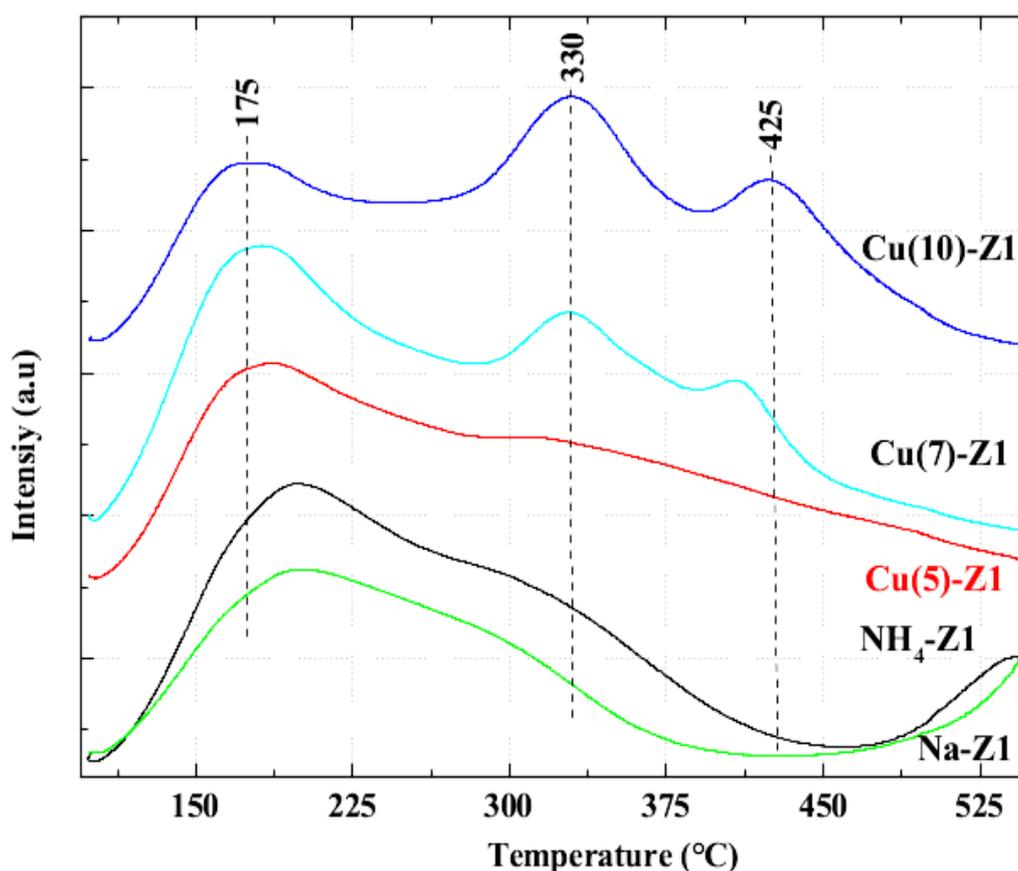
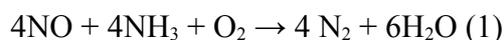


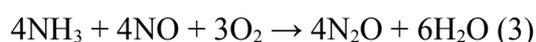
Figure 4: NH₃-TPD of Na-Z1 and NH₄-Z1 zeolites and Cu(x)-Z1 catalysts.

3.3 NH₃-SCR of NO catalytic activity measurements

The catalytic activity of the catalysts was evaluated in the NH₃-SCR of NO in the presence of oxygen and water vapor according to the following reaction:



The results collected are presented in **Fig. 5**. It should be noted that, for all the catalysts, the NO conversion increases with increasing temperature to reach a maximum and then decreases, excepted for Cu(10)-Z1. For this later, almost total NO conversion was observed in the temperature window studied with a space velocity of 333,333 h⁻¹. The presence of a maximum in the evolution of NO conversion reflects the existence of a competition between two reactions, the first concerning the reduction of NO and the second the oxidation of NH₃ by the oxygen present in the gaseous mixture. The competition between the two reactions takes place in favor of the oxidation of NH₃, which explains the lower conversion of NO at high temperatures. This behavior is also general for all the catalysts used in the elimination of NO by NH₃ in the presence of oxygen. The decrease in NO conversion can also be linked to the formation of N₂O according to the two non-selective reactions (2) and (3):



On the other hand, the NH₄-Z1 exhibits limited NO conversion, while the introduction of copper increased the NO conversion. Indeed, Cu(x)-Z1 catalysts show good catalytic performance at low temperatures, reaching 98% and 50% NO conversion at around 200 °C for Cu(10)-Z1 catalyst and Cu(7)-Z1, respectively. While NO conversion was about 45% at 260 °C for Cu(5)-Z1. The behavior of Cu(5)-Z1, Cu(7)-Z1 and Cu (10)-Z1 catalysts at low temperature is principally due to the oxidation capacity of the catalyst to oxidize NO into NO₂. This capacity is enhanced by the redox couple Cu⁺/Cu²⁺ [2,6] but also by the presence of copper oxide small aggregates. Therefore, the copper content is important and explains the increase of activity. It should be noticed that Cu(10)-Z1 catalyst maintained its NO

conversion around 99% in the whole temperature range. To point out the efficiency of Cu(10)-Z1 catalyst for NH₃-SCR process, we compared our results with the literature data obtained copper exchanged small-pore zeolites: Cu-SSZ-13 [31]. Han et al prepared Cu/SSZ-13 catalysts with different Si/Al ratios via the in situ hydrothermal synthesis. The fresh and hydrothermally aged Cu/SSZ-13 with the Si/Al ratio of 6.5 tested in NH₃-SCR with reaction gas feed consisted of 500 ppm NO, 500 ppm NH₃, 5% O₂, 3% H₂O and N₂ in balance. The gas hourly space velocity (GHSV) was kept as 400,000 h⁻¹ showed the best SCR activity showed the best SCR activity within a broad temperature window of 200–550 °C, in which more than 90% NO_x was reduced.

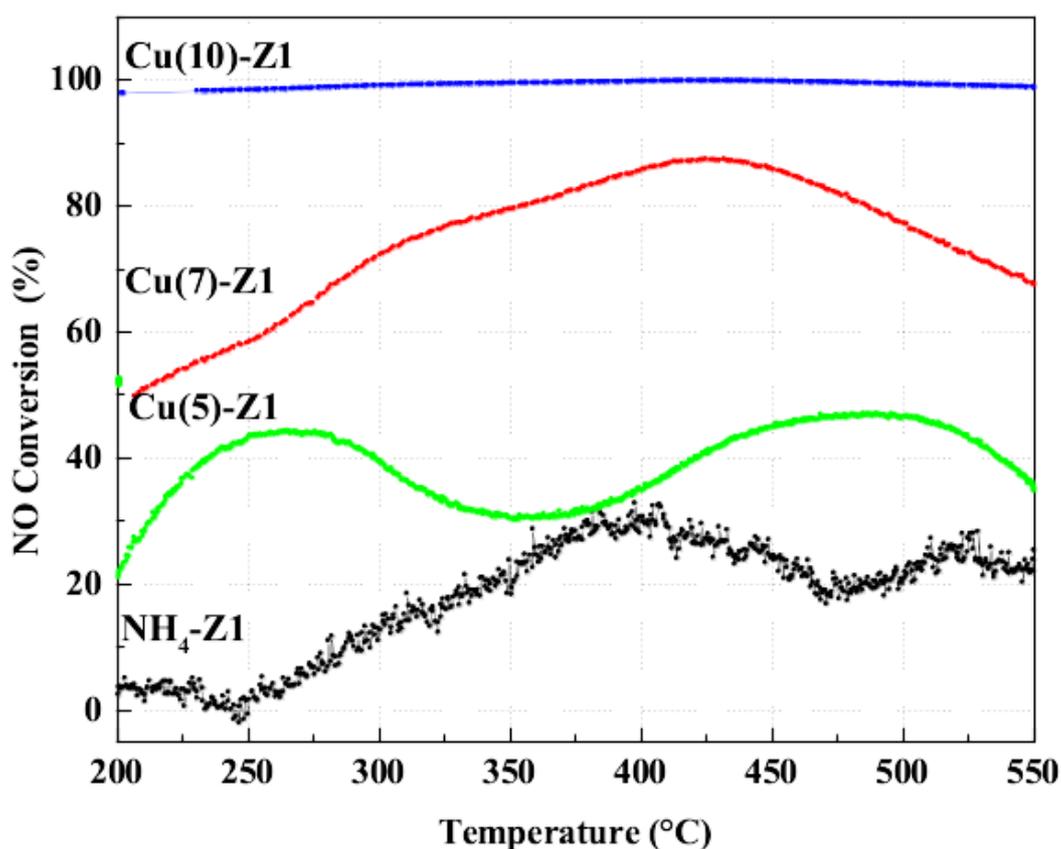


Figure 5: NO conversion profiles of NH₄-Z1 zeolite and Cu(x)-Z1 catalysts.

Also Martnez-Franco et al. evaluated the catalytic activity of three Cu-SSZ-13 materials in the SCR of NO_x, all materials demonstrate excellent activities in a wide range of temperatures when tested under severe catalytic conditions (the presence of 5% of water in the feed and high gas hourly space velocity (450 000 cm³/g.h)[32]. Taking into account that the GHSV used in our study we can conclude that Cu(10)-Z1 exhibits an excellent NH₃-SCR activity in temperature range 200–550 °C.

4. Conclusion

Zeolite type FAU called Na-Z1 was successfully prepared from glass waste and aluminum scraps collected from municipality disposal using alkaline fusion prior to hydrothermal synthesis technique. Ammonium exchanged zeolite Na-Z1 (NH₄⁺-Z1) was used as carrier to prepare copper exchanged catalysts with different copper content. The obtained catalysts were tested in ammonia Selective Catalytic Reduction using simulated diesel exhaust consisted of NO 1000 ppm, NH₃ 1000 ppm in an oxidizing atmosphere in the presence of excess oxygen (8%) and water vapor (3.5%). The XRD profiles of the Cu(x)-FAU showed change in the crystallinity related to the removal of aluminum species from zeolite framework without complete destruction of the zeolite structure. For high copper contents Cu(7)-Z1 and Cu (10)-Z1 catalysts, we note the presence characteristic peaks of CuO. From the results of nitrogen adsorption-desorption technique, it is noticed that the BET surface area decreased with the introduction of copper compared to the FAU zeolite. The conversion of NO increases with the increase of copper amount in the zeolite. The best catalytic activity is attributed for Cu(10)-Z1 reaching 98% NO conversion at 200°C.

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