Cu-exchanged 3D-printed Geopolymer/ZSM-5 Monolith for Selective Catalytic Reduction of NOₓ

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Cu-exchanged zeolites with MFI structure, such as ZSM-5, represent effective catalysts for SCR processes when the application requires a good thermal stability under a wide range of temperature as for the after-treatment of exhaust gas from diesel engine. The production of zeolite in a structured form, mandatorily required for mobile applications, is quite complex due to the poor adhesion of the material.

In this paper 3D-printed geopolymers containing about 37 % ZSM-5 are proposed as potentially structured catalysts for SCR applications. The production of the monolith and the pre-treatment necessary to introduce copper as active exchanged cation are investigated. The effect of pre-treatments on the physical and morphological structure of both geopolymer and zeolite and on the nature of copper introduced in the subsequent step was studied using characterization techniques such as SEM, XRD, N_2 physisorption and Temperature Programmed Reduction (TPR).

1. Introduction

Selective Catalytic Reduction (SCR) is the most widely used deNOₓ process for NOₓ removal from both stationary and mobile sources involving the reduction of NOₓ to N_2, generally with ammonia, over a suitable catalyst (Zhang et al., 2019).

The location of the deNOₓ unit downstream the electric precipitation and desulfurization unit in power plants (Zhang et al., 2019) or the application of the SCR process to the after-treatment of exhaust gas from diesel engine, typically exiting at a temperature <350 °C (Tamilselvan et al., 2017), require the development of catalysts operating at quite low temperature.

Furthermore, the location of the SCR unit in diesel exhaust gas after-treatment, downstream the DOC and DPF, requires a highly hydrothermally stable SCR catalyst due to cyclic regeneration taking place into the upstream DPF requiring a temperature increase up to 600 °C (Mohan et al., 2020).

The catalysts used for SCR consist of an active washcoat deposited on a metallic or a more porous ceramic substrate. The most active catalysts are based on platinum, vanadia/titania and zeolite (Mohan et al., 2020). Zeolites are excellent materials for catalytic processes as they consist of three-dimensional networks that allow them to preferentially adsorb molecules (Sarno and Scudieri, 2018).

Large and medium pore zeolites such as ZSM-5 (Lisi et al., 2009), MOR, FER, BEA (Leistner et al., 2015) and small pore zeolites as SSZ-13 (Hamoud et al., 2019) and SAPO-34 (Cao et al., 2016) are generally used for NH_3-SCR. Owing to an appropriate pore size, a strongly acidic character and the ability to resist deactivation, HZSM-5 is one of the most used zeolites as a catalyst (Namchot and Jitkarnka, 2015).

Fe and Cu are the most suitable metals for exchanged zeolites for NH_3-SCR since they provide good catalytic performance in a wide operating temperature range (Hamoud et al., 2019). Cu-CHA zeolite showed a superior deNOₓ activity over a wide temperature window and excellent hydrothermal stability as well (Martín-García et al., 2017). The limitation of conventional microporous zeolites for NH_3-SCR is mainly due to the difficulty of diffusion of the reagents and to the deactivation of the catalyst caused by the deposition of ammonium nitrates and sulphates in the pores and channels especially at low temperatures of reaction (Peng et al., 2020). For this reason, hierarchical zeolites show higher catalytic performances related to a greater distribution of pore

sizes. Furthermore, zeolite-type catalysts are currently limited by the inability to produce self-supported monoliths or foams (Gargiulo et al.2018). Zeolite washcoated ceramic substrate are generally produced with a consequent low zeolite loading and/or loss of the active phase due to poor adhesion and unmatched thermal expansion with the substrate especially in mobile applications (Lisi et al., 2009).

Composite TiO_2/zeolite materials have been proposed for photocalytic applications, addition of zeolite in the composite providing enhanced performance also related to an increased accessible porosity (Sarno et al. 2015). Geopolymers (GPs) are inherently micro/mesoporous materials and their pore architecture can be varied in a wide range of values (Colombo et al., 2010). Moreover, GPs show a high thermal stability with little network structural degradation up to 800 °C (Colombo and Degischer, 2010). The close similarity of the GP network with the zeolite one concerning ion exchange and presence of metal ions makes GPs amorphous analogues of zeolites for a lot of applications (Colombo et al., 2013).

In this work, structured catalysts consisting of zeolite with geopolymer obtained by Direct Ink Writing (DIW, an extrusion-based Additive Manufacturing technique) are proposed in order to provide the required geometric structure and, at the same time, a hierarchical porosity (from macro to micro pores) that can be involved in the catalysed reaction when a suitable active metal ion, such as Cu^{2+}, is incorporated or exchanged in the composite catalyst.

2. Experimental

Monoliths of Na-based geopolymer, with round section (diameter = 18 mm; height = 10-20 mm) (Figure 1a) were manufactured by DIW. The geopolymer slurry was prepared by mixing metakaolin, as an aluminosilicate source, and an activating solution, composed of sodium silicate (SS2942, Ingessil S.r.l., Montorio, Italy), sodium hydroxide NaOH (Sigma–Aldrich, Steinheim, Germany) and distilled water.

ZSM-5 was a commercial zeolite supplied by Zeolyst in ammonium form which was previously treated for 2 h at 550 °C to obtain the corresponding H-form, then it was added to the ink as a filler. To obtain a printable ink Na-bentonite (Sigma–Aldrich, Steinheim, Germany) and methylcellulose (Sigma–Aldrich, Steinheim, Germany) were added as rheological agents and distilled water was used to adjust the viscosity of the ink after the filler addition. The nominal composition of the monolith is reported in Table 1.
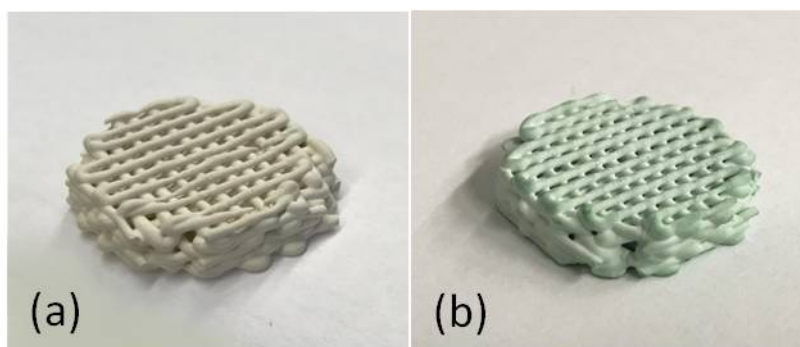

Figure 1: As prepared 3D-printed GP/ZSM-5 monolith (a); GP/ZSM-5 monolith after acid treatment and subsequent ionic exchange with $CuAc_2$ solution (b).

Table 1: Composition of GP monoliths.

Ratio between components in GP	Nominal weight composizion of monolith (%)	
SiO_2/Al_2O_3 = 3.8	GP	57.20
Na_2O/Al_2O_3 = 1.0	Zeolite	37.28
H_2O/Al_2O_3 = 25.0	Na bentonite	3.60
	Methilcellulose	1.92

The DIW equipment (Delta Wasp 2040 Turbo, Wasproject, Massa Lombarda, IT) used to fabricate the monoliths was equipped with a pressured vessel with a typical pressure of $1x10^5$ Pa to $5x10^5$ Pa and an infinite screw to extrude the ink through a tip of a conical nozzle of 840 µm (Nordson Italia S.p.a., Segrate, IT). The extrusion occurred at a predetermined flow rate and print speed, at room temperature and in air.

After printing the first layer, which was composed of filaments parallel to each other, the nozzle was raised by 600 µm in the z-direction to print the second layer which was composed of parallel filaments with a rotation of 90 °; this process was repeated until reaching the desired dimension. The printed samples were placed into the oven at 75 °C for 2 days in closed boxes to complete curing.

The crystalline phase assemblage was investigated by X-ray diffraction (XRD, Bruker AXS-D8 advance) with CuKα radiation at 40 kV and 40 mA on ZSM-5 and on powders obtained by grinding printed structures after curing and after acid treatment. Data were collected in the range of 5–60 ° 2θ with a scanning step of 0.05 ° and a scanning time of 1 s/step.

SEM analysis was carried out on both as prepared and treated monoliths using a a FEI Inspect Scanning Electron Microscope (SEM) to determine the possible morphological changes caused by the acid treatments.

Specific surface area measurements and micro- and meso-pore analysis were performed with a Autosorb 1-C by N_2 adsorption at 77 K after degassing the samples for 2 h at 150 °C. The specific surface area was evaluated through the BET method, whereas the PSD of micro- and meso-pores was evaluated through the DTF model.

3. Results and discussion

In Figure 2 the comparison of XRD patterns of the GP/ZSM-5 composite and of the zeolite are reported. The GP/ZSM-5 composite shows an amorphous halo centered at 27-29° which is typical of the geopolimeric matrix (Kim and Lee, 2020). All the main peaks of the ZSM-5 are present also in the composite confirming that their incorporation in a reactive geopolymeric matrix does not result in dissolution nor changes their crystalline structure.
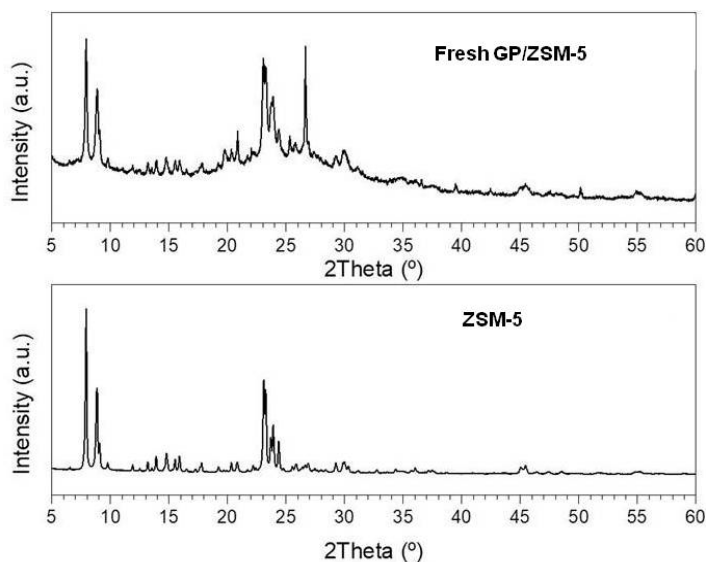

Figure 2: XRD patterns of the GP/ZSM-5 monolith and pure ZSM-5.

In Figure 3 a and b the SEM images of the inner portion of the tubular structures constituting the grid matrix is reported showing the presence of needle-like particles over a granular structure, the latter likely consisting of ZSM-5 (Lisi et al., 2009).
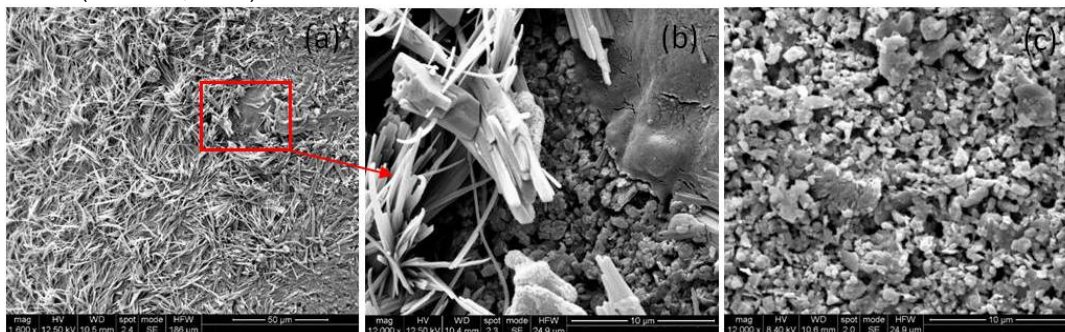

Figure 3: SEM image of the as prepared GP/ZSM-5 monolith (a). On the right (b) a magnification of the portion identified by the red rectangle in the left image. GP/ZSM-5 monolith after the acid treatment (c).

In order to introduce the active metal into the zeolite ionic exchange with copper acetate was firstly attempted directly on the as prepared GP/ZSM5 monolith using 0.02 M $CuAc_2$ solution and a zeolite/solution ratio 8 g/l, as reported in (Lisi et al., 2009). The white monolith quickly turns into blue but, after 2 h exchange and the following washing treatment, the inner section of the monolith is still white suggesting that $Cu(OH)_2$ precipitated on the surface due to the highly basic character of the GP hindering the exchange. Indeed, immersion of a fresh monolith (0.5 g) in 40 ml bi-distilled water results in a pH increase up to 10. In order to avoid the fast precipitation of copper hydroxide, the GP/ZSM-5 monolith was treated in a aqueous solution for 20 h adding two droplet of HNO_3 (37 %). The monolith was then washed again and pH of a 40 ml solution was 7.7 at the beginning, and stabilized at 8 after 3 h.

SEM analysis performed after the acid treatment showed the removal of needle-like particles (Figure 3c) confirming the attribution of these structures to sodium compounds from material preparation.

In Figure 4 the N_2 adsorption isotherms and the pore size distribution (PSD), evaluated according to the DFT method, are reported for the monolith before and after the acid treatment.
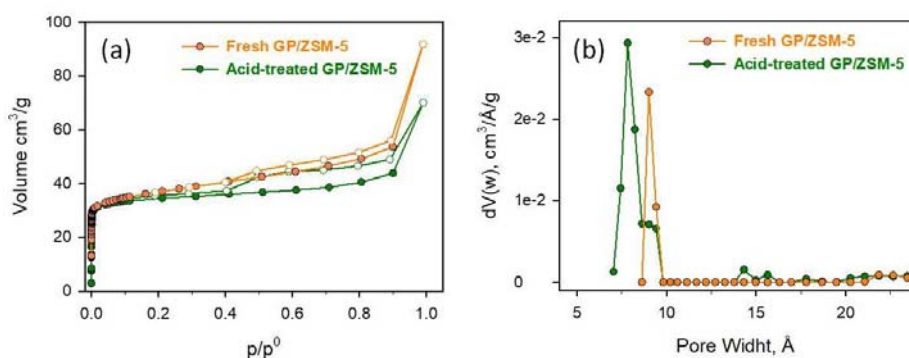

Figure 4: N$_2$ adsorption isotherms at 77 K of fresh GP/ZSM-5 and acid-treated GP/ZSM-5 (a). Corresponding PSD evaluated according to the DFT model (b).

Both the fresh and the acid treated monoliths give a type I isotherm with a hysteresis, larger for the acid-treated sample, indicating the presence of some mesopores in addition to micropores typical of the zeolite. The micropores are peaked at about 9 Å for fresh GP/ZSM-5 whereas the maximum shifts to 8 Å, approaching that found for pure ZSM-5, after the acid treatment. The presence of some mesopores, mostly associated to GP, is detectable at about 22 Å. The original value of the BET surface area (138 m^2/g) is rather unchanged after the acid treatment (134 m^2/g) and reasonably agrees with the value of the surface area of ZSM-5 of about 400 m^2/g and the zeolite fraction in the composite material of about 37 %, assigning a negligible surface area to the geopolymer. A slight reduction of the total pore volume from 0.083 to 0.068 cm^3/g was observed upon acid treatment.

XRD analysis was also repeated in order to verify the possible modifications induced by the acid treatment. In Figure 5 XRD patterns of the fresh and acid-treated GP/ZSM-5 monolith are compared.
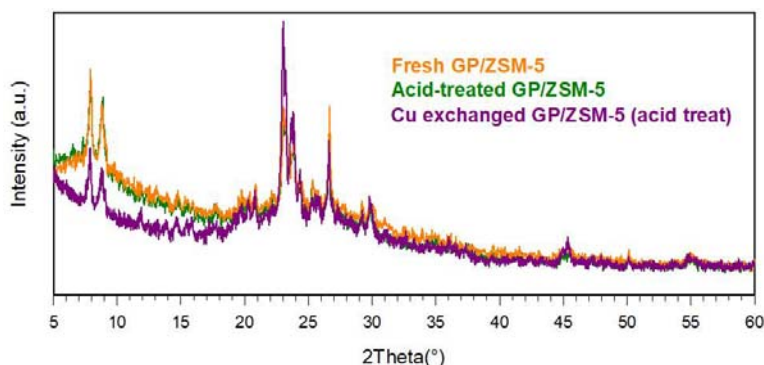

Figure 5: XRD patterns of the fresh, acid-treated GP/ZSM-5 and GP/ZSM-5 monolith after acid treatment followed by Cu exchange and calcination at 400°C.

No detectable loss of crystalline structure of the zeolite was detected after the acid treatment that led only to removal of sodium hydroxide residue.

The high stability of the geopolymer as well is in good agreement with results reported by Bakharev (2005) about geoplolymers exposed to an acid (sulfuric or acetic acid) solutions for two months, who concluded that more crystalline geopolymers prepared with sodium hydroxide were more resistant to aggressive environment. The acid-treated monolith was exchanged as above described. The homogeneous light blue color (Figure 1b) confirmed that an effective ion exchange occurred.

No modification of crystalline structure of ZSM-5 upon copper exchange and also upon subsequent calcination was observed, as shown by the purple pattern reported in Figure 5.

Temperature programmed reduction (TPR) was used to characterize copper present in the sample after the exchange followed by calcination under air at 400 °C. In Figure 6 TPR profiles of Cu-exchanged GP/ZSM-5 without and after the acid treatment are compared.

Exchanged copper provides a two-step reduction with corresponding signals peaked at 300 and 420 °C whereas the formation of copper oxide clusters gives rise to a single peak in the temperature range of the first step of exchanged copper (Lisi et al., 2009). The presence of a single peak for the sample exchanged without performing any acid treatment is in agreement with the supposed precipitation of copper hydroxide. On the other hand, the presence of two partially overlapped peaks suggests that copper was mostly exchanged in the acid-treated sample whilst it is present as copper oxide for the sample exchanged without any preliminary treatment. The quantitative analysis confirmed that the amount ($4.49x10^{-4}$ mol/g) of copper evaluated by the integration of the TPR curve, according to the reaction $CuO + H_2 -> Cu + H_2O$, is close to the expected amount of copper exchanged in the zeolite ($5.75x10^{-4}$ mol/g).

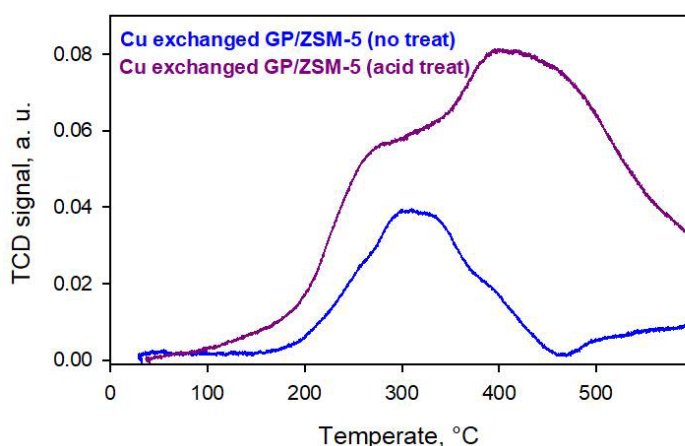*Figure 6: H$_2$ TPR profiles of Cu exchanged GP/ZSM-5 monolith without and after the acid treatment.*

4. Conclusions

In this paper the synthesis of a 3D printed ZSM-5/geopolymer was proposed as catalytic structured substrate for SCR application, such as after-treatment of diesel engine, after a suitable ion exchange with an active metal like copper. The pre-treatment necessary to strongly reduce the basic character of the geopolymer, strongly hindering the exchange of copper, was investigated together with the nature of copper and the chemical stability of the composite material to the acid treatments. On the basis of these results a procedure to correctly exchange the structured substrate was provided involving an acid pre-treatment of the ZSM-5/geopolymer up to neutralize the aqueous solution where the composite monolith is dipped before performing the Cu^{2+} exchange. The acid pre-treatment removes the sodium hydroxide residue without significantly affecting the crystalline structure and the porosity of ZSM-5. The following exchange step allows copper to be mostly located in the exchangeable positions rather than on the monolith outer surface as copper hydroxide, which is inactive for the SCR reaction. New attempts to load higher fraction of active zeolite into the 3D printed geopolymer are in progress.

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