



Cu-ZSM5 based monolith reactors for NO decomposition

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ABSTRACT

Micronic ZSM5 (Si/Al = 25) powder has been deposited on cordierite monoliths by dip-coating technique using colloidal alumina or silica as binders with different zeolite/binder ratios in aqueous suspension determining the parameters to obtain the best adhesion and mechanical resistance of the washcoat layer. For monolithic catalysts with washcoat containing 10 wt% SiO₂ the following alternative preparation procedures have been used: (i) deposition of a pre-exchanged Cu-ZSM5 powder on the ceramic monolith; (ii) deposition of a H-ZSM5 powder on the ceramic monolith followed by copper exchange of the structured catalyst.

The monolithic catalysts have been investigated by morphological (SEM), physical (BET and porosity), chemical (ICP-MS, EDX, XRD, H₂ TPR) and catalytic (NO decomposition tests in flow reactor under dry and wet conditions) analyses. Results have been compared with those obtained on the corresponding Cu-ZSM5 powder sample with the same copper content and Si/Al ratio in order to define the effect of the preparation procedure on the chemical and catalytic properties of the monoliths.

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1. Introduction

Monolith catalysts are widely used in environmental applications due to the several advantages they offer, like low pressure drop even at high space velocity, high geometric surface area, good mechanical strength and durability [1–3]. In particular, monolith catalysts are used in DeNO_x catalysis for both mobile and stationary source.

Since zeolites are promising materials for environmental catalysis, deposition of a zeolite layer on a structured support is required for a lot of applications. Many methods of deposition of an active layer on monoliths exist depending on the properties of the ceramic substrate and of the catalyst that has to be deposited [4]. Various preparation techniques have been developed including washcoating and incorporation of active species by different methods [3]. Nevertheless, the methods used to deposit a zeolite layer on a structured support can differ from deposition of other compounds [4].

Dispersion of zeolites on ceramic monoliths can be basically made into two different ways: by in situ hydrothermal synthesis or deposition from a slurry of fine pre-synthesized zeolite powder [2,4,5]. The advantage of the first method is the stronger adhesion of the coating to the support avoiding the use of a binder or a washcoat [6]. Nevertheless, it is more complex and diffusion

limitations can occur through the dense layer with small intercrystalline pores. In addition, formation of zeolite coatings with a high Al content is hindered by a Al-rich substrates as cordierite [7]. On the other hand, the main advantage of the washcoating method are the shorter diffusion distances. Moreover, since many zeolites are commercially available, the washcoating technique represents a quite simple method to obtain a zeolite based structured catalyst. Schematically, the method consists in dipping the structured substrate in a suspension of zeolite crystals also containing a binder and other possible additives followed by drying and calcinations [4]. Small particle sizes of the zeolites generally lead to a more effective anchoring to the structured support due to the comparable dimension with the macropores of the ceramic monolith [2]. Zamaro et al. [5] found a good correlation between zeolite particle size and adhesion, the lower the particle dimension the higher the stability of the washcoat layer. The use of a binder material, such as alumina or silica, to improve the zeolite adhesion is widely reported [3,8–10]. Nevertheless, the amount of the binding material should be carefully chosen, since active regions could be covered or active pores blocked [11]. The use of a surfactant is also reported to better disperse the zeolite in the suspension [8]. Due to its organic nature, it generally burned off during calcinations [11]. Zamaro et al. [5] reported an improved adhesion of three different zeolites by using colloidal silica both increasing contact between particle aggregates and allowing the formation of bondings with zeolite crystals after calcination due to the high concentration of hydroxyl groups. The enhanced adhesion of zeolite upon use of a silica binder was also demonstrated by Beers et al. [8].

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Nevertheless, the use of a binder is not always recommended. Boix et al. [12] reported that the addition of an alumina based binder for the deposition of PtCoZSM5 on monolith promoted the formation of nonselective CoAl_2O_4 spinel from Co^{2+} , originally located at exchange positions, and Al_2O_3 .

Zamaro et al. [5] also investigated the relationship of suspension concentration and number of immersion of the monolith with the zeolite loading. In the range 4–27 wt% ZSM5 washcoat they found a non-linear correlation between washcoat load and these parameters.

In general, pre-exchanged zeolites are used to washcoat the ceramic monolith [9,13–15] but sometimes the exchange is carried out after zeolite deposition on the monolith [16]. The possible effect of the order of the dip-coating and exchange steps in determining the final properties of the monolith catalyst has been always neglected. Nevertheless, Boix et al. [12] observed a different activity in the SCR of NOx of monolith catalysts prepared by exchanging Co and Pt after NaZSM5 washcoating or by washcoating the structured support directly with Pt/CoZSM5. No explanation is proposed for that, although the release of active cations from the zeolite powder suspended in the solvent during the coating step or a bad control of the exchange of a zeolite layer deposited on a structured support, due to the complexity of the system ceramic monolith/binder/zeolite, could be hypothesized.

This paper is focused on the scale-up of catalyst from Cu-ZSM5 powders (fixed bed reactor) to a structured reactor, in order to analyze the possible modification of physico-chemical and catalytic properties and define the procedure to obtain a stable and mechanical-resistant monolith catalyst. Structured catalytic reactors have been prepared by depositing a washcoat zeolitic layer on the internal channels of monoliths, through a dip-coating method; the adhesion of the zeolite to the monolith has been optimized by changing all parameters involved in the preparation of the structured catalyst such as type of binder, binder/zeolite ratio, pH of the suspension. Moreover, the copper ionic exchange has been carried out before (directly on the powder sample) or after monolith dip-coating in order to determine the possible influence on the nature of copper. The catalytic properties of the monolith catalysts have been compared with those of the corresponding powder sample in the decomposition of NO both under dry and wet conditions.

2. Experimental

2.1. Catalysts preparation

The Cu-ZSM5 powder sample was prepared by ion exchange of a commercial H-ZSM5 zeolite (Zeolyst CBU-5020, Si/Al = 25, BET specific surface area = 400 m²/g, particle size < 10 μm) in aqueous solution at 50 °C for 2 h with a 20 mM solution of copper(II) acetate monohydrate (Aldrich purity 99.8%) using a zeolite/solution ratio = 8 g/l. After ion exchange the sample was centrifuged, washed twice with double distilled water and dried at 120 °C overnight. Finally, the Cu-exchanged sample was calcined according to the following procedure: (a) heating under helium flow at 5 °C/min up to 550 °C keeping this temperature for 2 h; (b) cooling down to room temperature under He flow; (c) switching the gas flow to 1% O₂/He and heating 5 °C/min up to 550 °C keeping this temperature for 4 h.

Cordierite (2Al₂O₃·5SiO₂·2MgO) honeycomb monoliths provided by Corning Inc. with cell density 200 and 400 cpsi were cut to obtain samples with 5 × 5 channels section and about 24 mm length. The monoliths were coated by dipping the structured support into a ZSM5 fine powder (<1 μm) water suspension containing or not a defined amount of a binder. Pseudo-boemite (Disperal, Condea Chimie) or 30% colloidal silica (Ludox, Sigma–Aldrich) was used to obtain Al₂O₃ or SiO₂ binders, respectively. A binder/zeolite ratio 1:4 and 1:10 were used. After removing excess liquid with pres-

surized air, the monoliths were dried at 120 °C and then calcined at 550 °C under air flow. Several cycles were required to obtain the target amount of washcoat.

The exchange was carried out before or after the monolith coating. In the former case a copper-exchanged ZSM5 powder was added to the water suspension for the dip-coating; in the latter case the cordierite monolith was firstly coated with a H-ZSM5, then the exchange was made directly on the monolith sample under the same conditions described for the powder sample taking into account the amount of deposited ZSM5. A different device was used to stir the exchange solution in order to avoid crushing the monolith. Washcoat of the structured catalysts investigated for the NO decomposition contain 10% silica or consists of pure zeolite. In the following catalysts with the washcoat containing ZSM5 + SiO₂ will be referred to as monolith A and monolith B to indicate that the support has been coated with H-ZSM5 and then exchanged or directly with Cu-ZSM5, respectively. Monolith C indicates the structured catalyst prepared without using any binder and exchanged after the zeolite deposition.

2.2. Catalysts characterization

Copper content was quantitatively determined by inductively coupled plasma spectrometry using a Agilent 7500 ICP-MS instrument, after MW-assisted dissolution of copper in nitric acid solution.

ZSM5 washcoat adhesion was verified by measuring the weight loss of the monolith after 30 min ultrasounds treatment.

XRD patterns at room temperature were collected using a PW 1100 Philips XRD 6000 diffractometer with CuKα radiation.

SEM/EDS analysis was performed using a Philips XL30 microscope equipped with an EDAX detector for EDS analysis.

Meso- and micropores analysis of powder and monolith samples was performed using a Quantachrome Autosorb-1C analyzer by Ar adsorption at 87 K.

TPR experiments were carried out with Micromeritics TPD/TPR 2900 apparatus equipped with a TCD. Fresh samples were treated at 550 °C under air flow before starting the experiment. All samples were reduced with a 2% H₂/Ar mixture (25 cm³ min⁻¹) heating 10 °C min⁻¹ up to 550 °C. A sample amount corresponding to the same quantity of copper was used in all tests having been preliminarily verified that cordierite gives a nondetectable contribution to the reduction.

2.3. Catalytic activity tests

Powder and structured catalysts were tested for NO decomposition, this reaction having been widely investigated on Cu-ZSM5 [24,31–34]. Catalytic tests were carried out using a tubular quartz reactor, supplied with a porous disk supporting the catalyst particles (Ø200–400 μm) only for powder samples, heated in a three controlled zones electrical furnace (LENTON). The temperature of the catalytic bed was measured by a Chromel–Alumel thermocouple. Mass flow controllers (BROOKS 5850S) were used to control and measure the flow rates of high purity gases: 1 vol.% NO/He (NO₂ impurity about 150 ppm) and pure He (99.995%). Before each experiment, the catalyst was treated under He (500 cm³/min) for 2 h at 550 °C in order to promote Cu²⁺ self-reduction to Cu⁺ [17–21]. The inlet and the outlet streams were analyzed by Hartmann & Braun continuous analyzers specific for NO, N₂O (URAS 10 E) and O₂ (MAGNOS 6G), while the NO₂ concentration was indirectly evaluated through a NO₂ to NO catalytic converter (Hartmann & Braun CGO-K). The standard conditions used for the activity measurements were W/F = 1.5 × 10⁻³ g min N cm⁻³ for powder catalyst and 1.8 × 10⁻³ g min N cm⁻³ for monolith sample (weight referred to zeolite only), T = 400–550 °C and NO concentration = 5000 ppm.

Table 1
Preparation conditions and mechanical properties of monolith (400 cps) samples.

Sample	Order of deposition/exchange	Binder	pH of the suspension	Average adhesion (wt% washcoat)–number of deposition cycles	Weight loss after ultra-sound treatment (wt% washcoat)
Monolith A	1-deposition 2-exchange	10%SiO ₂	9	23–4	<1
Monolith B	1-exchange 2-deposition	10%SiO ₂	5–6	17–5	<1
Monolith C	1-deposition 2-exchange	–	5–6	16–6	4

These conditions allowed the NO conversion to be enough low (<15% in all experiments) to assume a differential reactor behaviour. Wet gas feed was obtained by saturating a helium stream at room temperature. The effect of water vapour on the catalytic activity was determined by measuring the activity under dry conditions after the two ageing treatments reported below: (a) 80 min at 480 °C by adding 2.0 vol.% water to the reaction feed; (b) treatment (a) followed by restoring of dry conditions and a further ageing treatment under wet helium flow for 15 h.

The catalytic performance is expressed as TOF (turnover frequency = number of NO molecules converted to nitrogen per hour per copper atom) in order to better compare samples with different copper content.

3. Results and discussion

3.1. Monolith washcoating

The first attempt to deposit H-ZSM5 onto the 400 cps cordierite monolith was done using alumina as binder with an alumina/zeolite ratio 1:10 adjusting pH to 9 with NH₄OH, as suggested by Xu and Moulijn [22] in order to promote the hydrolysis of the hydroxide precursor. After four cycles for each monolith the average weight increase due to the washcoat deposition was 3.8%. The weight loss upon ultrasound treatment was higher than 80% for each sample indicating a bad adhesion to the cordierite monolith.

Silica was used as binder as well. Similarly to the preparation with alumina, a silica/zeolite ratio 1:10 was used. Four dip-coating cycles resulted in an average weight increase of 23% for 400 cps monolith and of 17% for 200 cps monolith. A sim-

ilar weight increase was obtained with a silica/zeolite ratio 1:4 (21% for 400 cps monolith). The very good washcoat adhesion was confirmed by a weight loss <1% measured with the ultrasound test for all samples. On the basis of these results, in order to minimize the SiO₂ loading which is inactive for the NO decomposition, the monoliths with silica/zeolite ratio 1:10 have been chosen for the subsequent exchange which was carried out with a copper acetate solution under the same operating conditions described for powder samples hanging the monolith in the stirred suspension.

The possibility to support a layer of pre-exchanged ZSM5, avoiding the exchange step of the zeolite coated monolith, was also evaluated. A preliminary test of copper release under the conditions used to deposit the zeolite layer was carried out to estimate the possible copper loss due to the occurrence of cation exchange in the suspension. Cu-ZSM5 powder was then added to a water suspension containing colloidal silica at pH 9 with the same zeolite/silica/water ratio used for the monolith coating. After 24 h the copper content in the suspension was measured by ICP-MS analysis. 13% of the initial copper content was released in the suspension due to the exchange of a fraction of Cu²⁺ for NH₄⁺. For this reason Cu-ZSM5 deposition was not carried out under these conditions but monolith washcoating with a pre-exchanged zeolite was performed without modifying pH by NH₄OH addition. In that case the pH of the suspension was in the range 5–6. The negligible copper release (<0.03% of initial Cu after 24 h) detected in the preliminary test on the Cu-ZSM5 powder, carried out at this pH, suggested that deposition of pre-exchanged material can be done under this condition. Therefore, a washcoat increase of 17% was obtained for a 400 cps monolith after five deposition cycles using a silica/zeolite ratio 1:10. The washcoat adhesion is as good as that obtained adjusting pH to

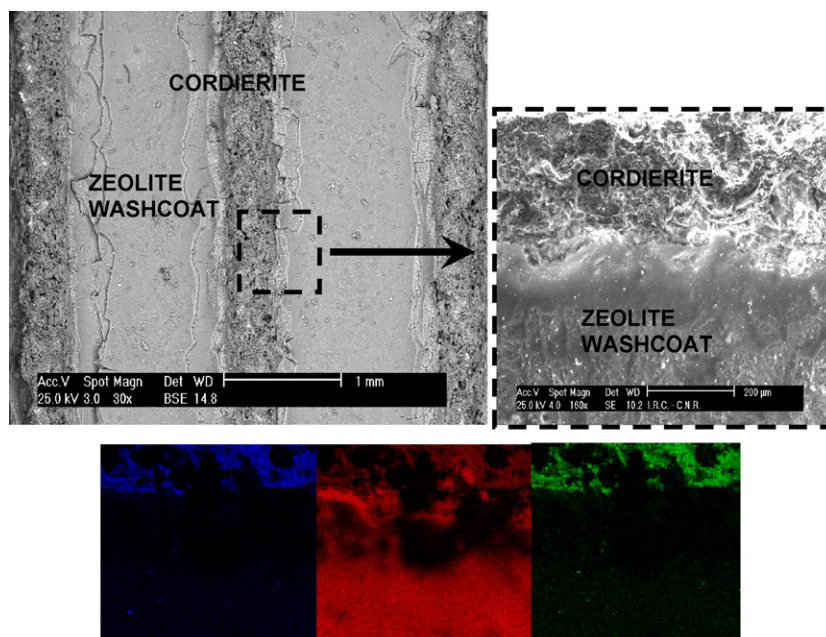


Fig. 1. SEM image of the ZSM5 monolith cross-section with magnification of the selected area (90° rotated) (upper image) EDS maps of Al, Si and Mg (lower image).

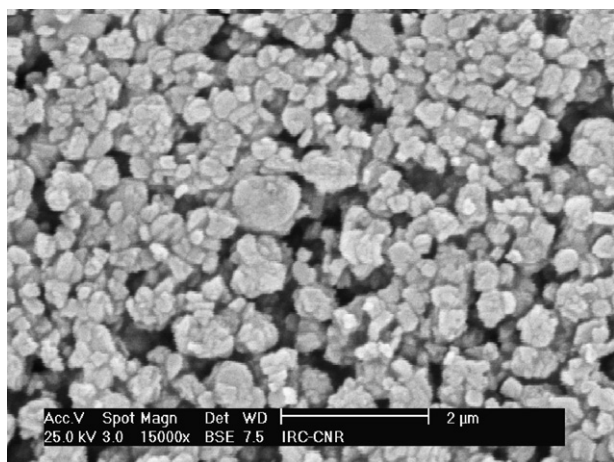


Fig. 2. SEM image of ZSM5 layer on cordierite monolith.

9. Thus, although, less effective than that carried out at pH 9, this kind of monolith preparation can be used for Cu-ZSM5.

Finally, deposition of a H-ZSM5 on a 400 cpsi monolith without adding any binder was also effected obtaining 16% washcoat deposition after six coating cycles. This monolith, which is mechanically less stable than the catalysts containing silica (4% washcoat lost upon ultrasonic treatment), was subsequently exchanged with copper as for the monolith containing the silica binder.

The results of the study of the preparation parameters on the mechanical properties of the ZSM5 monolith are summarized in Table 1.

3.2. Catalysts characterization

In Fig. 1a the SEM image of the monolith cross-section is shown. The cordierite channels with the large pores are clearly distinguishable from the more dense washcoat layer. In Fig. 1b the selected area of Fig. 1a (90° rotated) was magnified and EDS micro-analysis was performed (Fig. 1c) in order to observe the elements distribution in the washcoat. The large silicon enrichment inside the channel and, at the same time, the presence of Al and Mg (main components of cordierite together with Si) limited to the cordierite areas emerging from the crosscutting of the monolith, confirmed that a ZSM5 washcoat quite uniformly covered the monolith channels.

In Fig. 2 zeolite grains constituting the washcoat, with 1 μm or less, diameter are clearly visible.

Copper distribution (not reported in the figure) was also analyzed by EDX analysis. Results show a better distribution for monolith B whereas some Cu-enriched zones can be observed for monolith A caused by the deposition of CuO clusters on silica.

In Table 2 the actual copper content, as measured by ICP-MS analysis, in powder and monolith samples is reported. The data clearly show that the same copper amount is exchanged both for powder and structured samples and, furthermore, confirm that a negligible quantity of copper is lost during the deposition of the pre-exchanged zeolite. This copper content is close to the value corresponding to 100% exchange level (Cu/Al atomic ratio equal to 0.5).

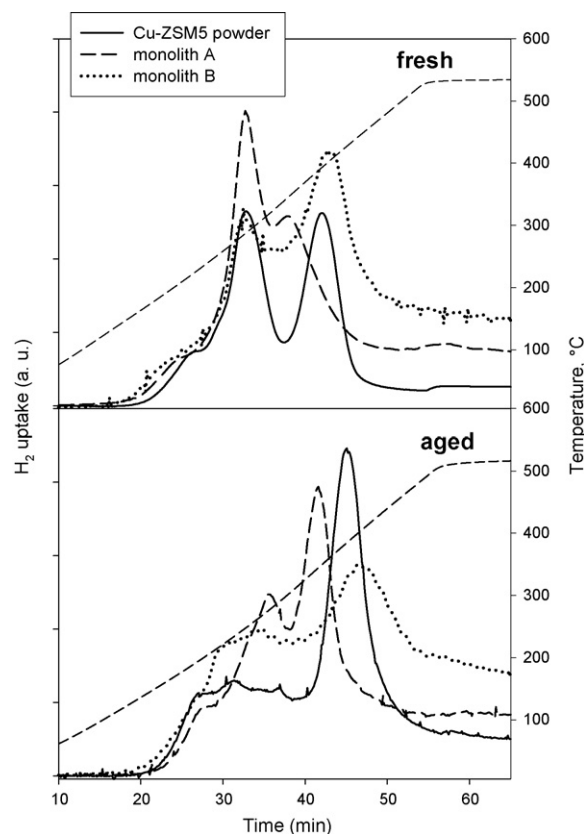


Fig. 3. TPR profiles of fresh and aged (catalytic test in the presence of water) monolith and powder catalysts.

Nevertheless, especially for the two structured samples the possibility that copper could be also present onto the cordierite or onto the silica added to the washcoat layer, in addition to that exchanged, cannot be excluded, as already reported for SEM/EDX analysis.

No significant modification of total pore volume and pore diameter was detected by Ar adsorption analysis. Micropores with the ZSM5 typical diameter around 5 Å were detected for both powder and monolith samples with the additional contribution of mesopores (diameter in the range 30–60 Å) for structured catalysts containing silica. This suggests that the preparation method does not cause pores occlusion.

In order to characterize the nature of copper in monolith samples and the influence of the exchange procedure, TPR experiments were carried out on fresh catalysts. A blank run with a H-ZSM5 powder sample showed that the zeolite that does not contain reducible ions does not show any H₂ uptake and consequently is not reducible. In Fig. 3 the TPR profiles of the powder sample and monoliths A and B, as fresh and as aged under wet condition, are reported. All curves consist of two partially overlapped signals peaked at about 300 and 420 °C, respectively, with a small shoulder at about 200 °C. The overall H₂ uptake roughly corresponds for all samples to the stoichiometric amount required for the reduction of Cu²⁺ to Cu⁰, as indicated by the H₂/Cu ratios close to 1 reported in Table 2. The

Table 2

Copper content determined by ICP-MS and values of H₂/Cu ratio evaluated from TPR analysis for powder and monolith (400 cpsi) samples.

Sample	Cu content (wt% ZSM5)	H ₂ /Cu ratio from TPR experiments (fresh sample)	H ₂ /Cu ratio from TPR experiments (used sample)
Powder Cu-ZSM5	1.71	1.0	1.3
Monolith A	1.70	1.2	1.1
Monolith B	1.66	1.3	1.5
Monolith C	1.63	1.3	1.5

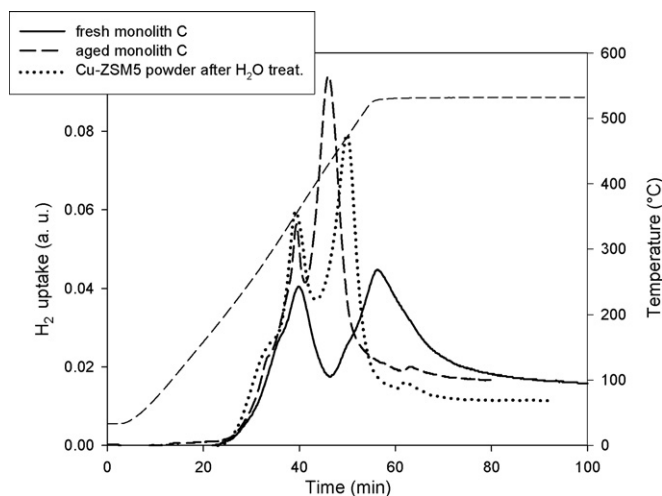


Fig. 4. TPR profiles of fresh and aged monolith C compared with Cu-ZSM5 powder sample upon treatment in water solution.

presence of two peaks is typical of Cu-ZSM5 and it is attributed to the two steps reduction of copper from Cu^{2+} to Cu^+ and from Cu^+ to Cu^0 , respectively [23]. Moreover, bulk-like copper oxide species can be reduced in the same temperature range of the low temperature peak [24,25]. As a consequence, when the intensity of the first peak is greater than that of the second one, the formation of some copper oxide aggregates, in addition to exchanged copper, can be supposed. The very similar area of the two reduction peaks of the powder sample used as reference material suggests that no significant formation of CuO aggregates occurs up to the 100% exchange level. Nevertheless, their concentration strongly prevails in monolith A that shows a first TPR peak with a significantly higher intensity compared to that of the second one, probably attributable to the interaction between copper acetate present in the solution and SiO_2 and/or cordierite giving rise to copper oxide clusters upon calcination. This was clarified by the TPR profile of the fresh monolith C (Fig. 4). Except for a shift towards higher temperatures, this catalyst shows the two peaks with comparable area typical of the powder sample indicating that no CuO formation occurs in the absence of silica binder and, therefore, that during the copper exchange step of monolith A copper interacts preferentially with silica rather than with cordierite which in addition to a very low surface area should be totally covered by the zeolite layer. Monolith B shows a different redox behaviour: the intensity of the high temperature peak is surprisingly slightly higher than that of the low temperature peak.

In order to better analyze the effect of the contact of Cu-ZSM5 with water solution excluding the possible influence of the cordierite monolith, a Cu-ZSM5 powder was contacted with a water suspension, containing a colloidal silica in the same amount used for the preparation of the monolith for the same time necessary to obtain the structured catalyst. After drying and calcinations a TPR analysis was carried out. Also in this case we observe the same modification of the TPR profile (Fig. 4) with an enhanced intensity of the second peak as observed for monolith B. Therefore, we can suppose that, although no loss of copper occurs in the suspension, water unavoidably introduced into the zeolite pores can somewhat modify the nature of exchanged copper during the following calcinations at 550°C .

In conclusion, these results demonstrate that the order of the different steps for the preparation of a zeolite based monolith should be very carefully considered.

In Fig. 3 TPR profiles of catalysts aged under wet conditions are also reported. The dramatic change of TPR curve of the powder sam-

ple is similar to that observed by Yan et al. [23]. Migration of copper ions from exchangeable positions to form copper oxides clusters upon treatment with water vapour has been assumed by many authors [26–29]. Yan et al. [23] proposed the formation of different copper species in deactivated Cu-ZSM5, like as copper ions dispersed in Al_2O_3 and CuAl_2O_4 , related to a partial dealumination not XRD detectable, which were responsible for TPR signals observed at higher temperature compared to fresh Cu-ZSM5 samples. The determination of the nature of the copper species providing the TPR main signal of the aged powder zeolite is not easy, due to the superimposition of XRD patterns of fresh and deactivated samples, as also shown in [27]. The different temperature of this signal with respect to that corresponding to CuO aggregates in fresh samples can be related to a larger size of copper oxide particles [30,31]. On the other hand, it could be due to the formation of CuAl_2O_4 , as proposed by Yan et al. [23]. The shift of the temperature of maximum towards higher values was also observed in the TPR profile of the used monolith A where an inversion of the intensity of the two signals is shown. Modification of the TPR profile of monolith B upon water treatment is more similar to that observed for the powder sample, although no increase of the second peak was detected. The very high H_2/Cu ratio (see Table 2) calculated for this monolith is likely related to the difficult evaluation of the area due to the bad recovery of the baseline of the TPR curve. An increasing slope of the baseline was also observed for the powder zeolite treated in water suspension. Finally, two peaks are still present in the TPR profile of used monolith C (Fig. 4) although with a different relative intensity, suggesting that some copper in the exchange positions is preserved when ZSM5 is dispersed on a monolith.

3.3. Catalytic activity tests

Preliminary tests performed by changing the total flow rate indicated that, under the conditions reported in Section 2, kinetic regime takes place diffusion limitations being negligible also for structured samples. No significant difference was found by changing the cell density of the monoliths provided that the zeolite content is the same. Therefore the following results are referred to 400 cpsi monoliths. All catalytic tests were performed under “differential reactor” conditions, namely by choosing the ratio between the catalyst load and the reactant flow rate as high as sufficient to have quite small NO conversion to correctly estimate the reaction rate and the turnover frequency. In Fig. 5 NO conversion is reported as a function of the reaction temperature for Cu-ZSM5 fresh powder sample. In the same figure conversion to N_2 is also reported. The trend is that typical of Cu-ZSM5 for NO decomposition, with maximum activity [32,33]. Selectivity to N_2 is not complete below 450°C

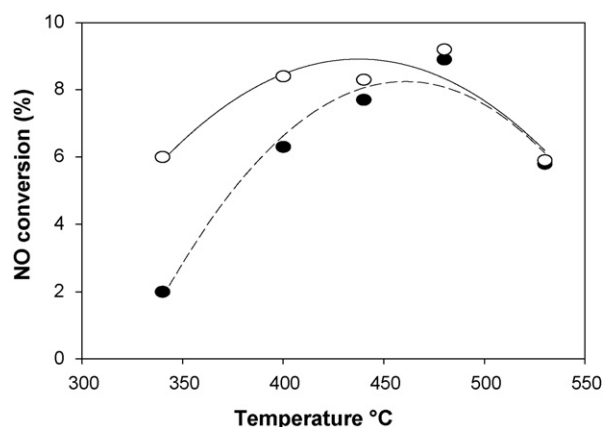


Fig. 5. Total NO conversion (○) and conversion to N_2 (●) for Cu-ZSM5 fresh powder sample ($W/F=0.09\text{ g s cm}^{-3}$).

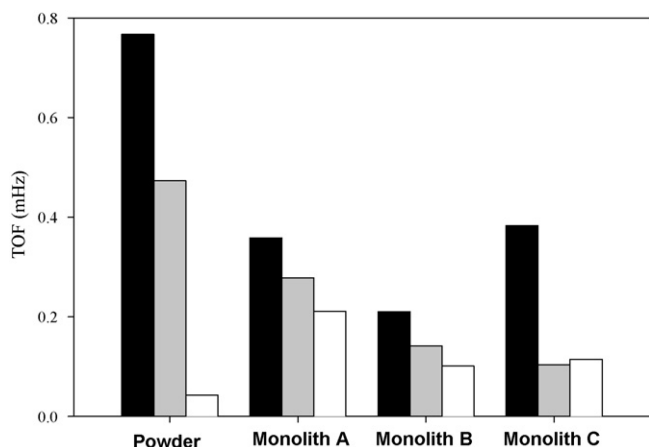


Fig. 6. Effect of the ageing treatments on the TOF evaluated under dry conditions at 480 °C (fresh sample (■), after 80 min in the presence water (■), after further 15 h in the presence of water (□)).

due to the occurrence of NO oxidation to NO₂, this reaction being promoted at lower temperature and depending on the production of O₂ via NO decomposition.

The catalytic behaviour of structured catalysts is qualitatively similar to that of the powder sample although the maximum NO conversion is slightly shifted at lower temperature. Nevertheless, it should be taken into account that the thermocouple is located in quartz tube coaxial and internal to catalytic bed for the powder sample whereas it is placed just upside the monolith for the structured catalysts. As a consequence, the temperature inside the monolith could be higher than that measured.

In order to compare the activity of all the catalysts on the basis of the actual copper content, thus excluding from the calculations the mass of the structured support and the binder, the TOF (moles of converted NO/moles of copper per hour) has been evaluated at 480 °C, chosen as temperature high enough to guarantee 100% selectivity to N₂. The values reported in Fig. 6 indicate that the best intrinsic activity among fresh catalysts is associated to the powder sample. This result could have been expected because copper introduced in the powder zeolite is mostly exchanged copper, i.e. that active for NO decomposition, whereas inactive copper could be present in the monolith, its nature depending on the preparation procedure.

In Fig. 6 the TOF values, evaluated after the weak and the strong ageing treatments under wet conditions, described in Section 2, are compared with those estimated for the fresh catalysts. As already reported in [27], the activity of powder Cu-ZSM5 is dramatically depressed upon water treatment at high temperature. On the other hand, although the activity of the fresh monolith catalysts is lower than that of the powder sample, they are less affected by the ageing treatment, i.e. the ceramic structure and the binder are able to partially preserve the activity of the zeolite likely protecting it from excessive water adsorption. The positive effect of cordierite substrate on the ZSM5 hydrothermal stability was also reported for SCR of NO_x with propane by Li et al. [34] who attributed to cordierite and to the in situ method they used to synthesize the zeolite on the monolith the property to depress copper species aggregation and ZSM5 dealumination. Although a dip-coating technique was used in the present work, the same effect was noticed which is then associated to the ceramic substrate.

4. Conclusions

Preparation of Cu-ZSM5 based ceramic monolith by dip-coating technique was investigated. The effect of the preparation conditions

on the final properties of the structured catalyst can be summarized as follows:

- the best adhesion and mechanical strength of the zeolite layer were obtained using colloidal silica as binder with a binder/zeolite ratio 1:10;
- an alkaline pH of the suspension containing the micronic zeolite powder improves adhesion to cordierite;
- the order of dip-coating and ionic exchange steps is crucial to determine the nature of copper in the monolith catalyst.

Structured catalysts show a lower intrinsic activity in NO decomposition compared to the powder sample which in some cases can be associated to the formation of inactive CuO in addition to exchanged copper. Nevertheless, they have a higher hydrothermal resistance likely related to an inhibiting effect of both silica binder and cordierite support which partly preserve copper migration promoted by water vapour at high temperature. This feature makes the structured catalysts more suitable for application under real conditions.

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