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# 1 Selective catalytic reduction of nitrogen oxides over a modified 2 silicoaluminophosphate commercial zeolite

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## A B S T R A C T

Nitrogen oxides (NO<sub>x</sub>: NO, NO<sub>2</sub>) are a concern due to their adverse health effects. Diesel 14  
 engine transport sector is the major emitter of NO<sub>x</sub>. The regulations have been 15  
 strengthened and to comply with them, one of the two methods commonly used is the 16  
 selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR), NH<sub>3</sub> being supplied by the in-situ 17  
 hydrolysis of urea. Efficiency and durability of the catalyst for this process are highly 18  
 required. Durability is evaluated by hydrothermal treatment of the catalysts at temperature 19  
 above 800°C. In this study, very active catalysts for the NH<sub>3</sub>-SCR of NO<sub>x</sub> were prepared by 20  
 using a silicoaluminophosphate commercial zeolite as copper host structure. Character- 21  
 izations by X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature 22  
 programmed desorption of ammonia (NH<sub>3</sub>-TPD) showed that this commercial zeolite was 23  
 hydrothermally stable up to 850°C and, was able to retain some structural properties up to 24  
 950°C. After hydrothermal treatment at 850°C, the NO<sub>x</sub> reduction efficiency into NH<sub>3</sub>-SCR 25  
 depends on the copper content. The catalyst with a copper content of 1.25 wt.% was the 26  
 most active. The difference in activity was much more important when using NO than the 27  
 fast NO/NO<sub>2</sub> reaction mixture. 28

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## 43 Introduction

45 The selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR)  
 46 process, using urea as ammonia source, is now an automotive  
 47 technology for removing NO<sub>x</sub> from Diesel exhaust gas  
 48 (Brandenberger et al. 2008; Granger and Parvulescu 2011;  
 49 Zhang et al. 2016a). Cu-, Fe-zeolite catalysts are commercially  
 50 used for this technology since a few years (Zhang et al. 2016a;  
 51 Kieffer et al. 2013). Among zeolite structures, zeolites with  
 52 small pores attract more and more attention (Zhang et al.  
 53 2016a; Beale et al. 2015). Chabazite (CHA) structure is one of  
 54 these and SAPO-34 zeolites are one of the possible choices. A  
 55 very interesting property of silicoaluminophosphates is their  
 56 high hydrothermal stability (Ishihara et al. 1997). Since SCR

catalyst ageing is usually realized by hydrotreatment at high 57  
 temperatures, the use of SAPO-34 as host structure allows 58  
 preparing more stable Cu-SAPO-34 catalysts for the NH<sub>3</sub>-SCR 59  
 process (Petitto and Delahay 2015; Wang et al. 2015). More- 60  
 over, the integration of SCR catalysts in the diesel particulate 61  
 filter (DPF) should be considered and requires that SCR catalysts 62  
 must be stable in increasingly drastic conditions. Hydrothermal 63  
 stability of SAPO-34 zeolites depends on chemical composition. 64  
 We have shown that among Cu-SAPO-34 catalysts, aged 5 hr at 65  
 850°C in a dynamic flow containing 10% H<sub>2</sub>O, the catalyst, with 66  
 the lowest silica content (1.2 wt.%) exhibited the highest 67  
 NH<sub>3</sub>-SCR of NO<sub>x</sub> activity by maintaining its initial structural 68  
 properties (Petitto and Delahay 2015). More recently, Wang et al. 69  
 (2012) using static hydrothermal conditions have reported that 70

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the stabilization of CHA structure is enhanced by the copper content.

In the present work, the effect of copper content on a commercial silicoaluminophosphate chabazite has been investigated. The catalysts have been tested both after calcination at 550°C and hydrotreatment at 850°C in the NH<sub>3</sub>-SCR of NO and NO/NO<sub>2</sub>.

## 1. Experimental section

The silicoaluminophosphate zeolite ( $S_{\text{BET}}$  (Brunauer Emmett Teller surface area) = 630 m<sup>2</sup>/g) with CHA structure (H-CZC) was graciously supplied by Clariant (Switzerland). The chemical composition given by Clariant is the following: 21.9 wt.% Al, 3.8 wt.% Si, 18.2 wt.% P and 1.97 wt.% Ti. According to the UV-visible spectroscopy spectrum of the H-CZC zeolite, the titanium possesses an octahedral coordination probably under the form of well-dispersed titanium oxide species. TiO<sub>2</sub> is known for its activity in the hydrolysis of the urea (Lundström et al. 2011).

The impregnation method, with an organic solvent, was used in order to introduce the adequate quantity of copper or iron. The use of an organic solvent instead of water was motivated by the possible negative effect of both pH and temperature during the evaporation phase (Parlitz et al. 1994). In a rotating evaporation flask, a desired amount of copper acetylacetonate or iron acetylacetonate was dissolved into 50 mL of acetonitrile and then 2 g of zeolite was added. Then, the flask was connected to the rotavapor and put in a bath heated at 60°C for 4 hr with a mild rotation speed. Then, a gentle evaporation, under vacuum, was made up to complete removal of acetonitrile. The final product was firstly dried in an oven at 80°C for 24 hr and then calcined overnight at 550°C in air. The catalysts were labelled Cu(x)- or Fe(x), x being the content in wt.%.

Hydrothermal treatment (HDT) was performed in dynamic flow (55 mL/min of 20% O<sub>2</sub>/He containing 10% H<sub>2</sub>O<sub>2</sub>) using 0.5 g of catalyst deposited on a porous frit of a U tube quartz reactor. The solid was heated at 850°C (or 950°C) with a ramp of 6°C/min. The injection of H<sub>2</sub>O(liq.) (0.0041 mL/min), by a syringe-pump was started and kept at this temperature for 5 hr. The injection of water was stopped during the cooling of the solid once the temperature reached 450°C.

Powder X-ray diffraction (XRD) data were obtained on a diffractometer apparatus (AXS D8, Bruker, United States) by using Cu K $\alpha$  radiation and a Ni filter.

The morphology of SAPO-34 catalysts was studied by scanning electron microscopy (SEM) (4800 S electron microscope, HITACHI, Japan).

The acidity measurements were evaluated by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) (AUTOCHEM 2910, Micromeritics, United States). NH<sub>3</sub> adsorption was carried out at 100°C for 45 min using 5 vol.% NH<sub>3</sub>/He with a flow rate of 30 mL/min. After NH<sub>3</sub> adsorption, the line was flushed with He (30 mL/min) during 45 min to remove physisorbed NH<sub>3</sub>. Finally, NH<sub>3</sub>-TPD was performed in helium flow (30 mL/min) from 100 to 550°C using a heating rate of 10°C/min.

The catalytic tests were performed in a dynamic flow reactor operating at atmospheric pressure. Catalyst aliquots

(0.024 g) were activated in situ at 550°C in air and cooled to 129 180°C. The catalytic tests were carried out from 180 to 550°C at 130 5°C/min with a space velocity of 312,500 hr<sup>-1</sup> using the 131 following feed concentration: 0.1% NO (or 0.0542% NO 132 +0.0458% NO<sub>2</sub>), 0.1% NH<sub>3</sub>, 8% O<sub>2</sub>, 3.5% H<sub>2</sub>O (*v/v*), and balance 133 with He. The effluent composition was monitored continu- 134 ously by sampling on line to a quadruple mass spectrometer 135 (Omnistar, Pfeiffer Vacuum, Germany) equipped with 136 Channeltron and Faraday detectors (0–100 amu). The possible 137 occurrence of intraparticle mass transfer limitations was 138 previously checked on copper Y zeolite using two aliquots 139 being grinding and sieving, in the ranges 63–125 and 140 250–400  $\mu\text{m}$ . These two aliquots were tested for the SCR of 141 NO by NH<sub>3</sub> in a temperature programmed surface reaction 142 (TPSR) protocol (Kieger et al. 1999). The plots of NO conversion 143 to N<sub>2</sub> were quasi-superimposed for the two aliquots, which 144 provides evidence that the intraparticle mass transfer is fast 145 enough and will not screen the chemical processes. The grain 146 size of the catalysts used for this study was in the same range. 147 Therefore, the possible occurrence of intraparticle mass 148 transfer limitations is unlikely since the catalytic study was 149 performed in the same set up, with less drastic reaction 150 conditions, and using catalysts in the same range of grain 151 size. 152

## 2. Results and discussion

### 2.1. Characterization and hydrothermal stability of the zeolite host structure

Our goal was to obtain active and stable catalysts in SCR of 157 NO<sub>x</sub> by NH<sub>3</sub>. Therefore, it was important to control the 158 hydrothermal stability of the zeolite itself before the deposi- 159 tion of copper or iron. Thus, three different characterizations 160 were carried out: XRD, SEM and NH<sub>3</sub>-TPD over calcined H-CZC 161 sample and hydrotreated H-CZC sample (850 and 950°C). 162

#### 2.1.1. XRD

Fig. 1 shows X-ray diffraction patterns of H-CZC after 164 calcination at 550°C and hydrotreatment at 850 and 950°C. 165 Fig. 1a–d shows typical powder diffraction patterns of a 166 chabazite (CHA) structure but with traces of AFI structure 167 (SAPO-5), pointed out by  $2\theta = 7.45^\circ$  (Baerlocher et al. 2001; 168 Nakhostin Panahi et al. 2015). However, the X-ray diffraction 169 patterns of H-CZC after hydrotreatment showed important 170 changes. The loss of crystallinity was evaluated close to 50%, 171 after hydrotreatment at 850°C whereas 67% of loss of 172 crystallinity is reached between calcination at 550°C and 173 hydrothermal treatment at 950°C for 5 hr. 174

#### 2.1.2. SEM

Zeolite crystals with an average size of 0.8–1.5  $\mu\text{m}$  were 176 observed for H-CZC calcined at 550°C (Fig. 2). As expected, the 177 zeolite displays a cubic morphology, which is typical for 178 SAPO-34 type zeolite (Xu et al. 2008). After HDT at 850°C, 179 apparently no change of morphology was observed. On the 180 other hand, amorphous phase was detected after hydrothermal 181 treatment at 950°C (Fig. 2). It should be emphasized that 182 the distribution, crystallized phase - amorphous phase, is not 183

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