



# Influence of lattice stability on hydrothermal deactivation of Cu-ZSM-5 and Cu-IM-5 zeolites for selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub>



Peter N.R. Vennestrom<sup>a,b,\*</sup>, Ton V.W. Janssens<sup>a</sup>, Arkady Kustov<sup>a</sup>, Marie Grill<sup>a</sup>, Anna Puig-Molina<sup>a</sup>, Lars F. Lundegaard<sup>a</sup>, Ramchandra R. Tiruvalam<sup>a</sup>, Patricia Concepción<sup>b</sup>, Avelino Corma<sup>b,\*</sup>

<sup>a</sup> Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark

<sup>b</sup> Instituto de Tecnología Química (UPV-CSIC), Universidad Politécnica de Valencia, Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain

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## ABSTRACT

Copper-exchanged zeolites are well-known catalysts for the selective catalytic reduction of nitrogen oxides by ammonia (NH<sub>3</sub>-SCR). To determine the influence of framework stability on catalyst deactivation, two zeolite frameworks, MFI and IMF, were used in this study. The two frameworks have similar window size and connectivities, but the IMF structure is less susceptible towards dealumination. In each zeolite, copper was introduced by aqueous exchange and the catalytic performance in the NH<sub>3</sub>-SCR reaction compared before and after hydrothermal ageing at 650 and 750 °C. The changes in state and local environment of Cu and the degradation of the zeolite structure were characterized using ammonia capacity measurements, solid state nuclear magnetic resonance, X-ray fine structure spectroscopy, temperature programmed reduction with hydrogen, infrared spectroscopy monitoring of adsorbed NO and CO probe molecules as well as the combination of transmission electron microscopy and energy dispersive X-ray spectroscopy to follow copper migration. The catalytic performance of Cu-ZSM-5 and Cu-IM-5 is similar in the fresh state, but after hydrothermal ageing the deactivation of Cu-IM-5 is less severe compared to Cu-ZSM-5 as a consequence of the higher framework stability. The changes in catalyst structure that occur during ageing are (i) partial dealumination of the zeolite, (ii) reversible migration of copper species, and (iii) irreversible formation of catalytically inactive and stable Cu–Al clusters, which have some resemblance to CuAl<sub>2</sub>O<sub>4</sub>, but without the symmetry of Cu in the spinel structure. As the Cu–Al clusters only form once Al is detached from the framework, the stability of Al in the zeolite framework is proposed to dictate the overall hydrothermal deactivation behaviour of Cu-ZSM-5 and Cu-IM-5 in the NH<sub>3</sub>-SCR reaction.

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## 1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) with NH<sub>3</sub> is an important technology for reducing environmentally harmful NO<sub>x</sub> in the exhaust gases from vehicles, ships, and power plants to the emission levels required by legislation. As legislation is becoming more stringent, further development of SCR-technologies and a better understanding of the catalytic materials are required.

Metal-substituted zeolites, in particular with Cu and Fe, are well known catalysts for SCR of NO<sub>x</sub> with NH<sub>3</sub>. They have recently been extensively reviewed [1] and are currently used in automotive applications. The most investigated zeolite material is Cu-ZSM-5

ever since Iwamoto and co-workers discovered its catalytic potential for direct and continuous decomposition of NO in 1986 [2]. Cu-zeolites are in general more active at lower temperatures, but also deactivate faster, than the Fe-equivalents.

Compared to other applications, use in the automotive sector requires high activity and selectivity in between 180 and 500 °C, together with a high hydrothermal resistance at even higher temperatures that can be reached when up-stream particulate filters are actively regenerated. Even though many zeolites are quite stable at elevated temperatures, the stability of materials like Cu-ZSM-5 is still an issue. To improve the stability of the metal-substituted zeolites, a better understanding of the mechanisms leading to catalyst degradation is required.

Several theories have been presented on the deactivation mechanism of metal-loaded zeolites. For Fe-zeolites, it was recently concluded that the deactivation is related to the stability of iron species within the zeolite and not to the zeolite framework itself [3,4]. For Cu-zeolites, the situation seems to be more complicated, and the degradation of the zeolite structure might also play a role

\* Corresponding authors. Addresses: Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark (P.N.R. Vennestrom), Instituto de Tecnología Química, Av. de los Naranjos, s/n 46022, Valencia, Spain (A. Corma).

E-mail addresses: [pnr@topsoe.dk](mailto:pnr@topsoe.dk) (P.N.R. Vennestrom), [acorma@itq.upv.es](mailto:acorma@itq.upv.es) (A. Corma).

for these systems. Grinsted et al. and Cheng et al. relate the deactivation of Cu-ZSM-5 to dealumination of the ZSM-5 framework [5,6], which is supported by Palella et al., who describe the formation of extra-framework Al<sup>3+</sup> together with a loss of monovalent copper ions when Cu-ZSM-5 is treated under wet conditions already at 550 °C [7]. Adding to this, Yan et al. discuss the simultaneous formation of CuO and Al<sub>2</sub>O<sub>3</sub> phases, which upon severe dealumination irreversibly transform into CuAl<sub>2</sub>O<sub>4</sub> [8]. This is corroborated by Kwak et al. who find that Cu and Al in Cu-ZSM-5, Cu-β, and Cu-Y show a stronger interaction after high-temperature hydrothermal treatment [9]. This is in line with the conclusion that copper species sinter to form CuO and perhaps Cu<sub>2</sub>O, which leads to local destruction of the framework [10] followed by formation of a copper aluminate-like phases. In contrast, Tanabe et al. reported that copper migrates to inaccessible sites but remains atomically dispersed [11], and in this case, the stability of the zeolite framework should be less important when copper is loaded into zeolite structures containing small pores, such as the CHA or AEI topologies, a more stable activity is observed, possibly because of the limited migration of detached aluminium moieties inside the pores [12,13]. Still, the deactivation mechanism of Cu-zeolites, in particular how dealumination and migration of Cu and Al occur, is not clear.

The aim of this study is to disentangle the contributions from dealumination and copper migration to deactivation and to clarify the outcome of high temperature hydrothermal ageing. In order to elucidate the deactivation mechanism, two zeolites, namely ZSM-5 and IM-5 (MFI and IMF topologies respectively), were selected. Both zeolites contain three-dimensional pore systems and 10-member-ring windows, but exhibit different stabilities towards dealumination [14,15]. This allows us to compare the aluminium stability in similar zeolite structures and to study its influence on deactivation of Cu-zeolites. To achieve this, the results from framework characterization, using N<sub>2</sub>-physisorption, NH<sub>3</sub>-TPD, and <sup>27</sup>Al-MAS-NMR, and copper speciation characterization, obtained by XAFS, NO + CO-FTIR and H<sub>2</sub>-TPR before and after hydrothermal ageing of Cu-zeolites at 650 and 750 °C, are combined and correlated with catalytic performance in the NH<sub>3</sub>-SCR reaction. Additionally, the migration of copper is studied from the SCR performance of different physical mixtures of copper-containing phases with Brønsted acidic H-ZSM-5 in combination with TEM/EDS.

## 2. Experimental

### 2.1. Synthesis of Cu-zeolites

For the synthesis of the IM-5 zeolite, a similar approach as in [14,16] was adapted, using a gel composition including IM-5 seeds to avoid contamination of impurity phases. The synthesis gel composition was 60 SiO<sub>2</sub>: 1.5 Al<sub>2</sub>O<sub>3</sub>: 17 Na<sub>2</sub>O: 6 NaBr: 10 R: 2400 H<sub>2</sub>O, where R is the template 1,5-bis(N-methylpyrrolidinium)pentane (1,5-MPP) prepared prior to zeolite synthesis. In a typical synthesis, 18.01 g 1,5-MPP was dissolved in 114.50 g H<sub>2</sub>O followed by addition of 15.41 g Si-aerosol (Degussa 200). In a second container, 2.78 g NaBr (98–100.5%, Scharlau) and 6.12 g NaOH (>98%, Scharlau) were dissolved in 68.12 g H<sub>2</sub>O. Afterwards, 0.36 g Al-foil was added and the mixture was left under stirring for 16 h to digest. This clear solution was then added slowly to the first solution under stirring and left under mechanical stirring for 30 min. Finally, 0.81 g of IM-5 seeds suspended in 12.00 g H<sub>2</sub>O were added. The zeolite synthesis gel was then transferred to Teflon-lined autoclaves, sealed and heated to 175 °C where they were kept for seven days. The zeolite product was recovered by suction filtration and calcined at 580 °C for 3 h after drying. To convert the zeolite into the NH<sub>4</sub>-form, it was

ion-exchanged two times in 2.5 M NH<sub>4</sub>Cl for 2 h at 80 °C under reflux in a solid-to-liquid ratio of 10 (w/w).

The NH<sub>4</sub>-ZSM-5 was obtained from a commercial supplier.

To introduce Cu into the zeolites, the NH<sub>4</sub>-form of the IM-5 and ZSM-5 zeolites was ion-exchanged with Cu(CH<sub>3</sub>COO)<sub>2</sub> · H<sub>2</sub>O (>99.0%, Sigma-Aldrich) with different molarities and consecutive times, to obtain Cu/Al ratios above 0.5, at room temperature using 250 mL/g under stirring for 24 h to obtain varying copper loadings on the two zeolites (see Table 1). After ion-exchange, the samples were calcined at 500 °C for 3 h. From these series, we selected three samples of each zeolite containing a comparable low, medium, and high Cu-loading, with Cu/Al ratios given in Table 1. Each sample was then divided into three portions. The first portion was used without further treatment; the second and third portions were aged in the exhaust of a diesel burner containing ca. 10% H<sub>2</sub>O and 8% O<sub>2</sub> for 16 h at 650 °C and 750 °C, respectively.

Reference samples were prepared by physically mixing CuO (Riedel de-Haën, >99%), Cu<sub>2</sub>O (Sigma-Aldrich, <5 μm, 97%) or CuAl<sub>2</sub>O<sub>4</sub> with the parent H-ZSM-5 zeolite in a mortar and grinding it for 10 min. The CuAl<sub>2</sub>O<sub>4</sub> was prepared by heating a mixture of CuNO<sub>3</sub> · 3H<sub>2</sub>O and pseudoboehmite (Al/Cu molar ratio 2:1), at 800 °C for 3 h.

### 2.2. Catalytic testing and hydrothermal ageing

The selective catalytic reduction of NO by ammonia (NH<sub>3</sub>-SCR) was carried out in a fixed-bed quartz reactor (i.d. 4 mm) using 40 mg catalyst (150–300 μm fraction) diluted with 180 mg SiC, connected to a Gasmet CX4000 FTIR analyser (8 cm<sup>-1</sup> resolution), for analysis of NO, NO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O and H<sub>2</sub>O. The reactant gas composition for NH<sub>3</sub>-SCR consisted of 500 ppm NO (from 4000 ppm NO, CRYSTAL mixture, Air Liquide), 530 ppm NH<sub>3</sub> (from 4000 ppm NH<sub>3</sub>, CRYSTAL mixture, Air Liquide), 10% O<sub>2</sub> (from Synthetic air, Air Liquide), and 5% H<sub>2</sub>O (from demineralized H<sub>2</sub>O), balanced with N<sub>2</sub> (Alphagaz, N<sub>2</sub> ≥ 99.999%, H<sub>2</sub>O ≤ 3 ppm, O<sub>2</sub> ≤ 2 ppm, C<sub>n</sub>H<sub>m</sub> ≤ 0.5 ppm); the small excess of NH<sub>3</sub> ensures that a complete conversion of NO could be reached. The concentrations of O<sub>2</sub> and H<sub>2</sub>O correspond to those under typical operating conditions. The total flow rate was maintained at 285 mL/min. Before the measurements, the catalysts were heated in the reaction gas mixture for 1 h at 550 °C, unless otherwise stated. The activity was measured by following the NO<sub>x</sub> conversion during cooling from 550 to 170 °C, at 2 °C/min. The hydrothermal ageing was carried out for 16 h at either 650 °C or 750 °C in real diesel exhaust containing approximately 10% of H<sub>2</sub>O and 8% O<sub>2</sub>.

### 2.3. Zeolite characterization

The zeolite phases and crystallinity were investigated by X-ray diffraction on a multisample PANalytical X'Pert diffractometer using the characteristic Cu Kα wavelength (1.542 Å).

Sample composition was measured after acid-digestion by ICP-OES on a Varian 715-ES instrument.

**Table 1**  
Ion-exchange concentrations and elemental composition after calcination of the Cu-zeolites.

Sample	Ion-exchange concentration (mM)	Cu/Al
ZSM-5	–	(Si/Al = 11.4)
Cu(0.29)-ZSM-5	1.0	0.29
Cu(0.43)-ZSM-5	10.0	0.43
Cu(0.62)-ZSM-5	3 × 10.0	0.62
IM-5	–	(Si/Al = 10.8)
Cu(0.28)-IM-5	2.0	0.28
Cu(0.44)-IM-5	10.0	0.44
Cu(0.62)-IM-5	3 × 10.0	0.62

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