



# NH<sub>3</sub>-SCR over Cu/SAPO-34 – Zeolite acidity and Cu structure changes as a function of Cu loading



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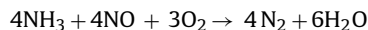
## ABSTRACT

A series of SAPO-34 catalysts with various Cu loadings (ranging 0.7–3.0 wt%) were prepared by the solid state ion exchange method (SSIE) and the acid properties of the catalysts were characterized by NH<sub>3</sub>-TPD and in situ DRIFTS. During synthesis, more Cu migrates and exchanges at the Brønsted acid sites with increasing amounts of Cu precursor during the SSIE, resulting in a monotonic reduction in the total number of Brønsted acid sites. Interestingly, the Lewis acid sites created by Cu ions linearly increased with increasing Cu loading up to 2.0 wt% and then only slightly increased with a further increase of Cu loading up to 3.0 wt%. XRD, H<sub>2</sub>-TPR, UV–vis and DRIFTS were used to probe Cu structures. From the DRIFTS, two different perturbed T–O–T vibrations were observed for both the zeolite skeleton and NH<sub>3</sub> adsorption spectra, indicating two different types of exchanged Cu species exist. This is also consistent with the results of NO adsorption DRIFTS spectra, in which two different Cu<sup>2+</sup> sites were observed to adsorb NO molecules. One of the sites was considered to be the isolated Cu<sup>2+</sup> species and the other could be another type of exchanged Cu site, possibly Cu<sub>x</sub>O<sub>y</sub> clusters (dimeric or oligomeric Cu species). The isolated Cu<sup>2+</sup> on each sample was further identified by UV–vis and quantified by H<sub>2</sub>-TPR experiments. Based on these results, isolated Cu<sup>2+</sup> species were found to be the active sites of NH<sub>3</sub>-SCR at low temperature. Furthermore, CuO phases were detected on the samples with high Cu loadings via XRD. The presence of Cu<sub>x</sub>O<sub>y</sub> may promote NH<sub>3</sub> oxidation by O<sub>2</sub>, leading to the observed decrease in standard SCR performance at high temperature.

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## 1. Introduction

Selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR) is widely applied in the treatment of NO<sub>x</sub> emissions from heavy duty diesel vehicles [1]. This approach involves an equivalent amount of NH<sub>3</sub> and NO reacting under oxidizing conditions to produce N<sub>2</sub> and H<sub>2</sub>O according to the reaction:



Zeolite-based SCR catalysts have been widely studied and used for NH<sub>3</sub>-SCR due to the high NO conversions that can be obtained in relatively wide temperature windows [2–4]. The traditional SCR catalysts are Fe- or Cu-exchanged medium pore zeolites, such as ZSM-5 and Beta [5–8]. In recent years, Cu-exchanged small pore zeolites, such as Cu-SSZ-13 and Cu-SAPO-34, have been commercially applied in diesel after-treatment systems. It has been extensively reported that Cu-SSZ-13 and Cu-SAPO-34

catalysts show excellent NO conversion and N<sub>2</sub> selectivity in a wide temperature window (250–550 °C), in comparison to medium pore zeolites [9–11]. Both of the SSZ-13 and SAPO-34 zeolites have the same chabazite (CHA) framework structure that contain a double six-membered ring prism (D6-MR) in the large cavities of the structure. Many authors have concluded that the isolated Cu<sup>2+</sup> sites located in the six-membered rings of Cu-CHA catalysts are the active sites responsible for their superior NH<sub>3</sub>-SCR performance [12–14]. In a previous study, nitrates and nitrites were shown to be the likely reaction intermediates for NH<sub>3</sub>-SCR over Cu-SAPO-34 and the enhanced activity could be explained by the higher reactivity between NO and surface nitrate [15].

In addition, the CHA framework structure has been discovered to be more hydrothermally stable than other zeolite frameworks [16–18]. For example, both Cu-SSZ-13 and Cu-SAPO-34 were reported to maintain their SCR activity after hydrothermal aging at 800 °C for 16 h [16,19]. This unique enhancement has been attributed to the small pore size of the CHA (3.8 Å) that eliminated the dealumination process by preventing the Al(OH)<sub>3</sub> (5.03 Å) from exiting the pores of the framework [17]. Interestingly, SAPO-34-based samples showed even higher NO conversion

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after hydrothermal aging than that of a corresponding fresh sample [17,20] while no such change was observed on Cu-SSZ-13 [16]. This was explained by the fact that the high temperature treatment could facilitate the migration of Cu from the external surface into the micropores of SAPO-34 and form isolated Cu [20]. However, the discrepancies between SSZ-13 and SAPO-34 upon hydrothermal aging are still not clear. Unlike SSZ-13, whose framework is built from aluminosilicate structures, with Si and Al as the tetrahedrals, the SAPO-34 framework is generated by the substitution of Si in the AlPO structure that was initially formed by P. The hydrothermal synthesis of SAPO-34 utilizes common zeolite structure directing agents (SDA) such as TEA, TEOH or MOR while SSZ-13 uses a very costly structural directing agent (SDA), *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH) [19]. The conventional wetness ion exchange (WIE) method has been extensively applied to prepare Cu-SSZ-13 [10,14,17,21], however, the preparation of Cu-SAPO-34 is not as straightforward. For example, Akolekar et al. found that both the surface area and pore volume of SAPO-34 significantly dropped after WIE, which is consistent with previous experimental results [22,23]. More recently, Feng et al. reported that more severe irreversible hydrolysis could occur with SAPO-34, resulting in a significant drop in zeolite crystallinity as well as surface area [19]. They also discovered that SAPO-34 synthesized by different SDAs underwent different levels of structural damage during the WIE process. Alternatively, Deka et al. designed a direct synthesis methodology to prepare Cu-SAPO-34 by incorporating Cu in a combination of SDAs, such as Cu<sup>2+</sup>-triethylenetetramine complex and tetraethylammonium cations [24]. Corma et al. used different SDAs, copper-tetraethylenepentamine (Cu-TEPA) and diethylamine (DEA), in a similar “one pot” synthesis method and the obtained catalysts showed good SCR activity and hydrothermal stability [25].

In this study, a family of Cu-SAPO-34 samples with different Cu loadings was prepared by a solid state ion exchange (SSIE) method. The as-prepared samples show good SCR performance, proving that SSIE can be used to prepare active Cu-SAPO-34 samples. The acid properties were investigated by NH<sub>3</sub>-TPD combined with in situ DRIFTS. Different Cu structures were characterized by XRD, DRIFTS, H<sub>2</sub>-TPR and UV–vis techniques and their various functionalities in NH<sub>3</sub>-SCR were also studied.

## 2. Experimental

### 2.1. Catalyst preparation by the solid state ion exchange (SSIE) method

The H-form SAPO-34 zeolite support used in this study was purchased from ACS materials. The H-SAPO-34 powder was first calcined at 500 °C in 10% O<sub>2</sub> before the ion exchange process. The solid state ion exchange was conducted in a tube furnace with 130 sccm of air flow. In each batch, one gram of the H-SAPO-34 powder sample was first physically mixed with a certain amount (10 mg–50 mg) of CuO nanosized particles (purchased from Sigma–Aldrich), the amount depending on the target Cu loading. The mixtures were then thoroughly homogenized and the color of the resulting samples was uniformly gray. The thermal treatment includes several steps and is described in Fig. S1. The furnace temperature was first maintained at 120 °C for 4 h and then was ramped to 600 °C at 2 °C/min and held there for 5 h. The temperature was then further increased to 800 °C at 2 °C/min and held for 12 h before cooling to room temperature. The 12 h thermal treatment enables the Cu ions to migrate inside the zeolite pores and exchange with protons. After the solid state ion exchange, the color of the samples was blue suggesting that the Cu ions were successfully exchanged into the zeolite.

### 2.2. Characterization of as-prepared Cu-SAPO-34

The elemental compositions of the as-prepared samples were analyzed by ICP (Galbraith Laboratories). The as-prepared samples are named in the format of SSIE-*x*, where *x* stands for the Cu wt% in each sample. X-ray diffraction (XRD) experiments were conducted using a Siemens D5000 Diffractometer equipped with a Cu-K $\alpha$  detector. UV–vis spectra were collected with a Hitachi UV-vis U-2001 Spectrophotometer. The NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-TPD) experiments were carried out by loading 120 mg of powder catalyst in the quartz tube reactor. The NH<sub>3</sub> effluent concentration was measured by FTIR (MultiGas 2030). The as-prepared samples were first pretreated in 10% O<sub>2</sub> in N<sub>2</sub> at 500 °C for 1 h. After pretreatment, a total flow of 300 sccm containing 500 ppm NH<sub>3</sub> in N<sub>2</sub> was metered into the reactor for 2 h at 35 °C to saturate the catalyst. Once the system reached steady state, NH<sub>3</sub> was switched off and only N<sub>2</sub> was fed to the reactor for another 2 h to remove any gas phase or weakly adsorbed NH<sub>3</sub>. The final stage involved a temperature ramp to 535 °C with a heating rate of 10 °C/min.

The H<sub>2</sub>-TPR experiments were performed by loading 100 mg of powder catalyst in a quartz tube reactor. The effluent H<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> concentrations were measured using a mass spectrometer (Hiden Analytical Inc. HPR-20). The samples were first pretreated in 150 sccm with 5% O<sub>2</sub> in He at 600 °C for 2 h followed by purging with pure He for 1 h at the same temperature. Subsequently, the reactor temperature was reduced to 50 °C and 1% H<sub>2</sub> in a total flow of 33 sccm (He balance) was metered into the reactor for 5 h in order to saturate the catalyst and stabilize the H<sub>2</sub> signal. An O<sub>2</sub> trap was used to remove any trace amount of O<sub>2</sub> from the gas supply. After saturation, the temperature was ramped to 1000 °C at 10 °C/min with flowing 1% H<sub>2</sub> in He and the H<sub>2</sub> consumption was calculated afterwards.

In situ DRIFTS experiments were performed using a Nicolet 6700 spectrometer equipped with a MCT detector and a high temperature reaction chamber (Harrick Praying Mantis) with ZnSe windows. In each experiment, powder samples were pressed into a 60 mg pellet placed in the sample cup with a porous screen at the bottom surface. The reactor temperature was measured with a K-type thermocouple located underneath the sample cup. The DRIFTS spectra were collected in the range of 4000–650 cm<sup>-1</sup> with the Kubelka–Munk (KM) format. Prior to each test, the catalyst sample was pretreated at 600 °C in a flow of 10% O<sub>2</sub> in He for 1 h before cooling to room temperature. For the skeleton vibration spectra, the background spectra were recorded in flowing He on pure KBr powder and subtracted from the absorption sample spectrum. For NH<sub>3</sub> and NO adsorption experiments, the spectra were collected by subtracting the background spectra recorded during exposure to the sample to pure He. NH<sub>3</sub> adsorption was conducted in a 50 cm<sup>3</sup>/min flow containing 500 ppm NH<sub>3</sub> in a balance of He and NO adsorption spectra were performed in a 50 cm<sup>3</sup>/min flow containing 200 ppm NO in a balance of He.

### 2.3. NH<sub>3</sub>-SCR and NH<sub>3</sub> oxidation reaction tests

The reaction data were collected using a micro-reactor system. In each experiment, 120 mg of sieved powder catalyst samples were mixed with 360 mg quartz beads and put into a quartz tube reactor (8 mm ID  $\times$  500 mm L). The powder catalyst was held in place with quartz wool. A thermocouple was inserted into the downstream quartz wool to monitor the temperature. The reactor was placed inside a Lindberg Minimate temperature-controlled furnace. Before testing, the catalyst was degreened at 600 °C for 2 h in flowing 10% O<sub>2</sub> in a balance of N<sub>2</sub>.

All the reactant gases were metered using MKS mass flow controllers and water vapor for the feed was supplied by a Bronkhorst

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