

## Euro Green Chemistry 2018- The reliability study on the Cu/CHA NH<sub>3</sub>-SCR Catalysts: SO<sub>3</sub> and Na ions poisoning-Chen Wang-North University of China

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### Introduction:

In the recent years most effective post-processing technology for incline NO<sub>x</sub> control in diesel is the specific catalytic reduction of NO<sub>x</sub> with ammonia (NH<sub>3</sub>-SCR). Cu/SSZ-13 catalysts, especially in the last five years, have gained much concentration because they exhibit good NH<sub>3</sub>-SCR results at low-temperature regions and outstanding N<sub>2</sub> selectivity. As a result, Cu/SSZ-13 catalysts could be a great SCR catalyst to meet with the harsh emission regulations in diesel vehicles. Actually, a number of necessary conclusions and contributions have been made to properly to understand the nature of copper ions and their impact on NH<sub>3</sub>-SCR mechanisms over Cu/SSZ-13 catalysts. The authors found that copper sulfate content decreased when increasing at 750 °C owing to copper migration and the contents of copper sulfate enhanced at 850 °C aging as CuO<sub>x</sub>/CuAlO<sub>x</sub> easy to react with SO<sub>2</sub>. Without any doubt, the above studies have provided important results to understand SO<sub>2</sub> poisoning. However, the impact of SO<sub>3</sub> should not be ignored because diesel oxidation catalysts (DOCs) will be applied upstream to SCR catalysts. As of now, few studies have reported on the influence of SO<sub>3</sub> on Cu-loaded Chabazite (Cu/CHA) catalysts.

### The Variation of the CHA Structure under SO<sub>3</sub> Poisoning:

It is normally accepted that SO<sub>2</sub> has no influence on the structure of zeolites as both SO<sub>2</sub> and zeolites show acidity. Hence, no modifications in the CHA framework on S-Cu-0 could be without difficulty understood. Most importantly, in this study, the data of Sox sulfated samples showed the identical results with S-Cu-0, indicating that the presence of SO<sub>3</sub> also had no authority on the CHA structure of SSZ-13. This is supported by the minor decline in the specific surface area, as well as the same relative crystallinity, the intensity of Si-O(H)-Al bonds and the chemical environment of Si and Al on the sulfated catalysts. It should be recalled from our preceding study on SO<sub>3</sub> poisoning in Cu/SAPO-34 catalysts that the CHA structure of Cu/SAPO-34 was spoiled during high contents of SO<sub>3</sub> poisoning (20% SO<sub>3</sub> in SO<sub>x</sub>) as the method of dealumination occurred. Considering the unbroken topological structure of Sox sulfated Cu/SSZ-13, Cu/SSZ-13 catalysts show better acid resistance than Cu/SAPO-34.

In fact, as SSZ-13 have a good peak of NH<sub>3</sub> at higher temperature compared with that of SAPO-34 (~420 °C for SSZ-13 vs. ~350 °C for SAPO-34) [15,39], SSZ-13 shows great acidity than SAPO-34.

### Materials and Methods

The Cu/SSZ-13s needed to completely dehydrate (300 °C for 24 h under vacuum), and then, the exact surface area of

Cu/SSZ-13s was measured using Brunauer–Emmett–Teller measurements

(Micromeritics, Norcross, GA, USA). The relative crystallinity of catalysts was calculated when the normalized whole areas of six peaks relative to that for a fresh one. A Nicolet 6700 FTIR (Thermo Fisher Scientific, Waltham, MA, USA) was used to probe the change of -OH vibration on Cu/SSZ-13s. KBr was selected as the standard substance to make the background for ex-situ tests. <sup>27</sup>Al and <sup>29</sup>Si NMR measurements were analysed on a Varian Infinity plus 300 WB spectrometer (Palo Alto, CA, USA) at resonance frequencies of 59.57 and 78.13 MHz, respectively, with samples pinning rates of 8 kHz for <sup>27</sup>Al and 4 kHz for <sup>29</sup>Si. A Mettler Toledo thermal gravimetric analyzer (Zurich, Switzerland) was used to recognize sulfur and give their amounts, and hence, 15 mg samples were examined within the temperature ranges from 40 to 850 °C at a ramping rate of 10 °C/min in a gas flow containing 10% O<sub>2</sub>/N<sub>2</sub>. The total copper contents on Cu/SSZ-13s were probed by H<sub>2</sub>-TPR methods. All samples were considered in a flow of 5% H<sub>2</sub>/N<sub>2</sub> (10 sccm) from 40 °C to 800 °C at a ramping rate of 10 °C/min. The contents of active sites were quantitative calculated by EPR at -150 °C when hydrated Cu/SSZ-13s and dilute CuSO<sub>4</sub>·5H<sub>2</sub>O aqueous solution with known concentration were used as a reference to standardize the copper amounts over Cu/SSZ-13. NH<sub>3</sub>-SCR activity at ordinary and kinetic conditions was performed on all Cu/SSZ-13 catalysts. The comprehensive description of the experimental process could be found in our previous studies.

SO<sub>2</sub> poisoning of NH<sub>3</sub>-SCR over Cu-SAPO-34 was studied, specifically to assess the forms/states of stored S and the effect of such species on low-temperature NO<sub>x</sub> lessening activity. Two primary sulfur species types were experimental and were found to be exchangeable depending on whether NH<sub>3</sub> was offered or not. Disperse reflectance infrared Fourier transform spectroscopy (DRIFTS) of NO adsorption was used to examine the nature and accessibility of the Cu species before and after sulfate formation, without the intrusion of ammonium sulfate; these data revealed that the Cu<sup>2+</sup> inside the six-membered rings was entirely blocked by sulfur and that the nature of the [CuOH]<sup>+</sup> close to the eight-membered ring altered.

### Conclusion:

The SO<sub>3</sub> effect on a Cu/SSZ-13 catalyst has been investigated as a function of Sox contents.

The main conclusions of this study are listed below: As a best acid-resistant ability, even at a high ratio of SO<sub>3</sub>/SO<sub>x</sub> flux, the CHA structure of Cu/SSZ-13 keeps intact. Copper sulfate form during sulfation with SO<sub>2</sub> alone or SO<sub>x</sub> at 250 °C and the

contents of sulfate show the linear relationship with the  $\text{SO}_3$  contents in  $\text{SO}_x$ .  $\text{Cu}(\text{OH})^+$  show the stronger response to sulfate, compared with  $\text{Cu}^{2+}$  ions, and no trace of  $\text{Cu}(\text{OH})^+$  has been found during sulfation. For sulfated catalysts, the loss of  $\text{Cu}^{2+}$  contents contributed to the inferior SCR activity at low temperatures.