

## Supplementary Material

# Rare-earth Ions Exchanged Cu-SSZ-13 Zeolite from Organotemplate-free Synthesis with Enhanced Hydrothermal Stability in NH<sub>3</sub>-SCR of NO<sub>x</sub>

Zhenchao Zhao<sup>a,1</sup>, Rui Yu<sup>a,1</sup>, Chuan Shi<sup>a</sup>, Hermann Gies<sup>b</sup>, Feng-Shou Xiao<sup>c</sup>, Dirk De Vos<sup>d</sup>, Toshiyuki Yokoi<sup>e</sup>, Xinhe Bao<sup>f</sup>, Ute Kolb<sup>g</sup>, Robert McGuire<sup>h</sup>, Andrei-Nicolae Parvulescu<sup>h</sup>, Stefan Maurer<sup>h</sup>, Ulrich Müller<sup>h,\*</sup>, Weiping Zhang<sup>a,\*</sup>

<sup>a</sup>*State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*

<sup>b</sup>*Institute für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany*

<sup>c</sup>*Department of Chemistry, Zhejiang University, Hangzhou 310028, China*

<sup>d</sup>*Center for Surface Chemistry and Catalysis, K. U. Leuven, Leuven, Belgium*

<sup>e</sup>*Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan*

<sup>f</sup>*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Dalian 116023, China*

<sup>g</sup>*Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, 55128 Mainz, Germany*

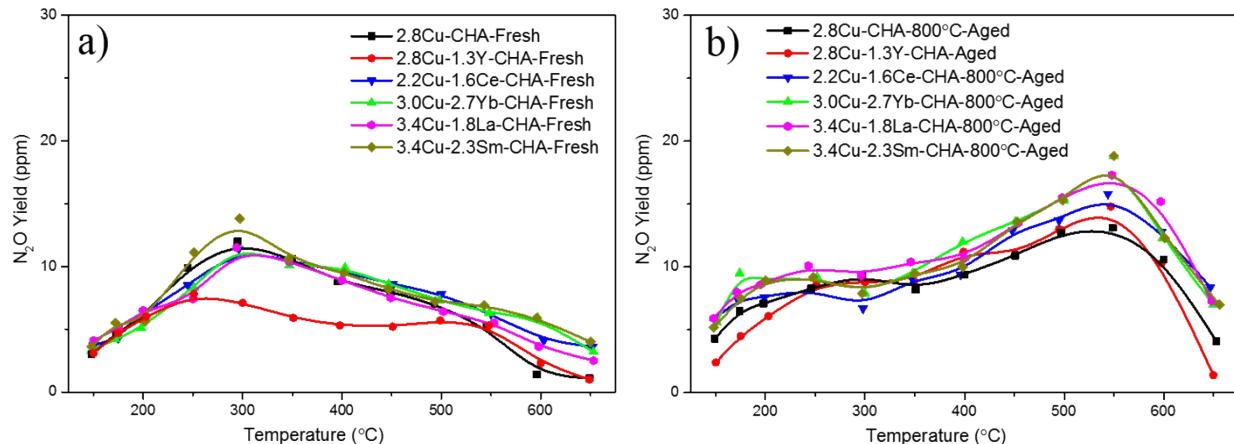
<sup>h</sup>*BASF SE, Process Research and Chemical Engineering, 67056 Ludwigshafen, Germany*

<sup>1</sup> Z.Z. and R.Y. contributed equally to this work.

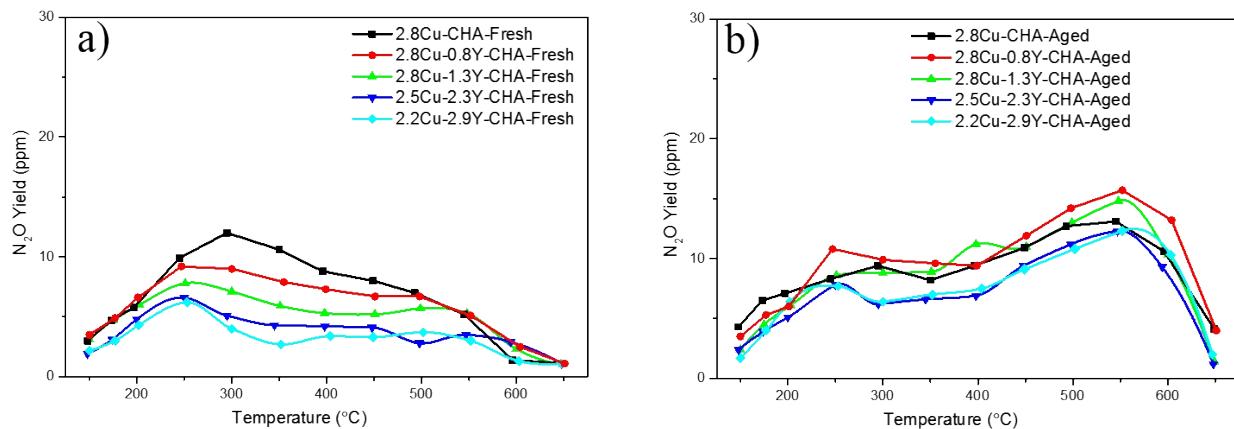
### \*Corresponding authors:

Ulrich Müller: E-mail: [ulrich.mueller@basf.com](mailto:ulrich.mueller@basf.com) Phone: + 49 621 60 56190

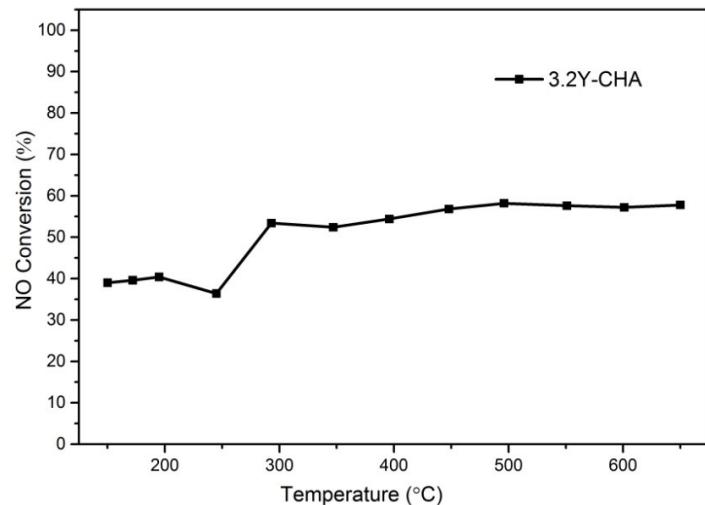
Weiping Zhang: E-mail: [wpzhang@dlut.edu.cn](mailto:wpzhang@dlut.edu.cn) Phone: +86 411 8498 6326



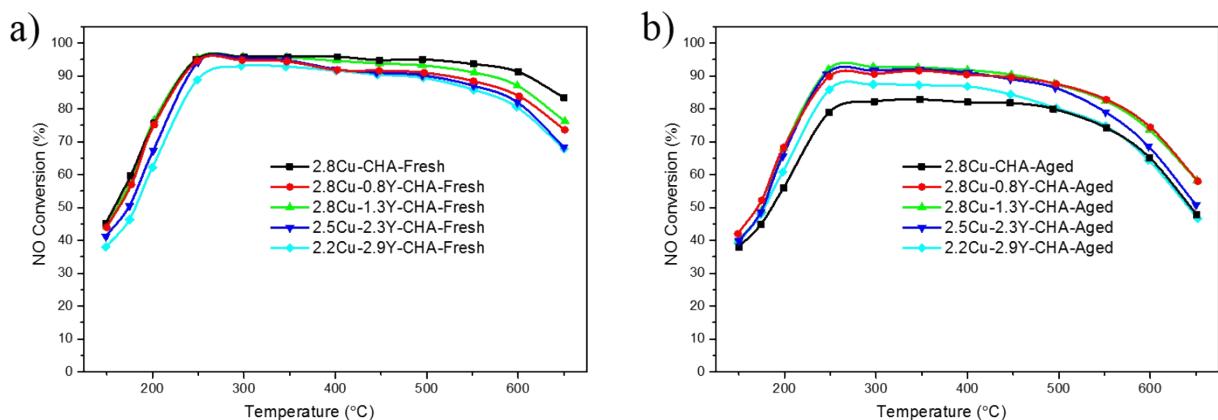
**Figure S1.**  $\text{N}_2\text{O}$  yields as a function of temperature on rare-earth ions exchanged Cu-SSZ-13(4): (a) Fresh and (b) 800 °C aged. Reaction conditions: 500 ppm NO, 500 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5 vol.%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ ; GHSV=80, 000  $\text{h}^{-1}$ .



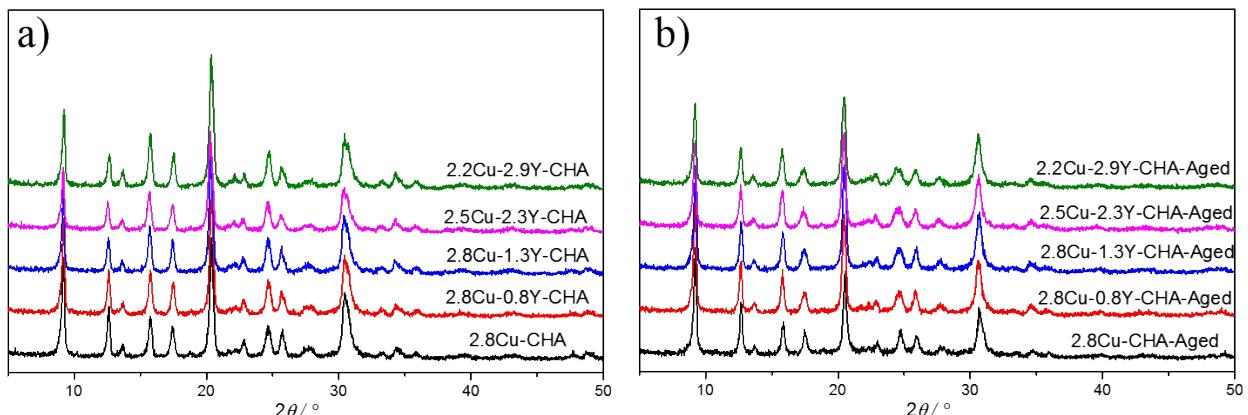
**Figure S2.**  $\text{N}_2\text{O}$  yields as a function of temperature on fresh and hydrothermally aged Al-rich Cu-Y-SSZ-13(4) catalysts with different amount of Y. Reaction conditions: 500 ppm NO, 500 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ ; GHSV=80, 000  $\text{h}^{-1}$ .



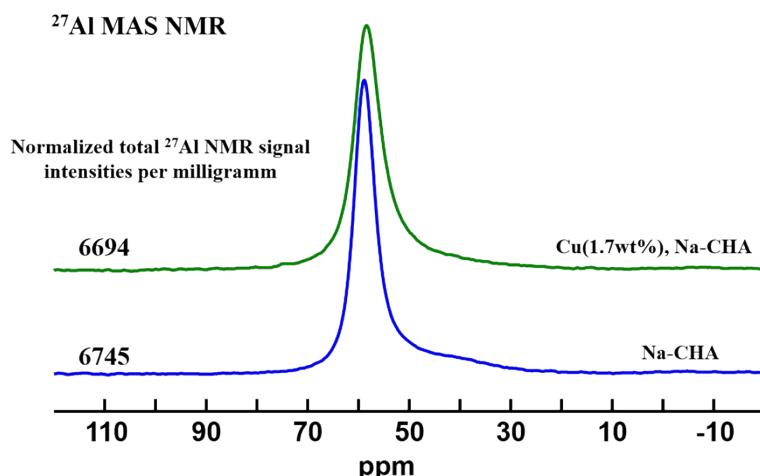
**Figure S3.** NO conversions as a function of temperature on Y-SSZ-13(4). Reaction conditions: 500 ppm NO, 500 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5 %  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ ; GHSV=80, 000  $\text{h}^{-1}$ .



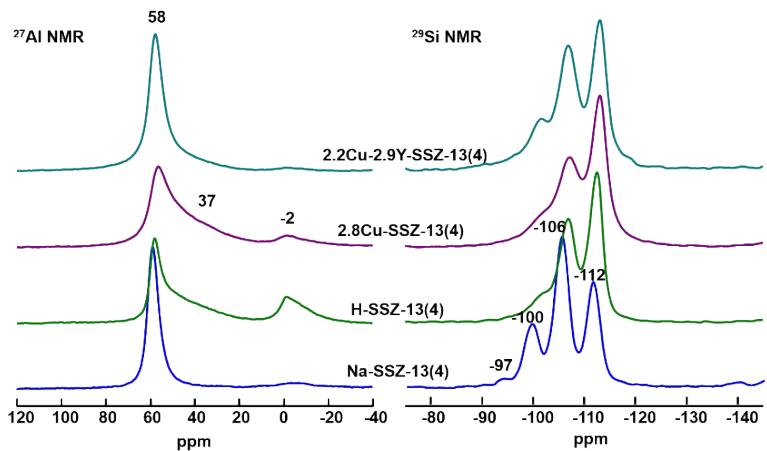
**Figure S4.** NO conversions as a function of temperature on fresh and hydrothermally aged Al-rich Cu-Y-SSZ-13(4) catalysts with different amount of Y. Reaction conditions: 500 ppm NO, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub>; GHSV= 400, 000 h<sup>-1</sup>.



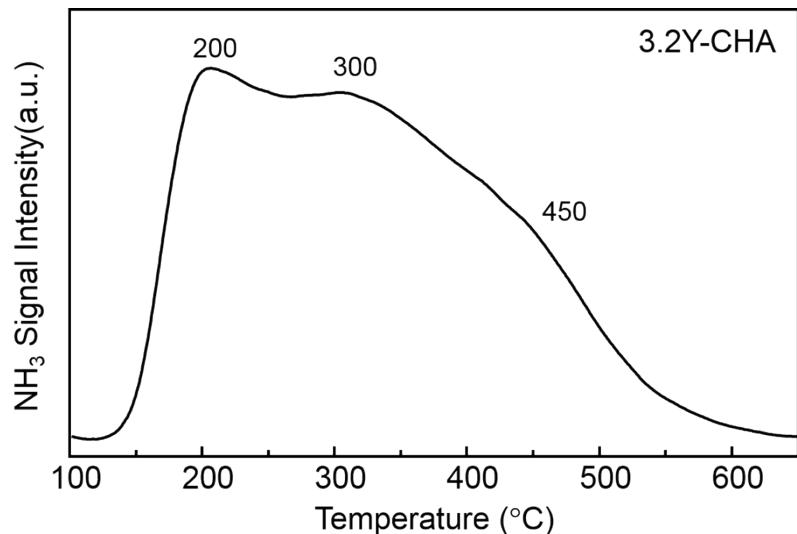
**Figure S5.** XRD patterns of Cu-Y-SSZ-13(4) catalysts: fresh (a) and hydrothermally aged (b).



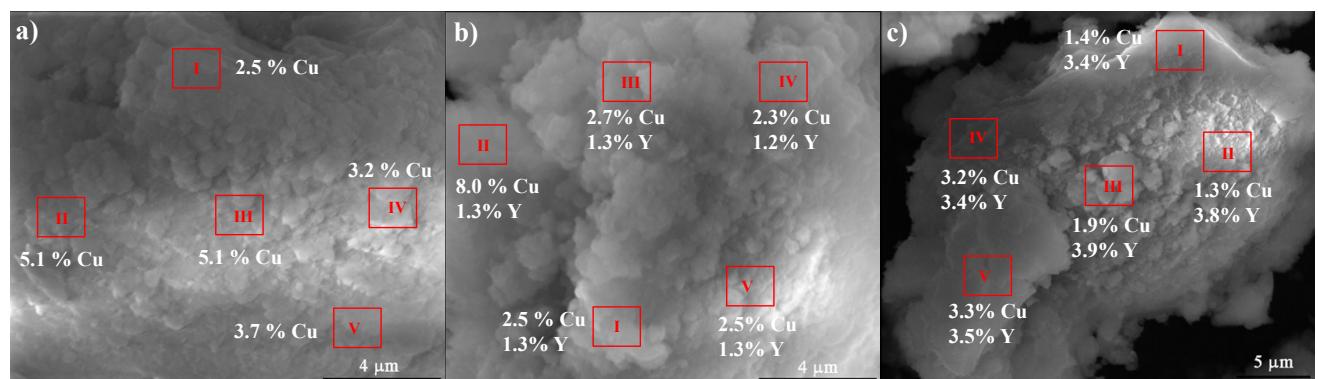
**Figure S6** <sup>27</sup>Al MAS NMR spectra of Na-SSZ-13 and Cu-Na-SSZ-13.



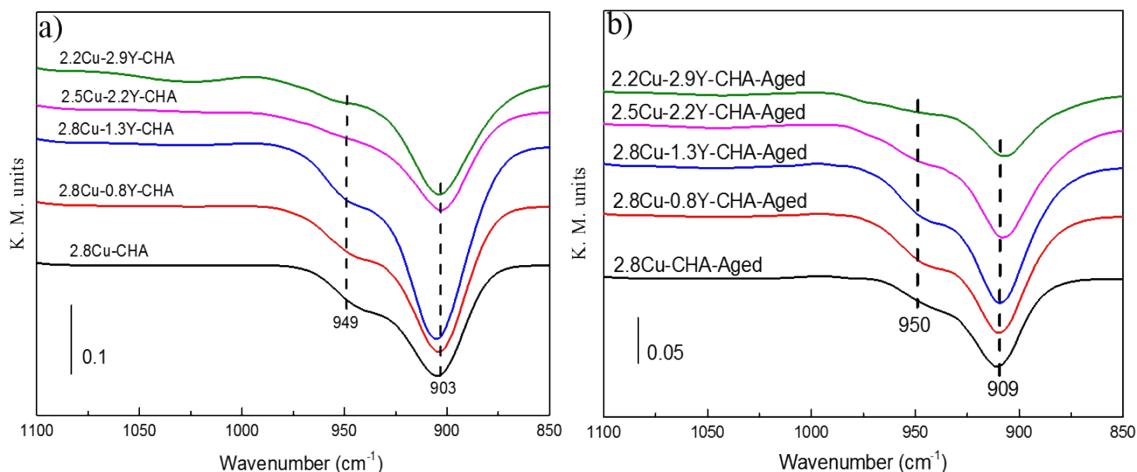
**Figure S7.**  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra of parent Na-SSZ-13(4), H-type SSZ-13(4) and Cu-exchanged SSZ-13(4) and Cu,Y-exchanged SSZ-13(4).



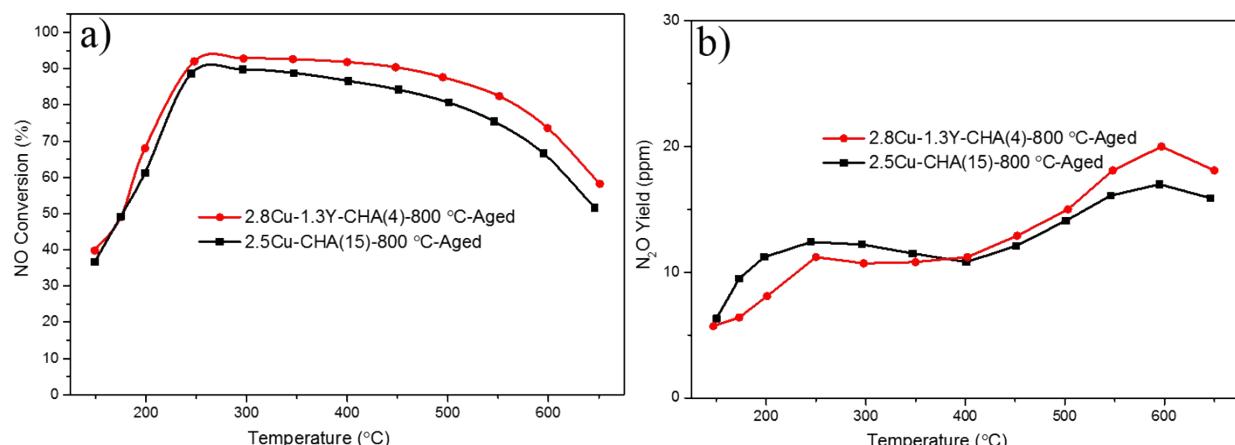
**Figure S8.**  $\text{NH}_3$ -TPD profiles of 3.2Y-H-SSZ-13(4).



**Figure S9.** SEM-EDX results of representative Cu-Y-SSZ-13 catalysts: (a) 2.8Cu-CHA; (b) 2.8Cu-1.3Y-CHA and (c) 2.2Cu-2.9Y-CHA. Cu distributions are inhomogeneous, and even unexpected high Cu contents above 5 wt% are observed for these catalysts, which may result from minor highly dispersed CuO species also identified by H<sub>2</sub>-TPR.



**Figure S10.** DRIFT spectra of fresh (a) and aged (b) Cu-Y-SSZ-13 zeolites with NH<sub>3</sub> exposure time of 30 min.



**Figure S11.** NO conversions (a) and N<sub>2</sub>O yields (b) as a function of temperature for hydrothermally aged Al-rich 2.8Cu-1.3Y-SSZ-13 and organotemplated high-silica 2.5Cu-SSZ-13(15) catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub>; GHSV=400, 000 h<sup>-1</sup>.

**Table S1** Concentration of Brønsted acid sites in fresh and aged Cu-Y-CHA catalysts derived from quantitative <sup>1</sup>H MAS NMR measurements

Sample	Fresh (mmol/g zeolite)	Aged (mmol/g zeolite)
<b>2.8Cu-CHA</b>	0.46	0.01
<b>2.8Cu-0.8Y-CHA</b>	0.41	0.01
<b>2.8Cu-1.3Y-CHA</b>	0.43	0.04
<b>2.5Cu-2.3Y-CHA</b>	0.41	0.04
<b>2.2Cu-2.9Y-CHA</b>	0.64	0.07

**Table S2** Normalized reaction rates ( $\times 10^{-3}$  mol NO · mol<sup>-1</sup>Cu · s<sup>-1</sup>) of Al-rich Cu-Y-CHA catalysts.

	2.8Cu-CHA	2.8Cu-0.8Y-CHA	2.8Cu-1.3Y-CHA	2.5Cu-2.3Y-CHA	2.2Cu-2.9Y-CHA
<b>150 °C</b>	4.3 <sup>a</sup> (3.6)	4.2(4.0) <sup>b</sup>	4.2(3.8)	4.4(4.3)	4.6(4.7)
<b>175 °C</b>	5.7(4.3)	5.4(5.0)	5.5(4.7)	5.4(5.2)	5.6(5.8)
<b>200 °C</b>	7.2(5.3)	7.2(6.5)	7.3(6.5)	7.2(7.0)	7.5(7.4)

<sup>a</sup>: Fresh catalyst; <sup>b</sup>: 800 °C aged catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub>; GHSV=400, 000 h<sup>-1</sup>.