Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2020

Why has to be residual Na as co-cation on Cu/SSZ-13?

Zexiang Chen [a], Xuguang Tan [b] , Jun Wang[a], Chen Wang[a,c], Jianqiang Wang[a], Wei Li[d] , Meiqing Shen[a,e,*]

a. School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, P. R. China

Email: mqshen@tju.edu.cn

b. State Key Laboratory of Engine Reliability， Weichai Power Co., Ltd, Weifang 261061, Shandong, P.R. China.

c. School of Environmental and Safety Engineering, North University of China, Taiyuan 030051, Shanxi, P. R. China

d. General Motors Global Research and Development, Chemical Sciences and Materials System Lab, 30500 Mound Road, Warren, MI 48090, USA

e. Collaborative Innovation Centre of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China

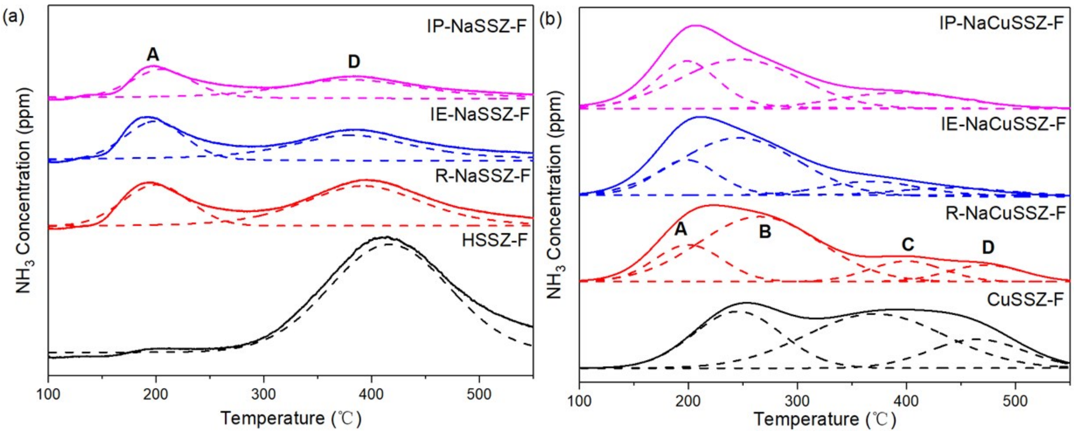

Fig. S1. Peak fitting of NH_3-TPD curves for the fresh supports and catalysts. The solid curves are the collected data and the dash curve represents fitting curves.

The fitting curves were obtained using the 'peak analyzer' in the ORIGIN software. Gaussian peak type was fitted for all curves. Peak A, B, C and D were marked on the figures and they were attributed to the NH_3 adsorbed on Na^+, weak Cu^{2+}, strong Cu^{2+} and Brønsted acid, respectively. The peak assignment was described in the explanation of the Fig. S2.

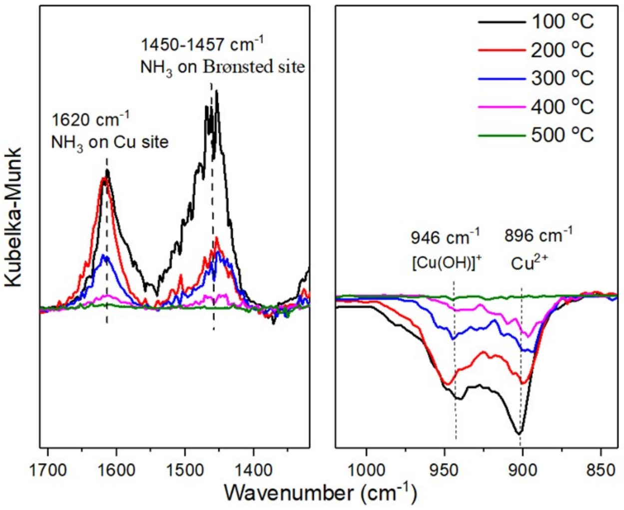

Fig. S2. Stepwise NH_3-DRIFTs of the model CuSSZ-F with increasing temperature from 100 °C to 500 °C. At each temperature, the background spectrum was collected under inert gas. The samples were exposed to NH_3 (500 ppm/N_2) for 1 h, then purged with N_2, during which the DRIFTs were continuously collected until they no longer changed with time.

The peak assignment is according to the previous literature[1] and our in-situ NH_3-DRIFTs results (Fig. S2). The support samples are easy to identify that the NH_3 adsorption at ~195 °C is assigned to Na ions and the peak from 300 °C to 500 °C is assigned to a strong Brønsted acid site. It is complicated to distinguish the NH_3 adsorption from Cu ions. As shown in Fig. S2, the NH_3 adsorbed on Cu ions will not desorb at 200 °C, as pointed by almost no change at 1620 cm^{-1}, although the band at 896 cm^{-1} decreases to some degree. From 200 °C to 400 °C the NH_3 is released continuously and above 400 °C it is limited. Therefore, we deconvoluted two desorption peaks in this temperature range to represent weak Cu site at 250-280 °C and strong Cu site 350-420 °C. We ignored the very weak Brønsted acid site when calculating the numbers of acidity because minor desorption before 300 °C as shown in Fig. S1a. Even though the band at 1450-1457 cm^{-1} drops a lot from 100 °C to 200 °C, we suggest that decrease is due to the release of a little surface weak bound NH_3.

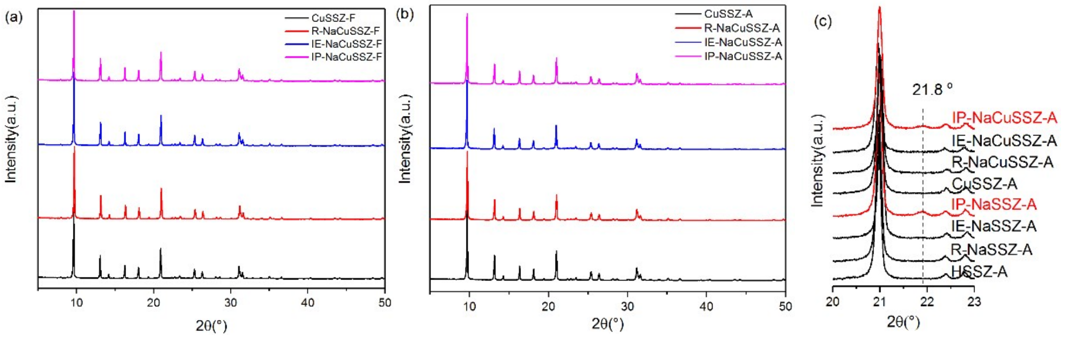

Fig. S3. XRD patterns of fresh (a) and aged (b) NaCu/SSZ-13 catalysts; (c) partial range of XRD in order to highlight the perturbation of 21.8 ° on IP-Na samples

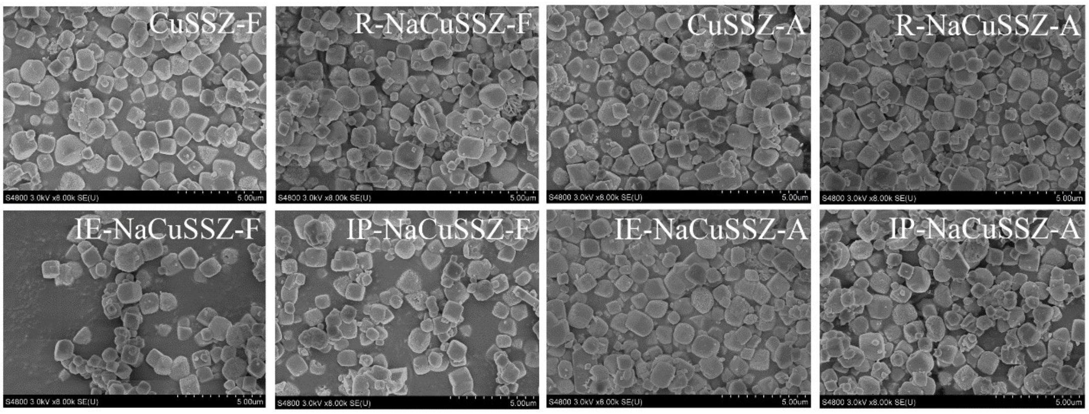

Fig. S4 SEM images of fresh and aged NaCu/SSZ-13 catalysts

CuSSZ-F R-NaCuSSZ-F IE-NaCuSSZ-F IP-NaCuSSZ-F

CuSSZ-A R-NaCuSSZ-A IE-NaCuSSZ-A IP-NaCuSSZ-A

Fig. S5. The pictures of the catalysts in the sample tube after TPR experiments. Copper red in all samples is observed.

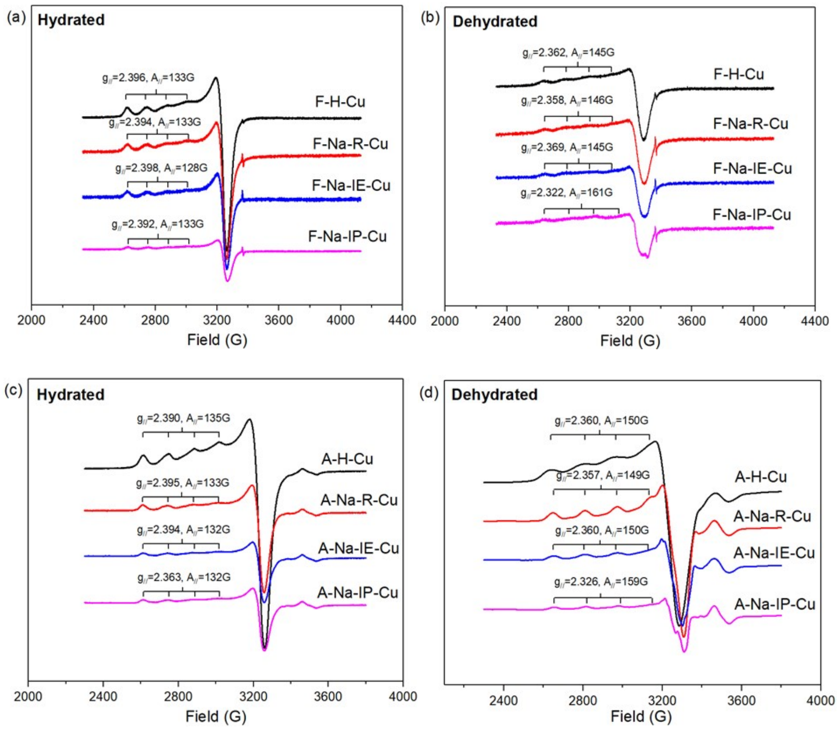

Fig. S6. EPR spectra of fresh (a-b) and aged (c-d) NaCu/SSZ-13 catalyst under hydrated and dehydrated

The g-factor and hyperfine coupling constant A are known to give information about a paramagnetic center's electronic structure and the interaction between the unpaired electron and the perturbing nuclei. Normally, experimental EPR spectra were fit using second-order perturbation equations[2] for axial A and g combined with a simplex least-squares fitting routine[3].

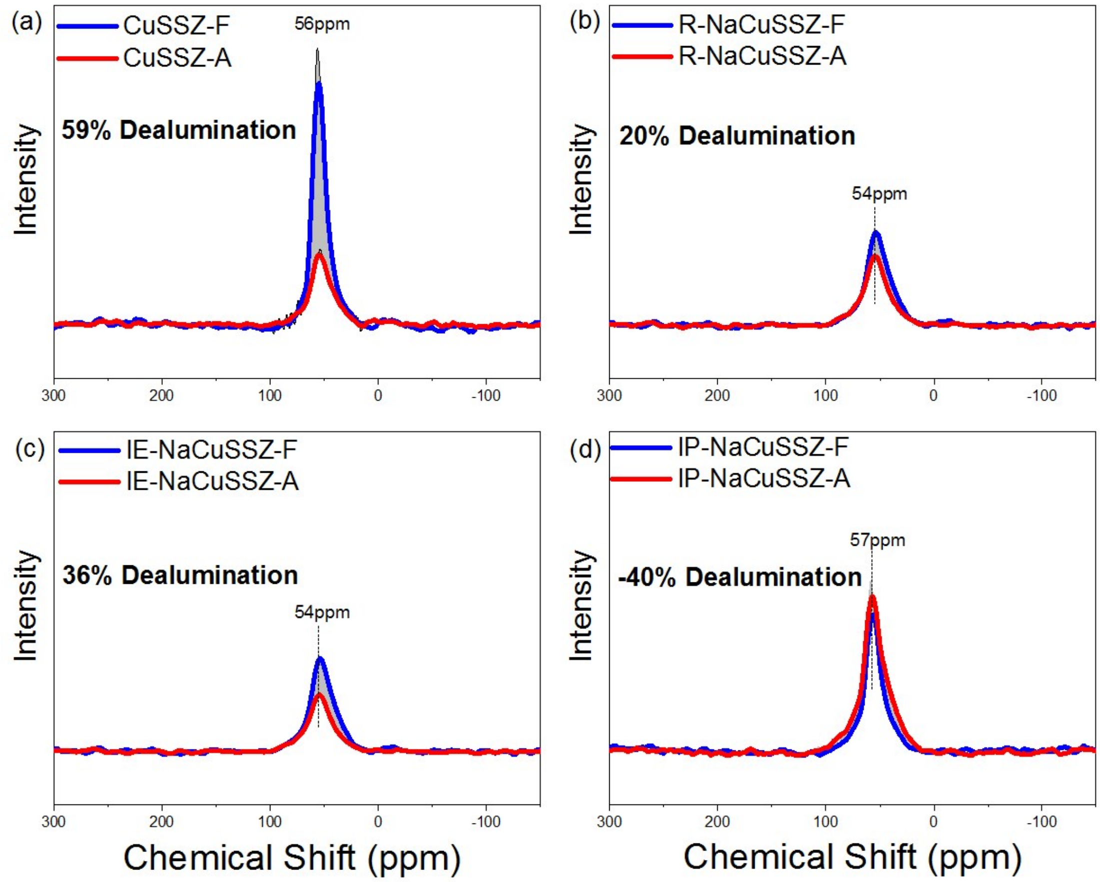

Fig. S7. Al^{27} NMR spectra of fresh and aged (a) H-Cu, (b) Na-R-Cu, (c) Na-IE-Cu and (d) Na-IP-Cu

^{27}Al MAS NMR measurements were conducted at room temperature on a Varian Infinity plus 300 WB Spectrometer at resonance frequencies of 78.13 MHz with samples spinning rates at 8 kHz. $Al(NO_3)_3$ aqueous solution was used as an external reference. The same quantity of samples in each test was controlled. The invisible Al at 54-57 ppm of chemical shift is caused by Cu nuclear spin polarization, which is normally seen in Cu/Zeolites[4]. The dealumination ratio is defined by the lost percent of peak areas centered at 54-57 ppm.

Table S1. The element composition of the fresh Cu/SSZ-13 cataylsts

Samples	Na content[a] (wt %)	Cu content[a] (wt %)	Si/Al[b] (mol/mol)
HSSZ-F	<5 ppm	-	14
R-NaSSZ-F	0.81	-	
IE-NaSSZ-F	0.79	-	
IP-NaSSZ-F	0.78	-	
CuSSZ-F	<5 ppm	1.73	
R-NaCuSSZ-F	0.77	1.70	
IE-NaCuSSZ-F	0.80	1.68	
IP-NaCuSSZ-F	0.83	1.73	

a. The Na and Cu contents are measured by ICP.

b. The Si and Al contents are measured by XRF.

Note: the element composition is no longer measured by assuming any change after hydrothermally aging.

Table S2. BET surface area of fresh and aged NaCu/SSZ-13 catalysts calculated from N_2 adsorption and desorption tests

Samples	Specific Surface Area (m^2/g)	Samples	Specific Surface Area (m^2/g)
CuSSZ-F	799	CuSSZ-A	795
R-NaCuSSZ-F	776	R-NaCuSSZ-A	739
IE-NaCuSSZ-F	782	IE-NaCuSSZ-A	650
IP-NaCuSSZ-F	775	IP-NaCuSSZ-A	662

Reference

1. K. Leistner, K. Xie, A. Kumar, K. Kamasamudram and L. Olsson, *Catal. Lett.*, 2017, **147**, 1882-1890.
2. N. D. Chasteen, in *Biological Magnetic Resonance: Volume 3*, eds. L. J. Berliner and J. Reuben, Springer US, Boston, MA, 1981, DOI: 10.1007/978-1-4613-3201-5_2, pp. 53-119.
3. S. A. Teukolsky, B. P. Flannery, W. Press and W. Vetterling, *SMR*, 1992, **693**, 59-70.
4. S. Prodinger, M. A. Derewinski, Y. Wang, N. M. Washton, E. D. Walter, J. Szanyi, F. Gao, Y. Wang and C. H. F. Peden, *Applied Catalysis B: Environmental*, 2017, **201**, 461-469.