Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY INFORMATION

Barium-Promoted Hydrothermal Stability of Monolithic Cu/BEA Catalyst for NH_3-SCR

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1. NH_3-SCR activity

Fig. S1 shows the NO_x conversion as a function of reaction temperatures in NH_3-SCR over the fresh and hydrothermally aged Cu/BEA and CuBa/BEA. The excellent and similar fresh activity could be achieved over all catalysts, and NO_x could be converted completely (higher than 90% NO_x conversion) between 175-550 °C. When the reaction temperature is above 350 °C, the decreased NO_x conversion could be due to the NH_3 oxidation.

The hydrothermal treatment at 600 °C for different time (24h, 48h, 72h) leads to a significant loss of NO_x conversion, but it could be found that it results in the less loss of activity over the CuBa/BEA than Cu/BEA (Fig. S1), demonstrating that the addition of Ba could improve the hydrothermal stability of Cu/BEA. Among these catalyst modified by the additive Ba, the best hydrothermal stability is obtained over $CuBa_3/BEA$. And the maximum NH_3-SCR activity over $CuBa_3/BEA$-(600, 48h) is 95% NO_x conversion at 250 °C and it still can remain above 87% NO_x conversion between 185-550 °C.

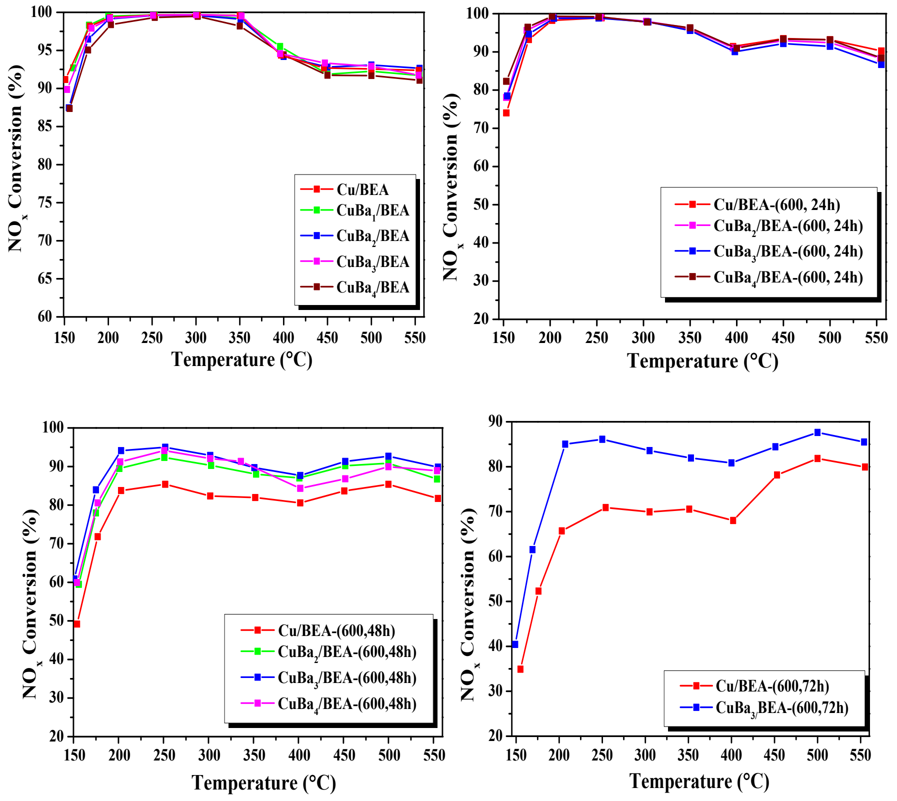

Fig. S1 NO_x conversion as a function of the reaction temperature over the fresh and hydrothermally aged Cu/BEA and CuBa/BEA during NH_3-SCR reaction conditions: 200 ppm NO, 200 ppm NH_3, 10 vol.% O_2, 5 vol.% H_2O, GHSV = 40,000 h^{-1}.

Table S1

The concentration of Cu and Ba over the fresh and hydrothermally aged Cu/BEA and CuBa/BEA analyzed by ICP-AES.

	Cu/BEA	$CuBa_1/BEA$	$CuBa_2/BEA$	$CuBa_3/BEA$	$CuBa_4/BEA$	Cu/BEA-(600, 48h)	$CuBa_3/BEA$-(600, 48h)
Cu (wt.%)	1.94	1.94	1.90	1.94	1.93	1.82	1.89
Ba (wt.%)	-	4.71	4.46	4.66	4.77	-	4.63

2. EPR

Fig. S2 displays the EPR of Cu/BEA and $CuBa_3/BEA$. Intensities of the hyperfine splitting peaks of Cu/BEA are lower than $CuBa_3/BEA$, indicating a reduction in the number of isolated Cu^{2+} species over Cu/BEA.

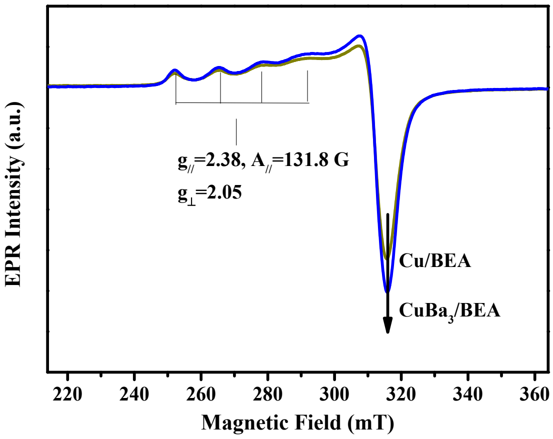

Fig. S2 EPR spectra of Cu/BEA and $CuBa_3$/BEA recorded at -150 °C.

Table S2

The surface chemical composition and contents of isolated Cu^{2+} species over Cu/BEA and $CuBa_3$/BEA.

Sample	[a] Isolated Cu^{2+} concentration on surface*
Cu/BEA	1.00
$CuBa_3$/BEA	1.25

[a] Calculated by EPR spectroscopy; * The isolated Cu^{2+} content on Cu/BEA is defined as 1.00.

3. TEM

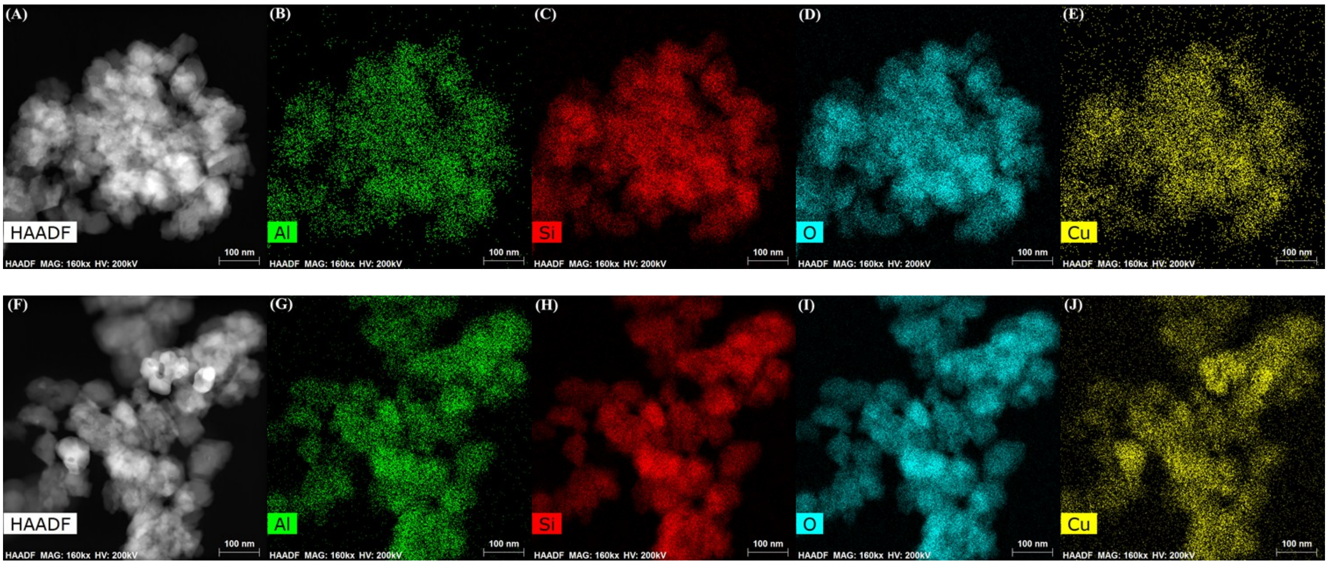

Fig. S3. HAADF-STEM image combined with the EDS elemental mapping over Cu/BEA (A)-(E) and CuBa/BEA (F)-(J).

Distributions of Al, Si, O and Cu species in the same region over fresh Cu/BEA and CuBa/BEA are simultaneously investigated by the HRTEM-STEM combined with EDS elemental mapping images (Fig. S3). Higher distributions of Al, Si, O and Cu species over Cu/BEA from elemental mapping image (Fig. S3B-E) could be observed than CuBa/BEA. Fig. S3B-D suggest that the better zeolite structure over Cu/BEA, which is consistent with the XRD. The more complete BEA structure is favor for more acid sites, which also corresponding to the

NH_3-TPD (Fig 3) and NH_3-adsorption (Fig 4). Furthermore, compared with CuBa/BEA, more bright copper region over Cu/BEA-HT are detected (Fig. S3J). Combined with the O element mapping image (Fig. S3I), some bright copper regions coincide with some rich O regions, which could be due to formation of the copper oxides during the preparation process. So it demonstrates that more copper oxides are presented in CuBa/BEA. But the H_2-TPR and XRD have no obvious presence of copper oxides, so a small amount of copper species is produced in the fresh CuBa/BEA. More copper oxides are disadvantaged for the higher activity of the hydrothermally treated catalyst.