

Supplementary information for

**Controllable positions of Cu²⁺ to enhance low-temperature SCR
activity on novel Cu-Ce-La-SSZ-13 by a simple one-pot method**

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S1. Experimental Section

S1.1 Preparation of catalysts by one-pot method

The Cu-Ce-La-SSZ-13 catalyst was synthesized by one-pot method. Briefly, 5.4111 g TEPA were slowly added into 35 ml 0.8M CuSO₄ aqueous solution under the stirring for 4 h, followed by the addition of 0.3040 g Ce (NO)₃·6H₂O and 0.3867 g La (NO)₃·6H₂O and stirred for another 1 h. The mixing solution of 25 ml of NaOH and NaAlO₂ and 38.2 g silica sol solution was added to the templating solution and aged for 12 h. Then, crystallized at 160°C for 96 h in Teflon-lined autoclaves. The composition of the reactant mixture was as follows: Na₂O: Al₂O₃: SiO₂: Cu-TEPA: H₂O = 4: 1: 10: 1.47: 280. After washing, centrifugation and calcination at 550°C for 6 h to remove organic templates, the obtained powder denoted as Cu-Ce-La-SSZ-13.

Cu-SSZ-13 and Cu-Ce-SSZ-13 were also synthesized according to these steps, only without the addition of Ce, La and La species, respectively.

S1.2 Preparation of catalysts by ion exchange method

The Cu-Ce-La/SSZ-13 catalyst was synthesized by ion exchange method. The composition of the reactant mixture was as follows: Na₂O: Al₂O₃: SiO₂: TMAdaOH: H₂O = 5: 1: 30: 5: 900. Briefly, 1.25 g of NaOH was added to deionized water. After the dissolution is completed, added 2.082 g of aluminum sulfate, continue stirring until the solution is clear, and then slowly add 13.28 g of silica sol (30 wt%) into the above solution. Then, a mixture of 6.2 g of N, N, N-trimethyl-1-adamantyl ammonium hydroxide (25 wt%) and 10 mL of deionized water was slowly added. After mechanical stirring at 25°C for 12 h, placed in a hydrothermal reaction kettle and homogeneously reacted at 160°C for 96 h at a rotation speed of 4 r/min. After the crystallization, the water was washed by centrifugation. The sample obtained by centrifugation was dried at 80°C. The dried sample was ground and placed in a calciner at a constant temperature of 550°C for 6 h to obtain a Na/SSZ-13 sample.

NH₄/SSZ-13 was prepared by exchanging Na/SSZ-13 in (NH₄)₂SO₄ (1 mol/L) solution at 70°C for 5 h. Then, 4 g NH₄/SSZ-13 were added into 400 ml Cu (NO₃)₂ solution (0.5 mol/L) under mechanical stirring at 30°C for 12 h. This step was conducted twice to make the Cu ion exchange entirely. And the Cu-Ce-La/SSZ-13 sample was further obtained by ion exchange of Cu-SSZ-13 in

Ce (NO₃)₃ solution (0.016 mol/L) and La (NO₃)₃ solution (0.01 mol/L) sequentially at 70°C for 2 h. Finally, this sample was calcined at 550°C for 6 h, the obtained powder denoted as Cu-Ce-La/SSZ-13.

The Ce/SSZ-13 was prepared by exchanging NH₄/SSZ-13 in Ce (NO₃)₃ solution (0.016 mol/L) sequentially at 70°C for 2 h. The La/SSZ-13 was prepared by exchanging NH₄/SSZ-13 in La (NO₃)₃ solution (0.01 mol/L) sequentially at 70°C for 2 h.

S2. Details on the analysis equipment

X-ray powder diffraction (XRD) patterns were recorded by a Bruker D8 advance diffractometer with Cu K α radiation under a voltage of 40 kV and a current of 100 mA. Scanning was conducted at a step of 0.02 and time of 0.01 s. X-ray photoelectron spectroscopy (XPS) measurements were conducted on PHI QuanteraII with Al K α radiation ($h\nu = 1486.6$ eV). Ultraviolet and visible diffuse reflectance spectroscopy (UV-Vis DRS) were determined on a Shimadzu UV-2550 UV-Vis spectrophotometer. Contents of Cu, Ce and La elements in synthesis solution were determined with ICP-AES (Thermo Electron Model IRIS Intrepid II XDL). Hydrogen temperature programmed reduction (H₂-TPR) experiments were performed on automated chemisorption analyzer (Quantachrome Instruments). In each experiment, 100 mg of samples were loaded into a quartz reactor and then pretreated in N₂ (50 mL/min) at 300°C for 1 h. The samples were then cooled to room temperature under a stream of N₂. The reduction of the samples was carried out from room temperature to 700°C under a flow of 10% H₂/N₂ (50 mL/min) at 10 °C/min. The consumption of H₂ was continuously recorded with a thermal conductivity detector. Electron paramagnetic resonance (EPR) measurements were obtained at 110 K by use of a Bruker EMX-10/12-type spectrometer in the X-band. The fresh samples were pretreated at 550°C for 6 h in N₂ to prepare dehydrated sample. Then, 100 mg of dehydrated samples were placed into quartz tubes for sealing measure. The spectra were simulated using the program Biomolecular EPR Spectroscopy Software. The line shape was Lorentzian for all simulated spectra. Note that the difference between ⁶³Cu and ⁶⁵Cu was not resolved and thus not taken into account.

S3. Catalytic activity measurements

The SCR activity measurements were conducted in a fixed-bed reactor under atmospheric pressure. The reaction temperature was controlled by a programmable temperature controller. 50

mg catalyst (60-80 mesh) was used in the fixed-bed reactor, and the total flow rate was 150 mL/min, corresponding gas hourly space velocity (GHSV) was 150000 h⁻¹. The mixture gas consisted of 500 ppm NO, 500 ppm NH₃, 10% H₂O (when used), 5% O₂ and balance N₂. The aging condition was as follows: the fresh samples were aged in the mixture atmosphere of N₂ and 10% H₂O for 12 h under 750°C. The concentration of NO was measured by a Germany Mruvario PLUS flue gas analyzer.

The NO_x conversion was calculated at steady state based on the inlet and outlet concentrations of NO, NO₂ and N₂. The NO_x Conversion was calculated based on Eq. (1):

$$NO_x \text{ Conversion} = \frac{(NO + NO_2)_{inlet} - (NO + NO_2)_{outlet}}{(NO + NO_2)_{inlet}} \times 100\% \quad (1)$$

S4. Catalyst Characterization

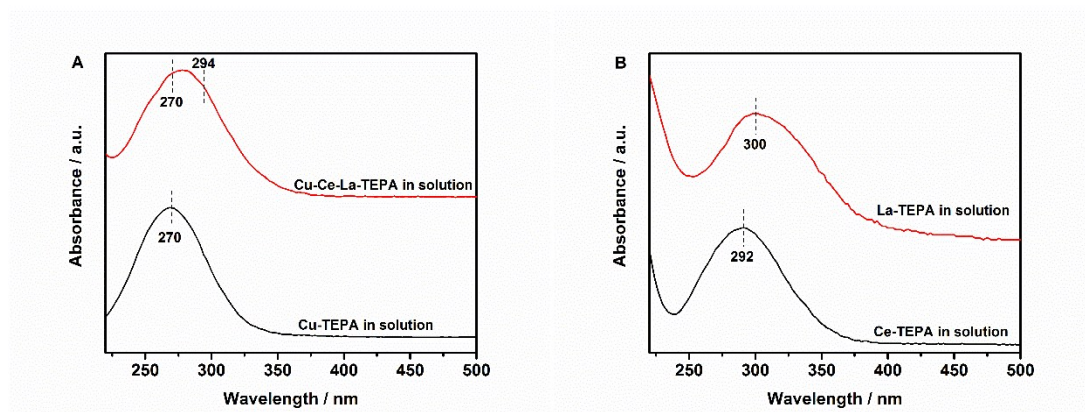


Figure S1 Liquid UV-Vis spectra of different samples in solution

The complexation of different metal cations (Cu^{2+} , Ce^{4+} and La^{3+}) with TEPA was studied using liquid UV-Vis spectra. As shown in Fig. S1, for Cu-TEPA in solution, the single band centered at 270 nm was assigned to the intact Cu-TEPA complex [1]. While the bands belong to the Ce-TEPA complex and La-TEPA complex appear at 292 nm and 300 nm, respectively (see Fig. S1B). For Cu-Ce-La-TEPA in solution, two bands centered at 270 nm and 294 nm were detected and assigned to the Cu-TEPA complex and Ce/La-TEPA complex, respectively. The results indicated that all metal cations (Cu^{2+} , Ce^{4+} and La^{3+}) were complexed with TEPA.

Table S1 Content of Cu, Ce and La elements in Cu-Ce-La-SSZ-13 synthesis solution at different reaction times

| Content | 0d | 1d | 2d | 3d | 4d |
|-------------------------|-------|----------------|---------------|---------------|--------------|
| Cu ^a (mg/kg) | 22700 | 1759.8 (7.75%) | 522.4 (2.30%) | 174.4 (0.77%) | 254.2 (1.1%) |
| Ce ^a (mg/kg) | 778.8 | 54.7 (7.02%) | 11.9 (1.53%) | 2.1 (0.27%) | 2.6 (0.33%) |
| La ^a (mg/kg) | 985.4 | 71.3 (7.24%) | 20.8 (2.11%) | 3.3 (0.34%) | 3.9 (0.40%) |

^a Elements content was determined by ICP-AES

The metal contents in synthesis solution at different reaction times was determined by ICP and the data were shown in Table S1. After reaction for 1d, the concentration of Cu, Ce and La elements was sharply decreased by 92.25%, 92.98% and 92.76%, respectively, indicating metal ions almost all are involved in crystal growth in the early stages of crystallization. As reaction proceeding for 4d, only a very small amount of metal ions were in the synthesis solution, this shows that almost all

metal cations enter the solid sample with the complex.

Table S2 Chemical compositions and BET surface areas of different samples

| Sample | Si/Al ratio ^a | Cu content (wt.%) ^a | Ce content (wt.%) ^b | La content (wt.%) ^b | S _{BET} (m ² /g) | V _p (cm ³ /g) ^c |
|-----------------|--------------------------|-----------------------------------|-----------------------------------|-----------------------------------|--------------------------------------|--|
| Cu-SSZ-13 | 4.53 | 3.73 | - | - | 191.1 | 0.0423 |
| Cu-Ce-SSZ-13 | 4.35 | 3.96 | 0.76 | - | 183.2 | 0.0411 |
| Cu-Ce-La-SSZ-13 | 4.27 | 3.84 | 0.78 | 0.75 | 199.9 | 0.0449 |
| Cu-Ce-La/SSZ-13 | 21.1 | 3.57 | 0.67 | 0.61 | 620.6 | 0.0612 |

^a Si/Al and Cu content was determined by EDS

^b Ce content and La content was determined by ICP-AES

^c V pore volume was calculated by t-plot method

Table S3 Relative proportion of different H₂ reduction peak.

| Sample | Peak a | Peak b |
|-----------------|--------|--------|
| Cu-SSZ-13 | 25.6% | 74.4% |
| Cu-Ce-SSZ-13 | 23.8% | 76.2% |
| Cu-Ce-La-SSZ-13 | 17.8% | 82.2% |
| Cu-Ce-La/SSZ-13 | 65.3% | 34.7% |

Table S4 EPR parameters of the low-field hyperfine structure signal indicated in the spectra of figure 3

| Sample | signal A (Cu^{2+} in Site III) | | signal B (Cu^{2+} in Site I) | |
|-----------------|--|----------|---|----------|
| | $g_{//}$ | $A_{//}$ | $g_{//}$ | $A_{//}$ |
| Cu-SSZ-13 | 2.35 | 150G | 2.29 | 135G |
| Cu-Ce-SSZ-13 | 2.35 | 150G | 2.32 | 139G |
| Cu-Ce-La-SSZ-13 | 2.35 | 150G | 2.30 | 135G |
| Cu-Ce-La/SSZ-13 | 2.32 | 151G | 2.36 | 141G |

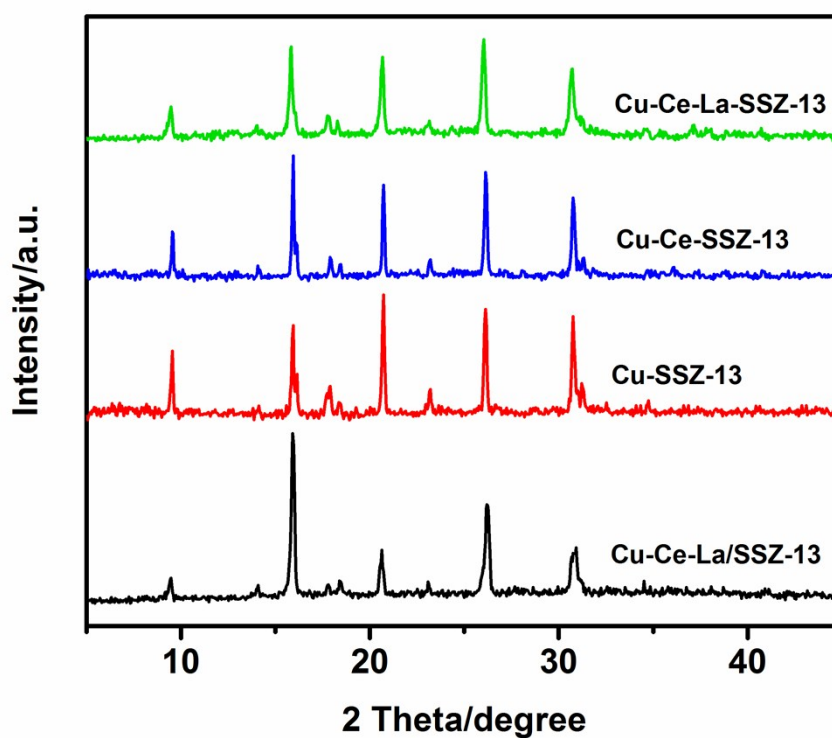


Figure S2. XRD patterns of Cu-Ce-La/SSZ-13, Cu-SSZ-13, Cu-Ce-SSZ-13 and Cu-Ce-La-SSZ-13 catalysts.

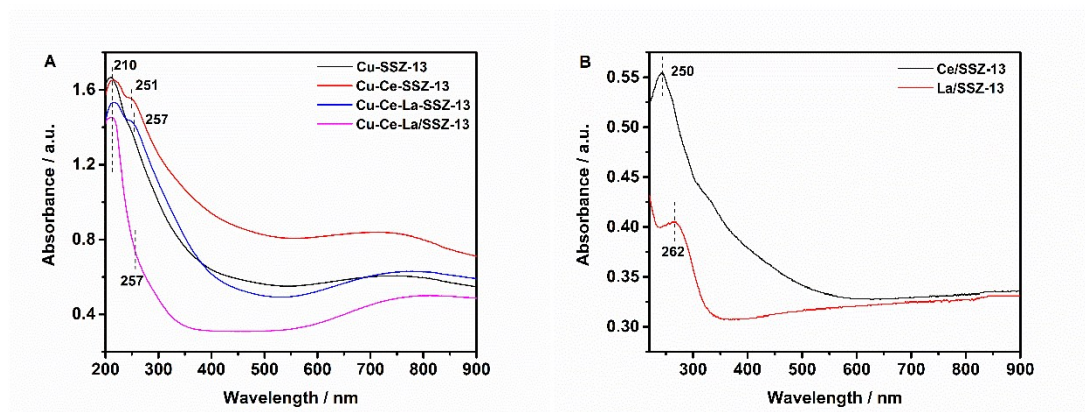


Figure S3. UV-Vis DRS spectroscopy of different catalysts.

UV-Vis DRS was utilized to study the coordination of metal species and the metal-oxygen environment of solid samples. As shown in Fig. S3A, an intense absorption band at near 210 nm and a broad band between 600 nm and 900 nm could be observed over all the samples, which corresponded to the transfer from O^{2-} to isolated Cu^{2+} ions and the d-d transition of the isolated Cu^{2+} ions, respectively [2, 3]. For Cu-Ce-SSZ-13 sample, an additional band centered at 251 nm was detected and was assigned to the charge transfer from O^{2-} to Ce^{3+} ions on the cation sites of SSZ-13, which corresponded to the band centered at 250 nm of Ce/SSZ-13 sample (see Fig. S2B) [4, 5]. For Cu-Ce-La-SSZ-13 sample and Cu-Ce-La/SSZ-13 sample, after the addition of La^{3+} ions, the additional band was a little shifted and centered at 257 nm. This is because the band of the charge transfer from O^{2-} to La^{3+} ions appears at 262 nm (see Fig. S2B) [4], and the addition amounts of Ce^{3+} ions and La^{3+} ions are similar, which caused the band to partially overlap and centered at 257 nm. The results indicate that most metal ions exist on the cation sites of SSZ-13.

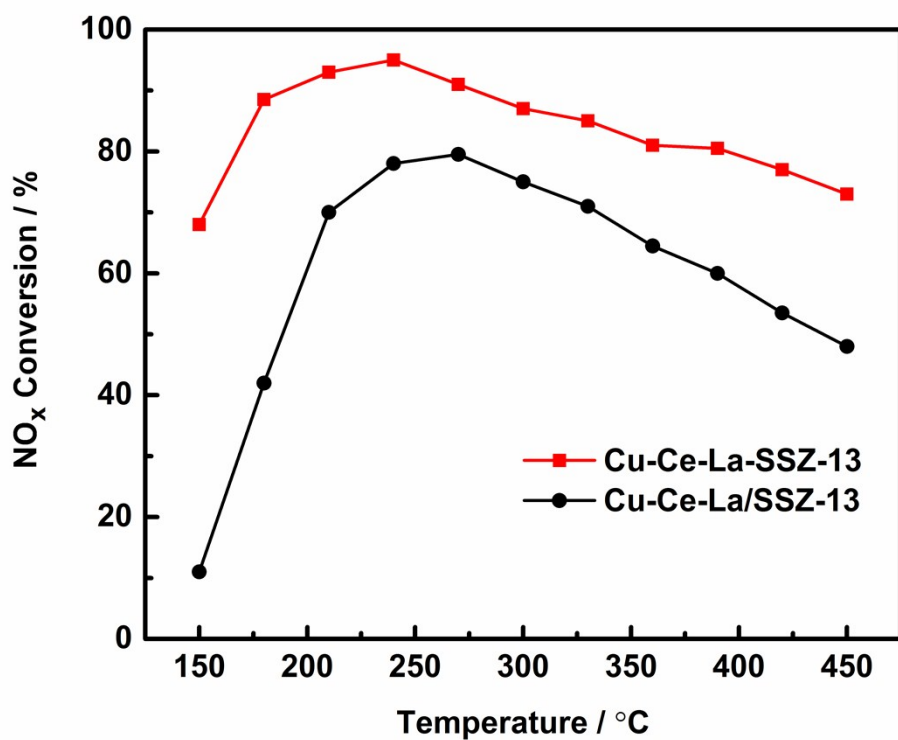


Figure S4. NO_x conversion of Cu-Ce-La/SSZ-13 and Cu-Ce-La-SSZ-13 catalysts after hydrothermal aging (750°C, 12 h) treatment. Reaction Conditions: 500 ppm of NO, 500 ppm of NH₃, 5% of O₂, balance N₂ and GHSV= 150000 h⁻¹.

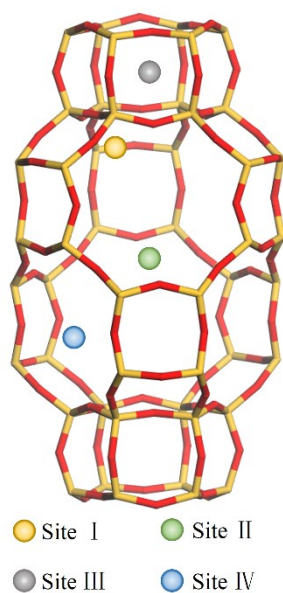


Figure S5. Skeleton structure diagram of the unit cell of SSZ-13 and possible Cu²⁺ locations.

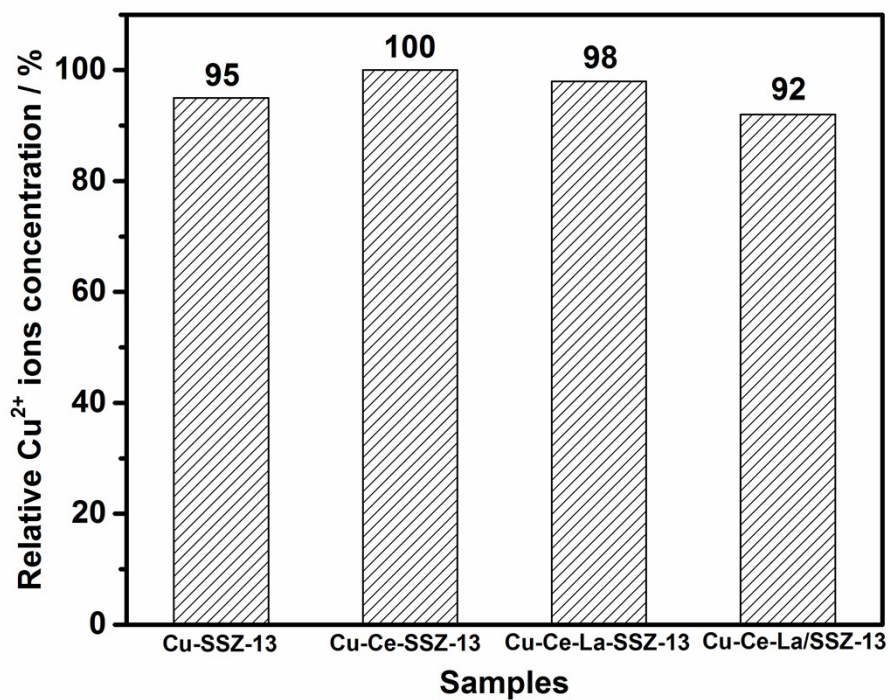


Figure S6. The relative Cu^{2+} ions concentration of dehydrated samples. The Cu^{2+} ions concentration was measured with double integrating the EPR spectra.

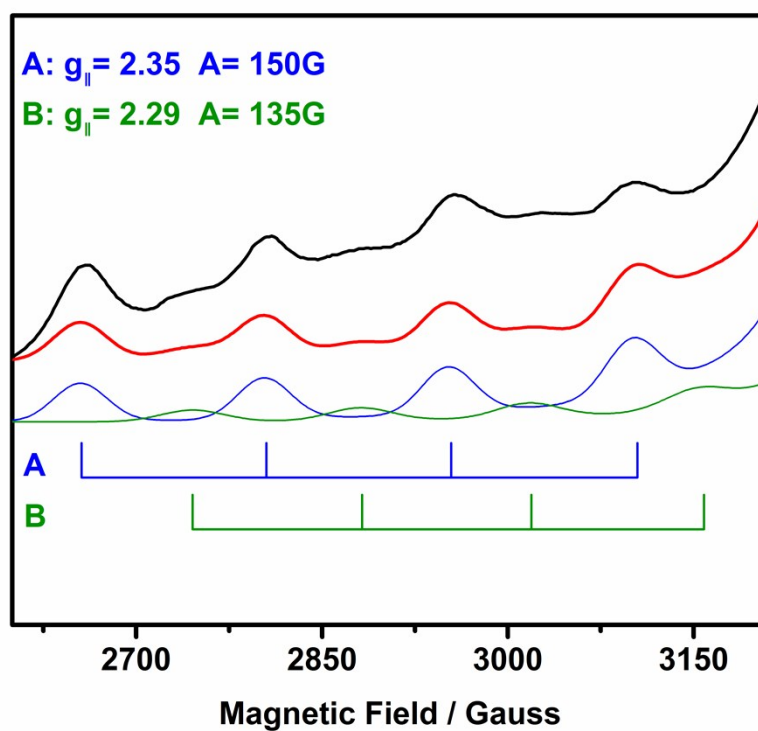


Figure S7. The low-field hyperfine structure signal of the experimental (black) and simulated spectra (red) of dehydrated Cu-SSZ-13 catalyst. The total simulated spectrum is the sum of two different simulated spectra A (blue) and B (green).

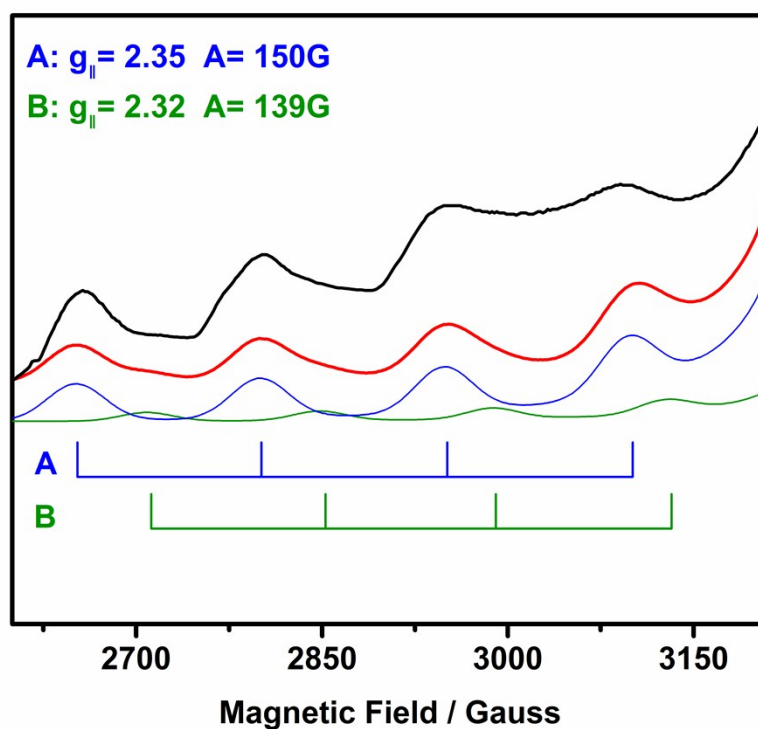


Figure S8. The low-field hyperfine structure signal of the experimental (black) and simulated spectra (red) of dehydrated Cu-Ce-SSZ-13 catalyst. The total simulated spectrum is the sum of two different simulated spectra A (blue) and B (green).

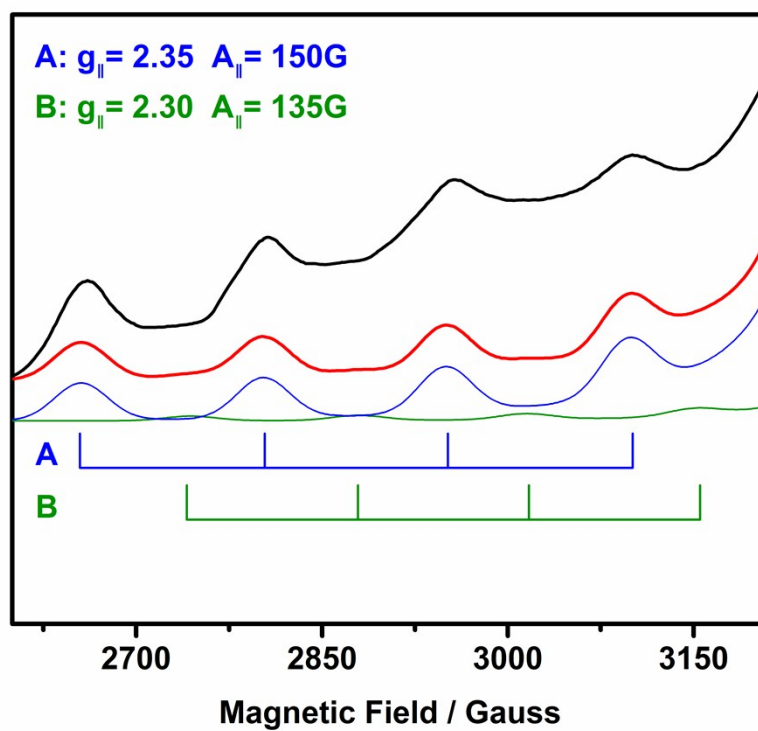


Figure S9. The low-field hyperfine structure signal of the experimental (black) and simulated spectra (red) of dehydrated Cu-Ce-La-SSZ-13 catalyst. The total simulated spectrum is the sum of two different simulated spectra A (blue) and B (green).

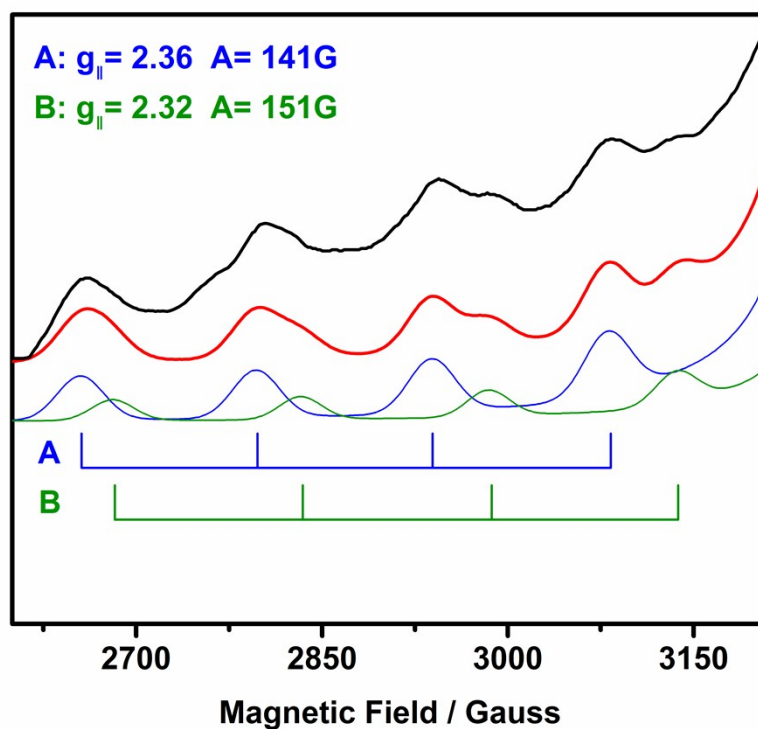


Figure S10. The low-field hyperfine structure signal of the experimental (black) and simulated spectra (red) of dehydrated Cu-Ce-La/SSZ-13 catalyst. The total simulated spectrum is the sum of two different simulated spectra A (blue) and B (green).

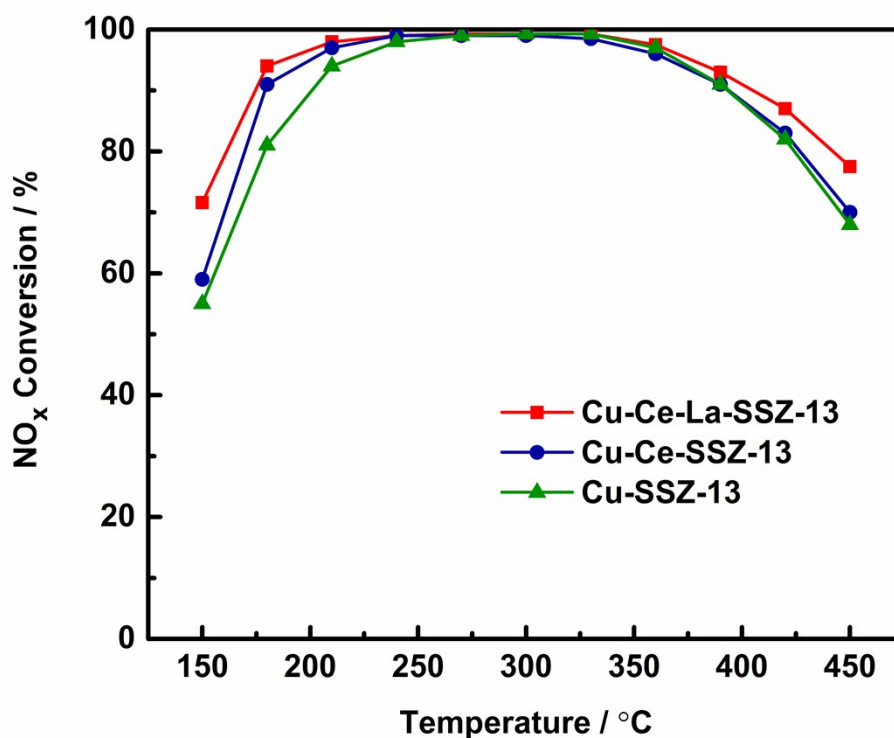


Figure S11. NO_x conversion of Cu-SSZ-13, Cu-Ce-SSZ-13 and Cu-Ce-La-SSZ-13. Reaction Conditions: 500 ppm of NO, 500 ppm of NH₃, 5% of O₂, balance N₂ and GHSV = 150000 h⁻¹.

References

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