Supporting Information

Low-Temperature Solid-State Ion-Exchange Method for Preparing Cu-SSZ-13 Selective Catalytic Reduction Catalyst

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Using Cu(NO₃)₂-im as a starting material, a cycled SCR test was performed and the results are shown in Figure S1, which is similar to that of CuAc₂-im in Figure 1a in the main text. Cu(NO₃)₂-im requires slightly lower activation temperatures compared with CuAc₂-im, as its significant activation starts at 225 °C (in the 2nd run) and completes at 275 °C (after the 4th run). After that, further increasing the treatment temperature does not affect its low-temperature SCR activity.



Figure S1. SCR activities of Cu(NO₃)₂-im in cycled SCR tests (the highest temperature of each run was shown in brackets). Reaction conditions: 500 ppm of NO/500 ppm of NH₃/5% O₂/3% H₂O/N₂, GHSV = 120,000 h⁻¹.

Before calcination, Cu-SSZ-13 prepared by a traditional solution ion-exchange method with *ca.* 2 wt.% Cu loading (Figure S2a) already shows much better low-temperature SCR activity compared with CuAc₂-im without calcination (Figure 1b). A thorough activation of the solution ion-exchanged catalyst can be obtained after 300 °C calcination. It is inferred that most of Cu²⁺ ions have located at the ion-exchange sites of SSZ-13 after the solution ion-exchange process, while the further calcination produces more active Cu²⁺ ions from residual CuAc₂. The residual CuAc₂ after solution ion-exchange is confirmed by a C to Cu ratio of 1.4 (C/Cu = 4 in CuAc₂) determined by elemental analysis. As CuAc₂-im gives an identical C/Cu ratio to neat CuAc₂ (Table 1) and shows poor low-temperature SCR activity before calcination, it is proved that solution ion-exchange can almost be excluded during impregnation, and the catalyst activation can be attributed mainly to the thermal treatment, in other words, low-temperature solid-state ion-exchange (LT-SSIE).

Besides impregnation in a rotary evaporator under vacuum, incipient-wetness impregnation under ambient pressure can also be adopted to load CuAc₂ over SSZ-13 for preparing highly active Cu-SSZ-13 (Figure S2b). The as-impregnated catalyst shows poor activity, but can be fully activated after a 300 °C calcination for 30 min in air.



Figure S2. SCR activities of Cu-SSZ-13 catalysts prepared by (a) a traditional solution ion-exchange method and (b) an incipient-wetness impregnation method using CuAc₂·H₂O as the Cu precursor. Reaction conditions: 500 ppm of NO/500 ppm of NH₃/5% O₂/3% H₂O/N₂, GHSV = 120,000 h⁻¹.

As shown in Figure S3a, $Cu(NO_3)_2$ -im shows poor SCR activity similar to $CuAc_2$ -im, while it is fully activated after 300 °C calcination. $Cu(NO_3)_2$ -im+cal also maintains high SCR activity upon aging in a steam-containing air at 750 °C for 16 h. Surprisingly, $Cu(NO_3)_2$ -mix+cal gives similiar low-temperature activity to $Cu(NO_3)_2$ -im+cal, but its high-temperature activity is quite poor, implying that some CuO species have formed along with the active isolated Cu^{2+} ions. Thus, loading Cu precursors by impregnation is crucial for activating Cu-SSZ-13 at low temperatures.

Using CuSO₄·5H₂O as a Cu precursor (Figure S3b), highly active Cu-SSZ-13 cannot be obtained by 300 °C calcination. CuSO₄-im+cal* was further calcined at 550 °C for 30 min, but still acts poorly in SCR. Again, CuSO₄-mix+cal shows poor SCR activity. The comparison among CuAc₂, Cu(NO₃)₂ and CuSO₄ indicates the necessity of using readily decomposible precursors in our novel method.



Figure S3. SCR activities of Cu-SSZ-13 catalysts using (a) $Cu(NO_3)_2 \cdot 3H_2O$ and (b) CuSO₄·5H₂O as Cu precursors. CuSO₄-im+cal* was calcined at 550 °C for 30 min. Reaction conditions: 500 ppm of NO/500 ppm of NH₃/5% O₂/3% H₂O/N₂, GHSV = 120,000 h⁻¹.

In order to test the feasibility of this method in large scale preparation of monolithic catalysts, Cu-SSZ-13 powders with 2 wt.% Cu loading were prepared as a washcoating material. In conderation of the convenience in industrial process, Cu precursor was loaded by an incipient-wetness impregnation method. Cu(NO₃)₂·3H₂O was chosen as the precursor instead of CuAc₂·H₂O due to the low solubility of the later one. In a typical preparation, 300 g SSZ-13 powders were impregnated with a Cu(NO₃)₂ solution containing 22.7 g Cu(NO₃)₂·3H₂O, followed by calcination in a muffle at 300 °C for 30 min. The obtained catalyst powders were mixed with water and binder, and then washcoated on a cordierite honeycomb with a cell density of 400 cpsi. The catalyst loading was 160 g/L. After that, the monolith was calcined in a muffle at 550 °C for 1 h.

For SCR test, a core sample containing 10×10 channels (with a cross area of 1.27 $\times 1.27 \text{ cm}^2$) with a length of 4 cm was cut from the monolith. The core sample was loaded in a reaction tube with a diamater of 1.27 cm and the space around the core sample was filled by quartz wool. The SCR test was performed in a gas mixture of 350 ppm of NO/350 ppm of NH₃/14% O₂/3% H₂O/5% CO₂/N₂ to simulate the exhuast gas of diesel vehicles. The total flow rate was 5 L/min with a GHSV of 50,000 h⁻¹. The SCR activities were measured between 150 and 500 °C at a temperature ramp rate of 10 °C/min.

The monolithic catalyst shows excellent SCR activity in a wide operation window between 175-500 °C in Figure S4, similar to a monolith loaded by commercial Cu-SSZ-13 powders prepared by a traditional solution ion-exchange method. Therefore, it can be declared that this method is a promising industrial process for preparing monolithic Cu-SSZ-13 catalysts with significantly reduced preparation period, water pollution and energy consumption.



Figure S4. SCR activities of monolithic Cu-SSZ-13 catalysts. Reaction conditions: 350 ppm of NO/350 ppm of NH₃/14% O₂/3% H₂O/5% CO₂/N₂, GHSV = 50,000 h⁻¹,

temperature ramp = 10 °C/min.

During the calcination in air, the XRD patterns of CuAc₂-im and CuAc₂-sie+cal were collected as a function of temperature (Figures S5a and S5b). Both of them show typical diffraction patterns of CHA structure regardless of temperature. The increased intensity of the diffraction peaks at temperatures lower than 250 °C is attributed to the dehydration of the zeolite which leads to increased ordering of the structure.¹

The lattice parameters of the CHA structure during calcination were derived from the refinement of the *in-situ* XRD patterns (Figures S5c and S5d). For both CuAc₂-im and CuAc₂-sie+cal, the parameter *a* decreases gradually with increasing temperature due to the dehrdration of SSZ-13 and the negative thermal expansion coefficient of the zeolite.^{2,3} Enhanced Cu-zeolite interaction also contributes to the decrease in parameter *a*.^{3,4} However, a dramastic increase of the parameter *c* can be observed at temperatures lower than 300 °C over CuAc₂-im, implying the change of Cu species. An increase in parameter *c* also takes place over CuAc₂-sie+cal but finishes at a temperature as low as 225 °C, attributed to the dehydration of Cu²⁺ ions.⁴ After all the Cu²⁺ ions are bonded with the SSZ-13 framework, the parameter *c* decreases for the two catalysts due to the negative thermal expansion with further increasing the temperature.²



Figure S5. *In-situ* XRD patterns of (a) CuAc₂-im and (b) CuAc₂-sie+cal during calcination in air, and the derived variations of lattice parameters a and c for (c) CuAc₂-im and (d) CuAc₂-sie+cal as a function of temperature.

Figure S6 shows more STEM images and EDS mappings of CuAc₂-im and CuAc₂-im+cal, confirming the homogenous Cu distribution over these two catalysts. Besides, CuAc₂-sie+cal was chosen as a reference sample for zeolite-bonded Cu²⁺ ions. The similarity of these mappings indicates that the impregnation method results in Cu species locating inside SSZ-13 channels.



Figure S6. STEM images of (a) CuAc₂-im, (f) CuAc₂-im+cal and (k) CuAc₂-sie+cal with EDS mappings of (b-e) CuAc₂-im, (g-j) CuAc₂-im+cal and (l-o) CuAc₂-sie+cal.

 CO_2 and CO are detected as the main carbon-containing gaseous products of acetate decomposition and oxidation in 21% O_2/N_2 in Figure S7. Other carbon-containing species (*e.g.*, acetic acid, methane, ethane and ethylene) are hardly detected by either FTIR or mass spectrometry (MS). Similar to the findings in TG (Figure 5), the transformation of the impregnated CuAc₂ shifts to higher temperatures compared with the mechanically mixed CuAc₂. After being kept at 300 °C for 30 min, about 85% of the impregnated acetate can be eliminated from CuAc₂-im, and the remaining acetate seems to have little influence on the low-temperature SCR activity (Figure 1b), confirming that 300 °C is a suitable activation temperature.



Figure S7. CO_x curves released from (a,b) CuAc₂-im and (c) CuAc₂-mix during temperature-programmed oxidation in 21% O₂/N₂ at 10 °C/min, where (b) CuAc₂-im experienced an additional isothermal treatment at 300 °C for 30 min.

Cu(NO₃)₂·3H₂O can be completely converted to CuO at 300 °C with a weight loss of 67%, but it shows a complex TG curve including multi-step decomposition and hydrolysis of nitrates in Figure S8a. Cu(NO₃)₂-mix shows a similar weight loss profile to neat Cu(NO₃)₂·3H₂O in the intial stage but the complete decomposition of Cu(NO₃)₂ lasts to slightly higher temperatures. After being impregnated on SSZ-13, the decomposition behavior of Cu(NO₃)₂ changes, probably due to the formation of basic copper nitrates and copper carbonates (as suggested by the release of some CO₂ detected by FTIR, not shown) during impregnation and the interaction between copper nitrates and zeolite framework.

CuSO₄·5H₂O loses its crystal water at temperatures lower than 250 °C, with four water molecules at temperatures below 110 °C (not shown) and the final water molecule at 200-250 °C in Figure S8b. However, neat CuSO₄ is so stable that it cannot decompose to CuO at temperatures lower than 650 °C. Although the decomposition temperatures of CuSO₄ decease to 550-700 °C over SSZ-13, CuSO₄ is still too stable to be adopted as a Cu precursor in the present method.



Figure S8. TG curves of (a) neat Cu(NO₃)₂·3H₂O and Cu(NO₃)₂-loaded catalysts and
(b) neat CuSO₄·5H₂O and CuSO₄-loaded catalysts in 21% O₂/N₂ at 10 °C/min.

CuAc₂·H₂O shows a strong triplet band at 3480, 3384 and 3280 cm⁻¹ (Figure S9a), which can be assigned to the crystal water of CuAc₂·H₂O and disappear after dyhydration at 150 °C. The doublet band at 2988 and 2942 cm⁻¹ is attributed to C-H vibration of acetate.^{5,6} The doublet band at 2470 and 2365 cm⁻¹ arises from the absorption of CO₂ in the atmosphere. Several bands are observed at wavenumbers lower than 2000 cm⁻¹, which are not pronounced over CuAc₂-im (Figure 6) and thereby are not discussed in the main text.

Over CuAc₂-mix (Figure S9b), the main band of C-H vibration occurs at 2930 cm⁻¹, with shoulders at 2990 and 2850 cm⁻¹. The minor band shift compared with CuAc₂-im (Figure 6) indicates the weaker interaction between the mechanically mixed CuAc₂ and the zeolite framework. The weak band at 2180 cm⁻¹ is assigned to Cu⁺-CO with a much lower intensity than that over CuAc₂-im, indicating a low dispersion of Cu loaded by mechanically mixing CuAc₂ with SSZ-13. Other strong bands (*i.e.*, those at 3670, 3283, 2520-2500, 2375 and 2200 cm⁻¹) are attributed to adsorbed water, as confirmed by the spectra of CuAc₂-sie+cal (Figure S9c).



Figure S9. DRIFTS of (a) copper acetate and *in-situ* DRIFTS of (b) CuAc₂-mix and (c) CuAc₂-sie+cal during temperature-programmed treatment at 10 °C/min in 21% O_2/N_2 .

CO (m/z = 28), CO₂ (m/z = 44) and CH₄ (m/z = 16) were detected as the main carbon-containing gaseous products during H₂-TPR of the CuAc₂-impregnated sample, while acetate acid (HAc, m/z = 60) was hardly detected in Figure S9. CH₄ curves were collected in the form of CH₃⁺ fragment (m/z = 15) to avoid the interference of O⁺ fragment (m/z = 16) deriving from H₂O, CO and CO₂. CO curves have different shapes compared with those of CO₂, indicating that CO is one of reduction products from CuAc₂ rather than merely a fragment of CO₂. For the sample pretreated at 110 °C, a CO release peak at 200 °C correlates well with the first reduction stage of CuAc₂-im, while CO, CO₂ and CH₄ are produced in the second stage. After a pretreatment at 250 °C, only the second reduction stage remains in much lower intensity, implying the existence of residual CuAc₂-related species. After 300 °C calcination, most of CuAc₂ has been converted, and only a little amount of carbon-containing species are released at 500-600 °C due to the residual strongly bonded acetates or carbonates.



Figure S10. Carbon-containing gaseous products in H₂-TPR of CuAc₂-im pretreated in 10% O₂/He at (a) 110 °C, (b) 250 °C and (c) 300 °C for 30 min.

Cu-SSZ-13 prepared by the traditional solution ion-exchange method using CuAc₂ as the precursor shows two H₂ consumption peaks at 175 and 510 °C, attributed to the reduction of isolated Cu²⁺ ions to Cu⁺ and Cu⁺ to Cu⁰, respectively (Figure S11a).⁷ Pretreatment temperature has little influence on the H₂-TPR curves of CuAc₂-sie+cal except that the reduction of Cu⁺ seems to be promoted after full dehydration. Cu(NO₃)₂-im+cal shows a similar H₂-TPR curve to that of ion-exchanged Cu-SSZ-13 with predominantly isolated Cu²⁺ ions, correlating with its high SCR activity (Figure S3a), while surface CuO species with different dispersions form over Cu(NO₃)₂-mix+cal, contributing to two sharp reduction peaks at 105 and 140 °C. Again, it is confirmed that Cu(NO₃)₂ is another suitable Cu precursor in the present method, and it is important to load the precursor by impregnation. In contrast, CuSO₄-loaded samples only show a strong peak at around 250 °C with a shoulder at 435 °C assigned to the reduction of dispersed and crystalline CuSO₄,⁸ and no obvious difference between the impregnated and mechanically mixed samples can be observed. Due to the high stability of CuSO₄, zeolite-bonded Cu^{2+} ions cannot be produced over the CuSO₄-loaded samples during 300 °C activation, resulting in very poor SCR activity (Figure S3b). Thus CuSO₄ is excluded as a Cu precursor in the present method.



Figure S11. H₂-TPR curves of (a) CuAc₂-sie+cal and the catalysts using copper (b) nitrate and (c) sulfate as the precursors.

Using CuAc₂-im as a starting material, spectra were collected at 100 °C after treatments at different temperatures for 30 min. In Figure S12, the CuAc2-im dehydrated at 110 °C was set as background instead of the 500 °C treated sample in Figure 9. A band at 940 cm⁻¹ (weakly bonded CuAc₂ in SSZ-13 channels) can be observed when the treatment temperatures are no higher than 250 °C, and it splits into two bands at 950 and 905 cm⁻¹ after treatments at higher temperatures reflecting zeolite-bonded Cu²⁺ ions at different sites, in accordance with Figure 10. The negative band at 870 cm⁻¹ is attributed to T-O-T vibrations of SSZ-13, and its intensity is influenced by the presence of zeolite-adsorbed water and zeolite-bonded Cu²⁺ ions.^{4,9} In Figure 9, the sample treated at 500 °C was used as background to show the evolutions of the bands related to zeolite-bonded Cu²⁺ ions more clearly. In this way, when deducting the spectrum collected after 500 °C treatment from those collected after treatments at lower temperatures (i.e., 150-250 °C), the band at 940 cm⁻¹ becomes invisible and the negative band at 950 cm⁻¹ shifts towards 960 cm⁻¹ due to the subtraction of the 940 cm⁻¹ band. In order to give more information on the Cu species in SSZ-13, in-situ DRIFTS of NH₃ adsorption is shown in Figure 10 as a supplement of Figure 9.



Figure S12. *In-situ* DRIFTS of CuAc₂-im collected at 100 °C after treatments in 21% O_2/N_2 at different temperatures for 30 min. The 110 °C dehydrated CuAc₂-im sample

was used as background.

Differential scanning calorimetry (DSC) curves (Figure S13) demonstrate that the decomposition and oxidation of CuAc₂ are strongly exothermic at 305-310 °C, in accordance with the literature.¹⁰ Some additional features are observed in the DSC curve of neat CuAc₂·H₂O (Figure S13b). The endothermic peak at 160 °C is attributed to the dehydration of CuAc₂·H₂O, which overlaps with the dehydration of SSZ-13 (Figure S13a). Two small endothermic peaks can be observed at 250-300 °C in Figure S13b, implying that the initial stage of CuAc₂ decomposition is endothermic, followed by strongly exothermic oxidation process.



Figure S13. DSC curves of (a) CuAc₂-im and (b) CuAc₂·H₂O in 21% O₂/N₂ at 10

°C/min.

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