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# Phosphorus modification to improve the hydrothermal stability of a Cu-SSZ-13 catalyst for selective reduction of NO<sub>x</sub> with NH<sub>3</sub>

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## Abstract

Phosphorus is introduced to modify the Cu-SSZ-13 catalyst via incipient wetness impregnation, with P/Cu-SSZ-13 = 1 and 2 wt.%, and Si/Al = 4, for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>. N<sub>2</sub> physisorption and XRD results show the incorporation of phosphorus as phosphate acid enhanced the hydrothermal stability of Cu-SSZ-13 significantly, during hydrothermal aging in 10 vol.% H<sub>2</sub>O/air at 750 °C for 16 h. NMR and Raman results suggest that phosphate ions migrate and coordinate with the framework-bonded Al species, forming a framework silicoaluminophosphate interface, thus impeding further dealumination and structure collapse. Before the hydrothermal aging, the isolated Cu<sup>2+</sup> ions partly interact with the phosphate ions, forming Cu-phosphate species and reducing the SCR performance. Nevertheless, the appropriate content of phosphate ions can prevent the structure collapse caused by the hydrothermal aging, remaining the isolated Cu<sup>2+</sup> ions as well as excellent SCR performance.

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**Keywords:** Cu-SSZ-13, NH<sub>3</sub>-SCR, Hydrothermal aging, Phosphorus modification, Emission control

## Introduction

Various catalytic technologies have been developed to eliminate the emission of engines [1-3]. For diesel vehicles, the emission of hydrocarbons and carbon monoxide is controlled by a diesel oxidation catalyst, whereas the particulate matter is removed with a diesel particulate filter (DPF) [4]. Subsequently, nitrogen oxides (NO<sub>x</sub>) can be removed with either a lean NO<sub>x</sub> trap for light-duty vehicles, or a NH<sub>3</sub> selective catalytic reduction (NH<sub>3</sub>-SCR) unit for heavy-duty ones [5, 6]. Typically, the DPF requires regeneration in hot vapor at above 650 °C, inducing hydrothermal condition to the SCR catalysts in the downstream [7-9]. Therefore, a high hydrothermal durability is required for the SCR catalyst to achieve effective NO<sub>x</sub> emission control [9-13].

Cu-chabazite (Cu-CHA) zeolites, including Cu-SSZ-13 and Cu-SAPO-34, have been successfully commercialized as catalysts for NH<sub>3</sub>-SCR reaction, to meet the stringent standards for diesel NO<sub>x</sub> emission in both North America and Europe, marking a significant breakthrough of catalytic technology in recent years [14-16]. Better hydrothermal stability has been shown with the Cu-CHA catalysts, as compared to the other zeolite-based catalysts, *e.g.*, Cu-ZSM-5, Cu-Beta and Cu-Y [17]. One well-accepted explanation is that the unique topology and the small pore size in Cu-CHA zeolites prevent the detached Al(OH)<sub>3</sub> moieties from escaping the CHA cavity [4, 11].

Cu-SSZ-13 has been found inferior to Cu-SAPO-34 in the hydrothermal stability [18, 19]. For the next generation Cu-SSZ-13 catalyst, stronger hydrothermal stability should

be achieved to prolong the lifetime and lower the cost [17, 20-23]. One approach is to maintain the content of two adjacent framework Al sites (Al pairs), such as Al-O-Si-O-Al or Al-O-(Si-O)<sub>2</sub>-Al, stabilizing the isolated Cu<sup>2+</sup> active sites in the six-membered rings (6MR) in the catalyst under hydrothermal conditions [24-28]. High content of the Al pairs requires a low Si/Al ratio, typically below 6 [22, 29, 30]. Nevertheless, the framework of the zeolite can be collapsed more easily with the low Si/Al ratio, caused the hydrothermal condition [31].

Phosphorus is well known for improving the hydrothermal stability of H-ZSM-5 as well as the other zeolites with similar multidimensional 10 MR structures, such as ZSM-11, MCM-22, ITQ-13 and IM-5 [32-36]. Meanwhile, phosphorus in SAPO-34 has been proposed critical to stabilize the CHA type framework in hydrothermal condition [37]. It is therefore interesting to investigate the effect of phosphorous on the hydrothermal stability of the other CHA type catalyst, *i.e.* Cu-SSZ-13.

In this work, phosphorous (P) is incorporated to modify the Cu-SSZ-13 catalyst with Si/Al ratio = 4. The effect of phosphorus on the framework structure, the cupric sites and the SCR performance will be discussed.

## 2. Experimental

### 2.1. Chemicals

Copper(II) sulfate (CuSO<sub>4</sub> > 99 wt.%), sodium aluminate (NaAlO<sub>2</sub> > 98 wt.%) and phosphoric acid (80 wt.%) were purchased from Guangfu (Tianjin). Tetraethylenepentamine (TEPA > 98 wt.%) and sodium hydroxide (NaOH > 98 wt.%) were purchased from Aladdin Industrial Corporation (Shanghai). Ammonium nitrate

( $\text{NH}_4\text{NO}_3 > 99 \text{ wt.}\%$ ) was purchased from Yuanli (Tianjin). Colloidal silica (JN-30,  $\text{SiO}_2 = 30 \text{ wt.}\%$ ) was purchased from Haiyang (Qingdao). All the aqueous solutions were prepared using ultra-pure water purchased from Yongqingyuan (Tianjin).

## 2.2. Catalyst preparation

The Cu-SSZ-13 was synthesized with one-pot hydrothermal synthesis using copper-tetraethylenepentamine (Cu-TEPA) as a structure-directing agent [38]. About 180 mL gel was prepared with a molar ratio of 2.5  $\text{Na}_2\text{O}$ :1  $\text{Al}_2\text{O}_3$ :10  $\text{SiO}_2$ :150  $\text{H}_2\text{O}$ :2 Cu-TEPA and then transferred into a 250 mL autoclave with a Teflon liner and crystallized at 140 °C for 96 h. The solid product was filtrated and washed with water, and then dried at 100 °C overnight. 15 g of the dried powder was immersed in 300 mL  $\text{NH}_4\text{NO}_3$  solution (1 mol/L) at 80 °C and kept for 6 h for ion exchange. The sample was then filtrated, washed and dried at 100 °C, followed by calcination in synthetic air at 600 °C for 6 h. The details of the synthesis for SSZ-13 and preparation of the H-SSZ-13 were shown in Section 1 and 2 in Supporting Information.

The P doped Cu-SSZ-13 catalysts (P/Cu-SSZ-13 = 1 wt.%, 2 wt.% and 5wt.%) were prepared with incipient wetness impregnation. The solution content in the impregnation was determined with the pre-tested water-absorption of the dry sample. Typically, 0.6 mL phosphoric acid solution with different concentrations (0.51, 1.02 and 2.55 mol/L) was dropped onto 1 g of the prepared Cu-SSZ-13, obtaining the catalysts with 1 wt.%, 2 wt.% and 5 wt.% P loading, respectively. The wetted catalyst was first dried at ambient conditions for 12 h, followed by drying at 100 °C overnight. Finally, the sample was calcined in synthetic air at 550 °C for 4 h. The fresh samples were hydrothermally aged in synthetic air flow containing 10%  $\text{H}_2\text{O}$  at 750 °C for 16 h. In order to figure out

the performance of the P doped Cu-SSZ-13 after hydrothermal treatment at low temperatures, Cu-SSZ-13, P<sub>1</sub>Cu and P<sub>2</sub>Cu were hydrothermally treated at 70 °C for 16 h with 30 vol.% moisture. All the catalysts were pelletized, crushed and sieved to 40-60 mesh before testing. Within the context of this article, the sample notations will be used as shown in Table 1.

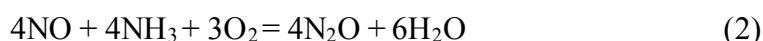
**Table 1.** Sample notations and details of preparation procedure<sup>a</sup>

| Samples             | Preparation procedure   |
|---------------------|---|
| Cu-SSZ-13           | Prepared with one-pot method and then ion-exchanged with NH <sub>4</sub> NO <sub>3</sub> solution       |
| P <sub>1</sub> Cu   | Cu-SSZ-13 impregnated with H <sub>3</sub> PO <sub>4</sub> solution, containing 1 wt.% P in the catalyst |
| P <sub>2</sub> Cu   | Cu-SSZ-13 impregnated with H <sub>3</sub> PO <sub>4</sub> solution, containing 2 wt.% P in the catalyst |
| P <sub>5</sub> Cu   | Cu-SSZ-13 impregnated with H <sub>3</sub> PO <sub>4</sub> solution, containing 5 wt.% P in the catalyst |
| Cu-H                | Cu-SSZ-13 hydrothermal aged in 10% H <sub>2</sub> O/air flow at 750 °C for 16h                          |
| P <sub>1</sub> Cu-H | P <sub>1</sub> Cu hydrothermal aged in 10% H <sub>2</sub> O/air flow at 750 °C for 16h                  |
| P <sub>2</sub> Cu-H | P <sub>2</sub> Cu hydrothermal aged in 10% H <sub>2</sub> O/air flow at 750 °C for 16h                  |

a. Note that the P<sub>1</sub>Cu and P<sub>2</sub>Cu samples are collectively named P<sub>x</sub>Cu. The P<sub>1</sub>Cu-H and P<sub>2</sub>Cu-H samples are denoted as P<sub>x</sub>Cu-H.

### 2.3. Standard NH<sub>3</sub>-SCR test

The activity of the catalysts for NH<sub>3</sub>-SCR was tested in a fixed-bed quartz reactor (10 mm in diameter) in steady flow operation. Possible reactions are shown in Equations 1&2:



Typically, 50 mg of the catalyst (40-60 mesh) was mixed with 950 mg quartz sand and packed in the plug flow reactor, and the temperature was controlled by a type K thermocouple inserted into the center of the catalysts bed. The catalyst was activated in reactant gas (shown in below) flow at 550 °C for 1 h before the SCR performance test. The gas flow was kept at 500 ml/min (50 mg of catalyst corresponds to gas hourly space

velocity = 300, 000 h<sup>-1</sup>) during reaction. The reactant gas contains 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, 5 vol.% H<sub>2</sub>O and N<sub>2</sub> as balance. For each run of testing, the reaction temperature was increased from 150 °C to 550 °C with step of 25 °C or 50 °C. At each step, the concentration of the products (NO, N<sub>2</sub>O and NO<sub>2</sub>) were recorded on FTIR (Thermo Nicolet iS10) with a 2 m gas cell when the reaction reached steady state (the concentration of the products changed less than 1 ppm in ten minutes). The NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) conversion was calculated with equation 3:

$$\text{NO}_x \text{ conversion} = \left(1 - \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}\right) \times 100\% \quad (3)$$

#### 2.4. Characterization

N<sub>2</sub> physisorption at -196 °C was used to determine the specific surface area and pore volume of the catalysts on Quantachrome Autosorb-1, with pre-degassing at 300 °C for 6 h. The specific surface area was calculated using BET equation and the pore volume was estimated using t-plot method.

The contents of the samples were determined via ICP-OES (VISTA-MPX, Varian). Before the ICP measurement, we treated the sample in 20% O<sub>2</sub>/N<sub>2</sub> at 300 °C for 1 h to totally remove the adsorbed water in the zeolite. The crystallization structure was measured via XRD (Rigaku, D/max-γ b-type X-ray) using monochromatic Cu Kα radiation (40 kV and 100 mA), with a scan speed of 2 °/min. 20 mg sample was used of each measurement. The relative crystallinity of the catalysts was estimated based on the method proposed by Yamanaka *et al.* [39], using peak intensities at 2θ = 9.4, 20.5 and 30.4° and the as-prepared Cu-SSZ-13 as a reference, with equation 4:

$$\text{Relative crystallinity (\%)} = \left( \frac{\text{the sum of the intensities of the peaks at } 2\theta=9.4, 20.5 \text{ and } 30.4 \text{ after treatment}}{\text{the sum of the intensities of the peaks at } 2\theta=9.4, 20.5 \text{ and } 30.4 \text{ before treatment}} \right) \times 100\% \quad (4)$$

<sup>27</sup>Al and <sup>31</sup>P solid-state MAS NMR were conducted on Varian Infinity plus 300 WB

spectrometer utilizing a 4 mm triple resonance probe operating with the resonance frequencies of 78.13 MHz and 121.37 MHz, respectively. Spectra of  $^{27}\text{Al}$  were acquired by using calibrated  $^{27}\text{Al}$   $\pi/20$  pulses of 0.5  $\mu\text{s}$ , a 40 kHz spectral window, a spinning speed of 8 kHz, and a 3 s pulse delay.  $^{31}\text{P}$  MAS NMR was conducted with a 40 kHz spectral window, a spinning speed of 9 kHz, and a 15 s pulse delay.  $\text{Al}(\text{NO}_3)_3$  aqueous solution (1 mol/L) was used for  $^{27}\text{Al}$  MAS NMR spectroscopy, and  $\text{H}_3\text{PO}_4$  aqueous solution (75 wt.%) was used for  $^{31}\text{P}$  MAS NMR spectroscopy, respectively, as references. Note that the NMR test condition and the sample amount are the same for all the samples. Hence, the NMR resonance intensity can be compared in each sample. The quantitative spectral analysis of the  $^{27}\text{Al}$  MAS NMR results was performed by fitting the spectra with mixed Gaussian/Lorentzian line shapes using the Peakfit software. All samples allow the fitting parameters in the deconvolution to be optimized.

The Raman spectra were acquired with a Thermo Fisher Scientific DXR spectroscope with an excitation wavelength of 532 nm.

EPR spectra in the X-band were recorded with a CW spectrometer JES-FA200 with a microwave power of 1 mW modulation frequency of 100 kHz. The EPR signals of isolated  $\text{Cu}^{2+}$  ions were recorded at -150  $^\circ\text{C}$  with the magnetic field being swept from 2000 to 4000 G with a sweep time of 5 min.

The  $\text{H}_2$ -TPR measurements were performed with an AutoChem 2920 apparatus with a TCD detector. 50 mg sample was heated to 550  $^\circ\text{C}$  in the 5%  $\text{O}_2/\text{N}_2$  for 1 h before the  $\text{H}_2$ -TPR test. After cooling down to room temperature, the sample was exposed to a flow of 5%  $\text{H}_2/\text{N}_2$ , and the temperature was increased at a rate of 10  $^\circ\text{C}/\text{min}$  until 800  $^\circ\text{C}$ . The different cupric species were assessed by deconvolution of the  $\text{H}_2$ -TPR curves



with Gaussian peak shapes, using the variable line shape for each respective peak across all samples and allowing the fitting parameters in the deconvolution software to be optimized.

### 3. Results

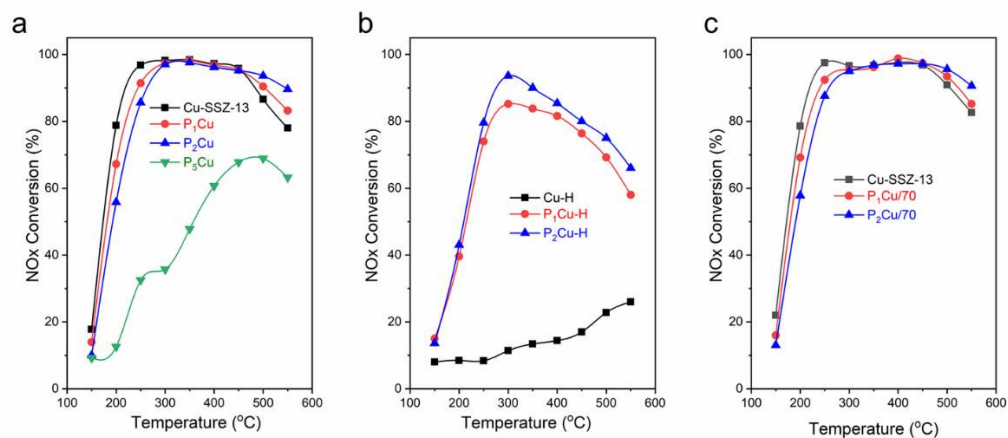
#### 3.1. Effect of phosphorus on the SCR performance

The activity of the as-prepared and doped Cu-SSZ-13 was compared in Fig. 1a. The NO<sub>x</sub> conversion was around 20% with the as-prepared Cu-SSZ-13 at 150 °C, and increased rapidly to 78% at 200 °C. The conversion remained above 90% from 250 to 450 °C, then decreased with the further increase of the temperature, to approximately 77% NO<sub>x</sub> conversion at 550 °C. The P loading caused decrease of the activity at low temperatures, with the NO<sub>x</sub> conversion of only 67% and 56% at 200 °C for the P<sub>1</sub>Cu and P<sub>2</sub>Cu samples, respectively. Nevertheless, the P doped catalysts (P<sub>1</sub>Cu and P<sub>2</sub>Cu) remained high activity at high temperatures, maintaining over 85% conversion even at 550 °C. The high P loading (5 wt.%) decreases the deNO<sub>x</sub> activities significantly in 150-550 °C, with only around 50% NO<sub>x</sub> conversion at 350 °C. This indicates that the high loading of P deactivated the Cu-SSZ-13 seriously, consistent with the previous works [40, 41].

The activities of the aged catalysts are plotted in Fig. 1b to compare the hydrothermal stability. The Cu-SSZ-13 catalyst without P doping showed less than 10% conversion at 150 °C, and reached only 20% conversion for the maximum from 150 °C to 550 °C. In contrast, P-doped aged catalysts (P<sub>1</sub>Cu-H and P<sub>2</sub>Cu-H) exhibited similar deNO<sub>x</sub> activity below 250 °C with a NO<sub>x</sub> conversion of around 40% at 200 °C, and maintained above 75% conversion in 250-500 °C. The doped catalyst with a higher P amount

(P<sub>2</sub>Cu-H) still got around 70% conversion at 550 °C, whereas only around 55% NO<sub>x</sub> conversion remained in the P<sub>1</sub>Cu-H. Apparently, the activity of the hydrothermally aged samples increased with the amount of P loading for the P<sub>1</sub>Cu and P<sub>2</sub>Cu samples.

A low temperature hydrothermal treatment (70 °C for 16 h with 30% H<sub>2</sub>O in air) has little effect on the SCR performance of the Cu-SSZ-13 and P doped samples, as derived from the comparing of Fig. 1a and 1c.



**Fig. 1.** NO<sub>x</sub> conversion during standard NH<sub>3</sub>-SCR as a function of the temperature (150-550 °C) of the (a) fresh (b) Cu-SSZ-13 and P<sub>x</sub>Cu catalyst samples hydrothermally treated at 750 °C for 16 h and (c) Cu-SSZ-13 and P<sub>x</sub>Cu catalyst samples hydrothermally treated at 70 °C for 16 h. Reaction conditions: 500 ppm NO, 500 ppm NH<sub>3</sub>, 5% O<sub>2</sub>, 5% H<sub>2</sub>O, balanced with N<sub>2</sub>; flow rate: 500 mL/min, GHSV: 300, 000 h<sup>-1</sup>.

### 3.2. Effects of phosphorus on Cu-SSZ-13 structure

#### 3.2.1. Textural properties and X-ray diffraction

The chemical composition and Si/Al ratios are almost identical in all the samples before and after the hydrothermal aging, according to the ICP results listed in Table 2.

**Table 2.** Al, Cu and Si contents and the relative crystallinity of the fresh and aged samples.

| Sample              | Cu content <sup>a</sup><br>(wt.%) | Al content <sup>a</sup><br>(wt.%) | Si content <sup>a</sup><br>(wt.%) | Si/Al ratio <sup>b</sup> | Crystalline size <sup>c</sup><br>(nm) | Relative crystallinity <sup>d</sup><br>100% |
|---------------------|-----------------------------------|-----------------------------------|-----------------------------------|--------------------------|---------------------------------------|---|
| Cu-SSZ-13           | 4.92                              | 9.97                              | 43.5                              | 4.36                     | 396                                   | 100   |
| P <sub>1</sub> Cu   | 4.91                              | 10.2                              | 43.5                              | 4.25                     | 389                                   | 92  |
| P <sub>2</sub> Cu   | 4.92                              | 10.4                              | 42.9                              | 4.14                     | 392                                   | 84  |
| Cu-H                | 4.89                              | 9.80                              | 42.8                              | 4.20                     | \                                     | 0   |
| P <sub>1</sub> Cu-H | 4.95                              | 9.90                              | 43.2                              | 4.20                     | \                                     | 52  |
| P <sub>2</sub> Cu-H | 4.93                              | 9.90                              | 43.3                              | 4.19                     | \                                     | 68  |

a, Determined with the ICP.

b, The mole ratio of the Si/Al determined with the ICP results.

c, The crystalline size was obtained with the XRD data using the Scherrer Equation.

d. Assuming crystallinity of the Cu-SSZ-13 sample to be 100% and the relative crystallinity of the other samples after acid or hydrothermal aging treatment calculated with the following equation:

$$\text{Relative crystallinity (\%)} = \left( \frac{\text{sum of the intensities of the peaks at } 2\theta=9.4, 20.5 \text{ and } 30.4 \text{ after treatment}}{\text{sum of the intensities of the peaks at } 2\theta=9.4, 20.5 \text{ and } 30.4 \text{ before treatment}} \right) \times 100\%$$

The data in Table 3 show a slight decrease of the surface area and the pore volume with phosphorus incorporation (P<sub>1</sub>Cu and P<sub>2</sub>Cu) as compared to the as-prepared Cu-SSZ-13.

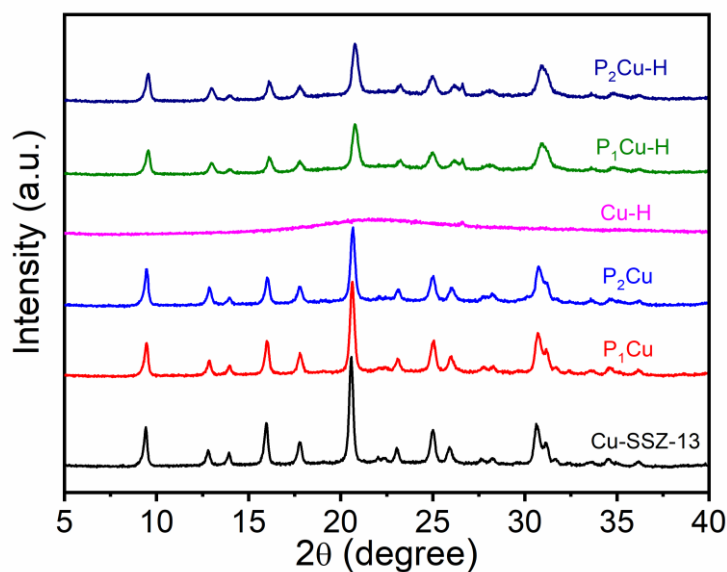
The Cu-H sample without phosphorus lost almost all the pore volume and surface area after the hydrothermal aging. In contrast, the P<sub>1</sub>Cu-H and P<sub>2</sub>Cu-H samples with phosphorus remained around 70% of the surface area as well as around 80% of the pore volume after the hydrothermal aging, as compared to their fresh counterparts.

**Table 3.** Surface areas and pore volumes acid amounts of Cu-SSZ-13 and P<sub>x</sub>Cu catalysts before and after hydrothermal aging

| Sample              | Micropore surface area <sup>a</sup><br>(m <sup>2</sup> /g) | External surface area <sup>a</sup><br>(m <sup>2</sup> /g) | Surface Area <sup>a</sup><br>(m <sup>2</sup> /g) | Pore volume <sup>b</sup><br>(cm <sup>3</sup> /g) |
|---------------------|--|---|--|--|
| Cu-SSZ-13           | 400  | 5   | 405  | 0.20   |
| P <sub>1</sub> Cu   | 382  | 2   | 383  | 0.19   |
| P <sub>2</sub> Cu   | 351  | 2   | 353  | 0.17   |
| Cu-H                | 4  | 4   | 8  | 0.00   |
| P <sub>1</sub> Cu-H | 259  | 9   | 265  | 0.14   |
| P <sub>2</sub> Cu-H | 270  | 6   | 276  | 0.15   |

a. Calculated using BET equation.

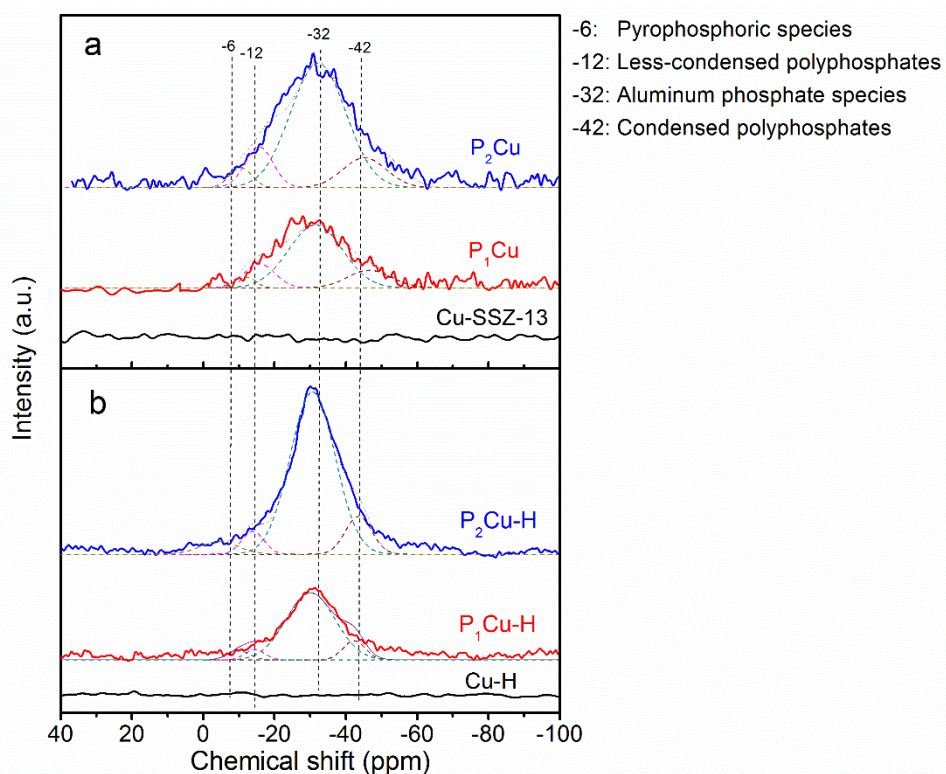
b. Determined using the t-plot method.



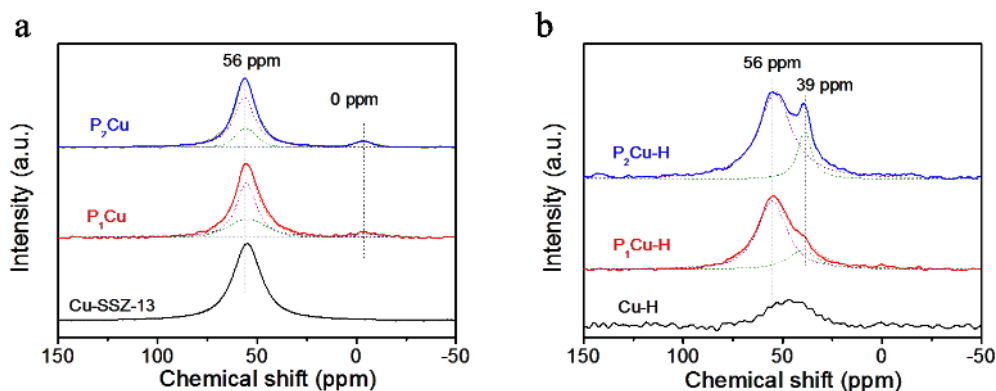
**Fig. 2.** XRD patterns of the fresh and aged catalysts

As shown in Fig. 2, XRD results show that the Cu-SSZ-13 and P doped samples show a typical CHA structure, and no new crystalline phase was detected. The crystalline size of the Cu-SSZ-13, P<sub>1</sub>Cu and P<sub>2</sub>Cu are 396 nm, 389 nm, and 392 nm, respectively, obtained with the XRD data using the Scherrer Equation, shown in Table 2. This is consistent with the SEM results, which shows the samples have a similar mean

crystallite size of around 400 nm, shown in Fig. S4. The XRD intensities slightly decreased with the incorporation of phosphorus on the catalysts  $P_1Cu$  and  $P_2Cu$ , as compared to the as-prepared Cu-SSZ-13. Data in Table 2 show the relative crystallinity decreased with the increase of the phosphorus content. This reveals minor destruction of the crystalline structure caused by the phosphorus incorporation.



**Fig. 3.** Solid state  $^{31}P$  MAS NMR spectra of the (a) fresh and (b) aged Cu-SSZ-13 and  $P_xCu$  samples. The original  $^{31}P$  MAS NMR profiles are represented with the solid lines. The fitted peaks are represented as dash lines and highlighted with different colours (wine, dark cyan, magenta and dark yellow) for comparison. The purple dash lines represent the sum of fitted peaks. The assignment of the resonance peaks is presented in the right part of the figure.



**Fig. 4.** Solid state  $^{27}\text{Al}$  MAS NMR spectra of the (a) fresh and (b) aged Cu-SSZ-13 and  $\text{P}_x\text{Cu}$  samples. The solid lines represent the original  $^{27}\text{Al}$  MAS NMR profiles. The fitted peak at 0 ppm highlighted with green dash line, and the green dash line represents the fitted peak at 39 ppm. The navy and olive dash lines stand for the fitted peak at 56 ppm. The sum of all fitted peak is shown as a gray dash line.

All the signature peaks of Cu-SSZ-13 disappeared after the hydrothermal aging (Cu-H), as shown in Fig. 2, indicating the complete collapse of the crystalline structure. Nevertheless, the typical CHA structure was still retained with the phosphorus incorporation after the hydrothermal aging, and 52% and 68% of the relative crystallinity remained for the  $\text{P}_1\text{Cu-H}$  and  $\text{P}_2\text{Cu-H}$ , respectively, as shown by the data in Table 2.

### 3.2.2. $^{31}\text{P}$ MAS NMR

In Fig. 3a, no phosphorous species were found in the as-prepared Cu-SSZ-13 according to the  $^{31}\text{P}$  MAS NMR spectra, whereas a broad resonance peak was observed from 0 to -60 ppm with the phosphorus loaded catalysts. The resonance peak can be deconvoluted into four at around -6 ppm, -12 ppm, -32 ppm and -46 ppm, respectively. The assignments for the peaks around -6 ppm, -12 ppm and -46 ppm have been studied intensively, which are the phosphorus atoms in pyrophosphoric species [41, 42], phosphorous in less-condensed polyphosphates such as polyphosphates or certain specially polymerized short-chain polyphosphates [43], and phosphorous in branching

groups in condensed polyphosphates such as  $P_4O_{10}$  [41, 43], respectively.

The assignment of the dominant broad peak centered at -32 ppm is relatively difficult. Similar resonance has been reported with phosphorus modified ZSM-5, and assigned to either phosphate species bonded with extra-framework aluminum or phosphate species connected with the framework aluminum [36, 42, 44]. Here, it is plausible to give a similar assignment for the broad resonance with the Cu-SSZ-13 samples, to phosphate species bonded with Al either in the framework or in the extra-framework. This will be further discussed in Section 4.2.

**Table 4.** Relative phosphate distribution observed with  $^{31}P$  MAS NMR for fresh and aged Cu-SSZ-13 and  $P_xCu$  samples

| Sample    | P atoms (%) <sup>a</sup>            |                               |  |                                  | Changed ratio                      |
|-----------|-------------------------------------|-------------------------------|--|----------------------------------|------------------------------------|
|           | -42 ppm<br>Condensed polyphosphates | -32 ppm<br>Aluminum phosphate | -12 ppm<br>Less-condensed polyphosphates | -6 ppm<br>Pyrophosphoric species |                                    |
| Cu-SSZ-13 | ND <sup>b</sup>                     | ND                            | ND                                       | ND                               |                                    |
| $P_1Cu$   | 14.1                                | 66.5                          | 13.6                                     | 5.8                              |                                    |
| $P_2Cu$   | 13.9                                | 67.3                          | 11.9                                     | 6.9                              |                                    |
| Cu-H      | ND                                  | ND                            | ND                                       | ND                               |                                    |
| $P_1Cu-H$ | 14.1                                | 75.5                          | 5.2                                      | 5.1                              | 9.1 <sup>c</sup> /9.0 <sup>d</sup> |
| $P_2Cu-H$ | 13.6                                | 76.1                          | 5.4                                      | 4.9                              | 8.5/8.8                            |

- The distribution of different phosphorous species based on the deconvolution of the  $^{31}P$  MAS NMR results.
- ND denotes not detected.
- The decreased ratio of the less-condensed polyphosphates and pyrophosphoric species after hydrothermal treatment.
- The increased ratio of the aluminum phosphate species after hydrothermal treatment.

As shown in Fig. 3b and Table 4, the shape of the  $^{31}P$  MAS NMR spectra narrowed with the hydrothermal aging on the  $P_xCu-H$  samples, caused by the decrease of the low-field signals (-6 and -12 ppm) and the increase of the broad signal centered at around -32 ppm. Note that the increased ratio of the phosphate species showing resonances at -32 ppm is equivalent to the decline of pyrophosphoric species (-6 ppm) and less-

condensed polyphosphates (-12 ppm) as shown in Table 4, suggesting the transformation between the different phosphate species during hydrothermal aging.

### 3.2.3. $^{27}\text{Al}$ MAS NMR

$^{27}\text{Al}$  MAS NMR is sensitive to the coordination of Al atoms in zeolites. As shown in Fig. 4a, the  $^{27}\text{Al}$  MAS NMR spectra of Cu-SSZ-13 and  $\text{P}_x\text{Cu}$  samples show a strong peak at around 56 ppm, assigned to the tetrahedral framework Al (TFAl) species in the zeolite framework [4, 9]. Meanwhile, a new peak at around 0 ppm appeared with the phosphorus loading on Cu-SSZ-13, assigned to the octahedral extra-framework Al (EFAl) in the phosphorus modified samples [22]. The relative contribution of the respective Al species is shown in Table 5. Around 94% and 86% TFAl remained in the  $\text{P}_1\text{Cu}$  and  $\text{P}_2\text{Cu}$ , respectively, using the integrated peak area at around 56 ppm in the as-prepared Cu-SSZ-13 as a reference, shown in Table 5 [4, 24]. Nevertheless, only around 3% of Al converted to EFAl in both the phosphorus-modified samples, indicating a part of Al was undetectable with the  $^{27}\text{Al}$  MAS NMR.

**Table 5.** Relative Al contribution of the TFAl, EFAl, distorted TFAl and undetected Al species observed with  $^{27}\text{Al}$  MAS NMR for catalyst samples

| Sample                  | Al distribution (100%)        |                              |   |                            |
|-------------------------|-------------------------------|------------------------------|---|----------------------------|
|                         | TFAl <sup>a</sup><br>(56 ppm) | EFAl <sup>a</sup><br>(0 ppm) | Distorted TFAl <sup>a</sup><br>(39 ppm) | Undetected Al <sup>b</sup> |
| Cu-SSZ-13               | 100                           | 0                            | 0                                       | 0                          |
| $\text{P}_1\text{Cu}$   | 94                            | 1                            | 0                                       | 5                          |
| $\text{P}_2\text{Cu}$   | 86                            | 3                            | 0                                       | 11                         |
| $\text{P}_1\text{Cu-H}$ | 48                            | 0                            | 10                                      | 42                         |
| $\text{P}_2\text{Cu-H}$ | 57                            | 0                            | 17                                      | 26                         |

a. Assuming the  $^{27}\text{Al}$  MAS NMR resonance peak area in the Cu-SSZ-13 sample to be 100% and the relative contributions of the respective Al species in the samples according to the deconvolution result of NMR spectra.

b. The percentage of the Al species undetected with the  $^{27}\text{Al}$  MAS NMR measurement, calculated with the one hundred percentage subtract the contribution of the TFAl, EFAl and distorted TFAl.



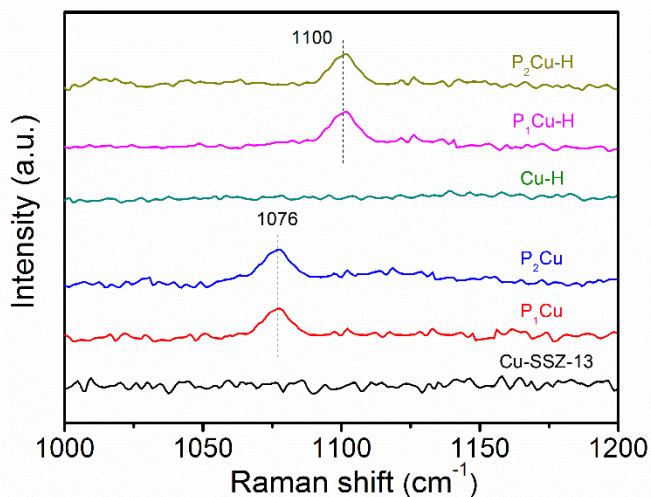
A significant change was observed in the  $^{27}\text{Al}$  MAS NMR spectra after the hydrothermal treatment, as shown in Fig. 4b. The intensity of the TFAl peak centered at 56 ppm almost vanished over the sample Cu-H. Meanwhile, the decrease of the TFAl signal intensity with the P-loaded sample indicates significant degradation after the hydrothermal treatment, whereas about 48% and 57% of the TFAl species still remained in the  $\text{P}_1\text{Cu-H}$  and  $\text{P}_2\text{Cu-H}$  samples, respectively (Table 5).

Interestingly, a new peak at 39 ppm exclusively appeared after the hydrothermal aging with the phosphorus-doped catalysts. According to previous works [24, 45], the peak at 30 ppm was clearly assigned to the penta-coordinated Al for Al in SSZ zeolite. As is known, the chemical shift of  $^{27}\text{Al}$  nuclear moves to a lower position with the increasing number of ligands, which was caused by the increased shielding effect [46, 47]. Therefore, pentahedral framework Al with more ligands than the distorted tetrahedral framework Al should show a lower chemical shift. Along this line, the signal of 39 ppm is likely ascribed to the distorted TFAl, consistent with previous works of P modified Y and ZSM-5 [36, 43, 48, 49].

#### 3.2.4. Raman

Raman spectra were used to verify the structural changes of the phosphate and aluminate entities in the samples, as shown in Fig. 5. The Raman band at around  $1076\text{ cm}^{-1}$  with the  $\text{PxCu}$  samples was observed in the P doped samples. This may be ascribed to  $\text{P(OH)}_3$  or the stretching vibrations of P-O-Al bonds in amorphous aluminophosphate species [50, 51]. The  $^{31}\text{P}$  MAS NMR measurement in Fig. 3 rules out the existence of the  $\text{P(OH)}_3$  in the P doped samples. Therefore, the band at  $1076\text{ cm}^{-1}$  indicates the

amorphous aluminophosphate exist in the fresh P doped samples. After hydrothermal treatment, the band at around  $1076\text{ cm}^{-1}$  with the  $P_x\text{Cu}$  samples upshifted to  $1100\text{ cm}^{-1}$ , as shown in Fig. 5. This can be explained by the emergence of the phosphorus-oxygen tetrahedron coordinated with the lattice  $\text{Al}^{3+}$  in the tetrahedral sites in the phosphorus loaded samples during the hydrothermal treatment [52, 53].

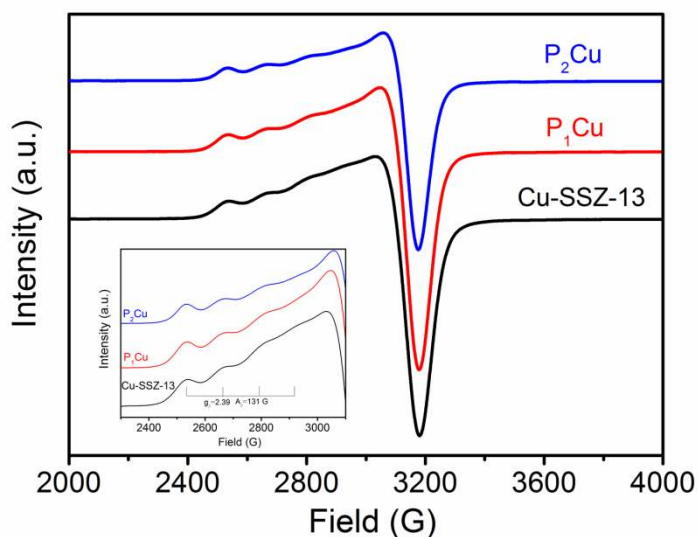


**Fig. 5.** The Raman shift at around  $1100\text{ cm}^{-1}$  of the fresh and aged catalysts.

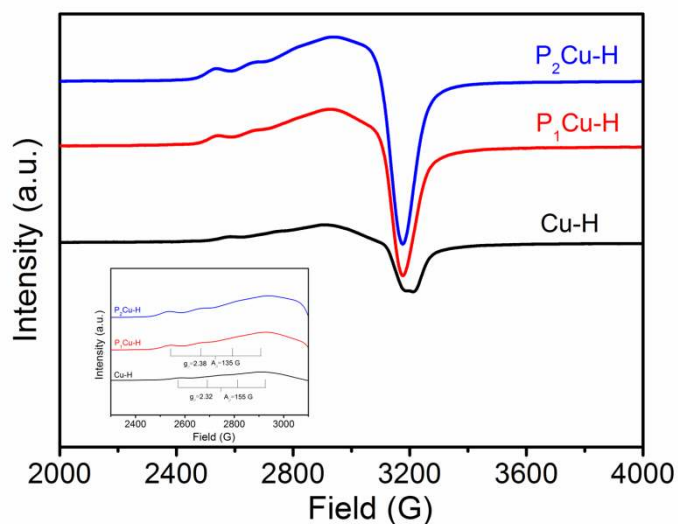
### 3.3. Effect of phosphorus on the cupric species

#### 3.3.1. EPR

Fig. 6 and 7 present EPR results of the fresh and the aged samples, respectively. The hyperfine structures of the EPR spectra were resolved and enlarged in the inset for the fresh and the aged samples.  $g_{//} = 2.39$  and  $A_{//} = 131\text{ G}$  were observed with all the fresh samples as well as the  $P_x\text{Cu-H}$  samples, ascribed to the octahedral coordination of isolated  $\text{Cu}^{2+}$  ions [54, 55]. Meanwhile,  $g_{//} = 2.32$  and  $A_{//} = 155\text{ G}$  was observed in the sample Cu-H, corresponding to the  $\text{Cu}^{2+}$  ions on  $\text{Al}_2\text{O}_3$  [23]. This indicates the change of the  $\text{Cu}^{2+}$  coordination in the undoped sample in the hydrothermal aging treatment.



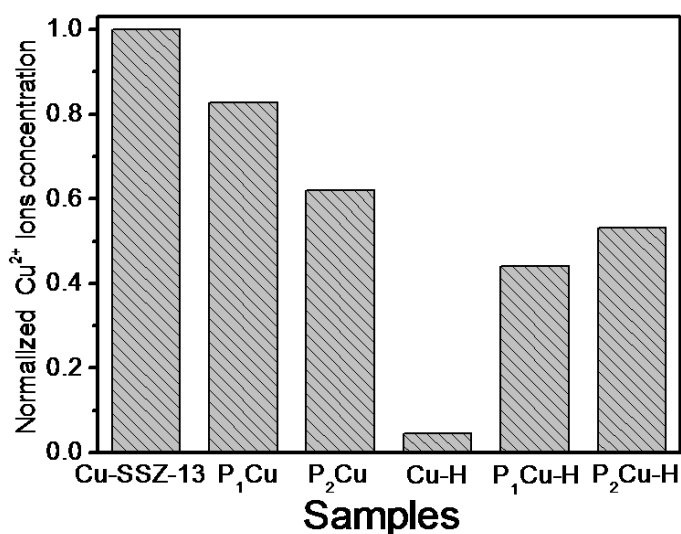
**Fig. 6.** Electron Paramagnetic Resonance (EPR) spectra of the fresh catalyst samples. The insert displays hyperfine features of the EPR spectra for the samples. Spectra were collected at  $-150\text{ }^{\circ}\text{C}$ .  $g// = 2.39$  and  $A// = 131\text{ G}$  was ascribed to the octahedral coordination of isolated  $\text{Cu}^{2+}$  ions [54]



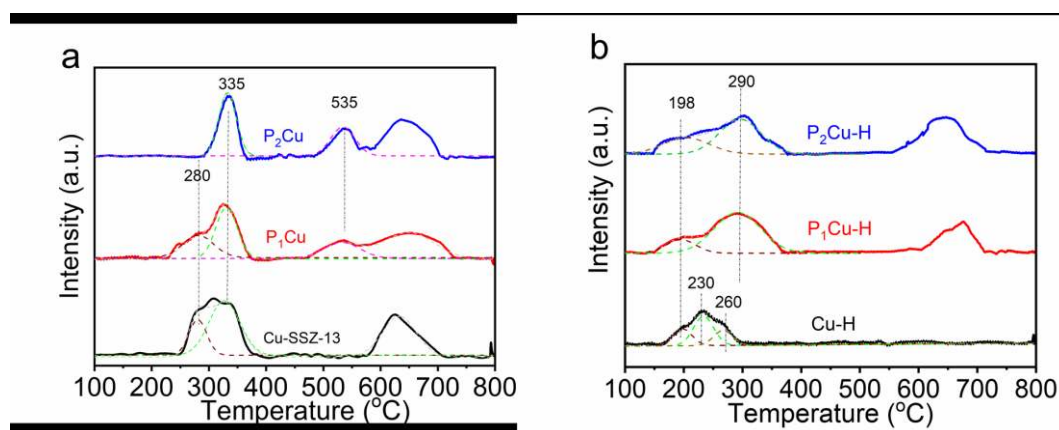
**Fig. 7.** Electron Paramagnetic Resonance (EPR) spectra of the aged catalyst samples. The insert displays hyperfine features of the EPR spectra for the samples. Spectra were collected at  $-150\text{ }^{\circ}\text{C}$ .  $g// = 2.39$  and  $A// = 131\text{ G}$  was ascribed to the octahedral coordination of isolated  $\text{Cu}^{2+}$  ions [30, 43], and  $g// = 2.32$  and  $A// = 155\text{ G}$  can be attributed to the  $\text{Cu}^{2+}$  ions on  $\text{Al}_2\text{O}_3$  [23].

The relative amount of  $\text{Cu}^{2+}$  ions in the samples were normalized using the isolated  $\text{Cu}^{2+}$  ions content in Cu-SSZ-13 as a reference, as shown in Fig. 8. The amount of isolated  $\text{Cu}^{2+}$  ions decreased by around 18% in  $\text{P}_1\text{Cu}$  sample and by around 35% for  $\text{P}_2\text{Cu}$  sample, respectively, as compared to the Cu-SSZ-13 without P. After

hydrothermal treatment, almost all the isolated  $\text{Cu}^{2+}$  ions vanished in the Cu-H sample. Nevertheless, about 45% and 53% of isolated  $\text{Cu}^{2+}$  ions still remained in the  $\text{P}_1\text{Cu-H}$  and the  $\text{P}_2\text{Cu-H}$  samples, respectively, as compared to the Cu-SSZ-13.



**Fig. 8.** The normalized  $\text{Cu}^{2+}$  ions concentration determined with double integrating the EPR spectra using the Cu-SSZ-13 as a reference.



**Fig. 9.**  $\text{H}_2$ -TPR spectra of (a) fresh and (b) aged samples. The fitted peak at 280 °C highlighted with purple dash line, and the green line represents the fitted peak at 335 °C. For the aged samples, the fitted peaks with tops at 200 °C, 250 °C, 535 °C and 290 °C are highlighted (orange, pink, wine and olive) for comparison. The violet dash line stands for the fitted peak above 600 °C. The sum of all fitted peak is shown as a gray dash line.

### 3.3.2. $\text{H}_2$ -TPR

Fig. 9 shows the  $\text{H}_2$ -TPR plots with the fresh and the hydrothermally aged samples.

Two peaks were recorded with the Cu-SSZ-13 in Fig. 8a, caused by  $\text{H}_2$  consumption of

Cu<sup>2+</sup> reduced to Cu<sup>+</sup> below 450 °C, and Cu<sup>+</sup> reduced to Cu<sup>0</sup> above 600 °C, respectively, as shown in Equation (5) and (6) [3, 9, 51, 54, 56].



Note that more reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> than the Cu<sup>+</sup> to Cu<sup>0</sup> was observed in the fresh samples, which can be ascribed to the reduction of a part of Cu<sup>+</sup> ions occurs at the temperature higher than 800 °C. This is consistent with the previous work by Xie *et al.* [9], in which the Cu-SSZ-13 synthesized with the one-pot method shows a H<sub>2</sub>-reduction peak of Cu<sup>+</sup> at around 900 °C.

The peak from 250 to 400 °C with the Cu-SSZ-13 sample was deconvoluted into two peaks around 280 °C and 335 °C, respectively. The peak at around 280 °C is assigned to the reduction of [Cu(OH)]<sup>+</sup> near the eight-membered ring (8MR), whereas the peak at around 335 °C is attributed to the reduction of the naked Cu<sup>2+</sup> ions coordinated to the paired Al in 6MR (Cu<sup>2+</sup>-2Al) [17, 22, 57]. The intensity of the peak at around 280 °C decreased with the increase of phosphorus doping content in the P<sub>x</sub>Cu sample, indicating the amount of isolated Cu<sup>2+</sup> ions decreased as compared to the Cu-SSZ-13.

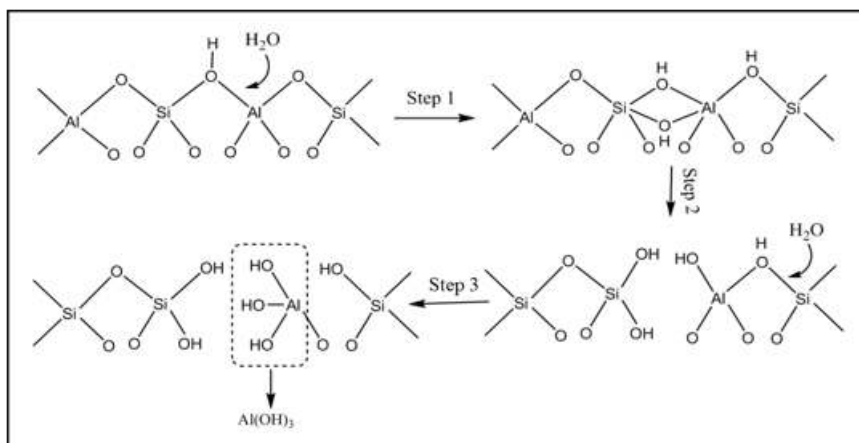
An H<sub>2</sub> consumption peak at around 535 °C emerged in the P<sub>x</sub>Cu samples, much higher than the reduction temperature of isolated Cu<sup>2+</sup> ions (below 400 °C). Probably, this new peak may be ascribed to the reduction of some newly formed Cu-phosphate species with lower redox capacity than the isolated Cu<sup>2+</sup> ions [9, 54, 56]. However, we have no further evidence on determining the exact state of the Cu-phosphate, since different phosphate species exist in the P doped samples according to the <sup>31</sup>P MAS NMR results in Fig. 3.

The H<sub>2</sub>-TPR plots of the hydrothermally aged samples are shown in Fig. 9b. For the sample Cu-H, the reduction peaks appeared at around 230 °C and 260 °C should be ascribed to the reduction of Cu<sup>2+</sup> on Al<sub>2</sub>O<sub>3</sub>, according to the EPR results in Fig. 7. The H<sub>2</sub> consumption peak at above 600 °C remained with the two P<sub>x</sub>Cu-H samples, indicating that they still contain a large amount of the isolated Cu<sup>2+</sup> ions. Meanwhile, a broad peak is shown between 180 °C and 400 °C with the P<sub>x</sub>Cu-H samples which can be deconvoluted into two peaks, at around 200 °C and 290 °C, respectively. The peak around 200 °C can be assigned to the reduction of aggregated CuO<sub>x</sub>, because a reduction peak at similar temperature was observed with CuO powder as a reference in Fig. S6. Another peak around 290 °C appeared exclusively with the samples with phosphorous, attributed to the reduction of the remaining isolated Cu<sup>2+</sup> ions. Only one reduction peak of isolated Cu<sup>2+</sup> ions was observed in the aged P doped samples. This can be ascribed to the overlap of the reduction profiles of the [Cu(OH)]<sup>2+</sup> and Cu<sup>2+</sup>-2Al or the transformation between Cu(OH)<sup>+</sup> and Cu<sup>2+</sup>-2Al during hydrothermal treatment [28, 58].

#### 4. Discussion

##### 4.1. Hydrothermal aging effect on the structure

The hydrothermal aging at 750 °C for 16 h destroyed the Cu-SSZ-13 structure completely for the sample without P loading (the sample Cu-H), according to the XRD pattern in Fig. 2a. The surface area and the pore volume of the sample lost almost completely as shown in Table 3.



**Scheme 1.** SSZ-13 zeolite hydrolysis process.

It has been well documented that Brønsted acid sites (*i.e.*, -Si-(OH)-Al-) in zeolites are the most vulnerable to H<sub>2</sub>O attack during hydrothermal aging, resulting in the collapse of the zeolite structure with dealumination [45]. The mechanism of the dealumination is summarized in Scheme 1. First, the framework acidic Si-(OH)-Al sites can be easily hydrolyzed, forming a vicinal disilanol defect as well as a new Brønsted acid site in the vicinity, as shown in Step 1 in Scheme 1 [31, 59]. In Step 2, the formation of vicinal disilanol defect results in weakening and cleavage of the Al-O bonding [31, 60]. Subsequently, as shown in step 3, the hydroxylation of Si-(OH)-Al framework continuously repeats the two steps above mentioned, eventually resulting in complete expulsion of the Al from the framework, causing the collapse of the structure [19, 60]. The mechanism is confirmed with NH<sub>3</sub>-TPD in this work, where almost no NH<sub>3</sub> desorption was observed with Cu-H (Fig. S5), indicating the complete disappearing of Si-(OH)-Al sites. Furthermore, <sup>27</sup>Al MAS NMR with the Cu-H sample in Fig. 4b shows the peak at around 56 ppm decreased significantly, suggesting the vanishing of the TFAI via dealumination.

## 4.2. Phosphorus effect on the structure

### 4.2.1. Phosphorus effect before aging

The XRD in Fig. 2a and the data in Table 2 show minor structural destruction in the phosphorus loaded samples. Meanwhile, the as-prepared Cu-SSZ-13 contains only TFAl, whereas the EFAl emerged in the  $P_xCu$  samples without hydrothermal treatment, according to  $^{27}Al$  MAS NMR in Fig. 4a. This indicates partial detachment of the TFAl from the framework. These observations suggest that the detachment of partial TFAl contributes to the structure destruction of the  $P_xCu$  samples.

The total Al content remained constant as confirmed with the ICP data in Table 2. Nevertheless, around 10% Al was undetectable via  $^{27}Al$  MAS NMR with the  $P_xCu$  samples shown in Table 5. This can be explained by the well-accepted theory that certain content of Al species was beyond the detection in the  $^{27}Al$  MAS NMR due to the second-order quadrupolar interactions in the Al nucleus [49, 61, 62]. The formation of highly distorted Al species and the paramagnetic  $Cu^{2+}$  species situated next to extra-framework Al can cause the "NMR invisible Al" in  $^{27}Al$  MAS NMR spectra [4, 24].

The  $^{31}P$  MAS NMR (Fig. 3a) and Raman (Fig. 5) spectra corroborate that the aluminum phosphate species exists in the  $P_xCu$  samples [36, 42, 44], while no such Al species was observed in the  $^{27}Al$  MAS NMR results (Fig. 3a). This clearly confirms that Al interacting with the phosphate caused a part of the Al species highly distorted, undetectable in  $^{27}Al$  MAS NMR with the  $P_xCu$  samples. No line broadening of the TFAl signal was observed in  $^{27}Al$  MAS NMR in Fig. 4a, ruling out the interaction between phosphate and the framework Al in the  $P_xCu$  samples [58]. Therefore, the undetectable Al can be ascribed to the extra-framework aluminum phosphates formed



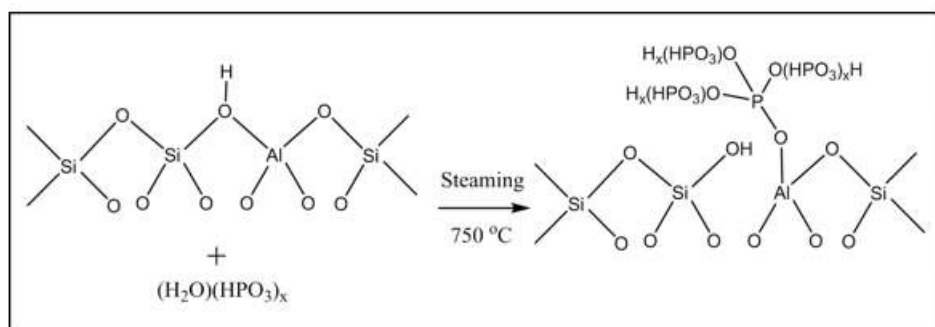
with part of the EFAl interacting with the phosphate, agreeing with the previous results with phosphorus modified Y and ZSM-5 [44, 63, 64]. However, the impact of the paramagnetic  $\text{Cu}^{2+}$  species on the measurement of extra-framework Al in  $^{27}\text{Al}$  MAS NMR is unavoidable [4]. Accordingly, we cannot discard the possibility that a part of invisible Al was caused by the influence paramagnetic Cu species in the  $^{27}\text{Al}$  MAS NMR measurement.

#### 4.2.2. Improvement of skeleton stability

The crystalline structure, as well as over 65% of the surface area and pore volume, retained with the  $\text{P}_x\text{Cu-H}$  samples after the hydrothermal treatment, according to XRD (Fig. 2 and Table 2) and  $\text{N}_2$  physisorption measurement (Table 3) data, significantly improved over the Cu-H sample without P loading. Moreover, the  $^{27}\text{Al}$  MAS NMR results in Table 5 demonstrate that around 50% of TFAl still remained in the aged phosphorus doped samples. In contrast, almost no TFAl retained in the Cu-H sample (Table 5). This clearly proves the stabilization effect of the phosphorus species on the Cu-SSZ-13 structure against dealumination during the hydrothermal aging.

The coordination environment of the Al and P changed in the  $\text{P}_x\text{Cu-H}$  samples after the hydrothermal treatment, if compared to that in the fresh samples. As shown in Fig. 4b and Table 5, the distorted TFAl species appeared in the  $\text{P}_x\text{Cu-H}$  samples, increasing with the increase of the phosphorus amount according to  $^{27}\text{Al}$  MAS NMR (Table 5). Meanwhile, the pyrophosphoric species (-6 ppm) and less-condensed polyphosphates (-12 ppm) transferred to aluminum phosphate species (-32 ppm) during the hydrothermal aging according to  $^{31}\text{P}$  MAS NMR in Fig. 3b and Table 4. There seems to exist a correlation between the formation of distorted TFAl and the transformation

of the phosphate species. This is confirmed by the shift of the peak assigned to the P-O-Al lattice vibration with phosphorus modified samples according to the Raman spectra in Fig. 5 [52, 53]. Additionally, no crystalline  $\text{AlPO}_4$  phase was observed via XRD in Fig. 2, ruling out any crystallization of the extra-framework aluminum phosphates [51, 52]. As a result, the shift of the Raman peak indicates the formation of distorted TFAl coordinating with the phosphate species, resulting in a framework silicoaluminophosphate interface, as shown in Scheme 2.

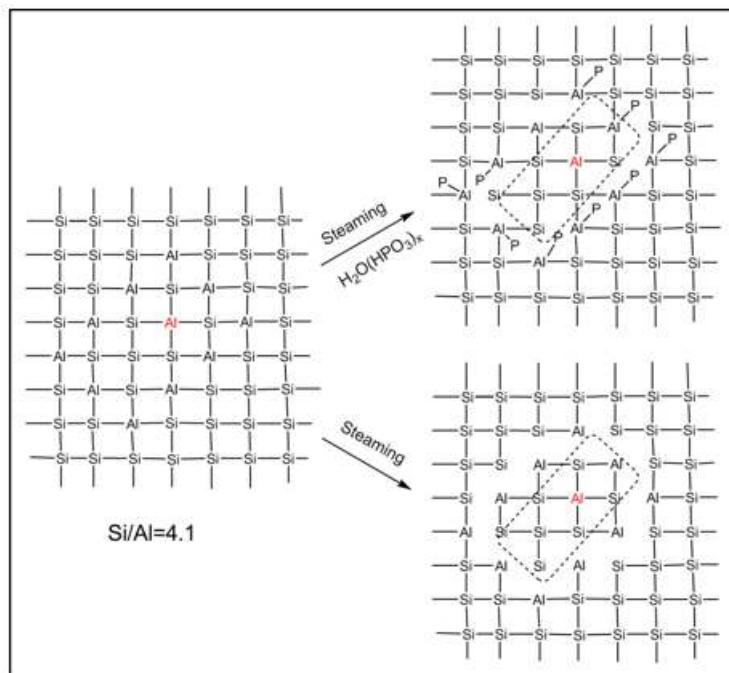


**Scheme 2.** The phosphorus stabilization effect on the phosphorus modified samples ( $x=0,1,2,\dots$ ).

The interaction between the distorted TFAl and the phosphate species probably caused by the well-known fact that the positively charged  $[\text{PO}_4]^+$  in the phosphate can neutralize the negatively charged  $[\text{AlO}_4]^-$  containing TFAl in the zeolite lattice, eliminating the Brønsted acidity as well as the ability to dissociate water, as shown in Scheme 2 [36, 63]. This prevents degradation of the distorted TFAl with further breakage of the residual Si-O-Al bond under hydrothermal condition (Step 3, Scheme 1).

Around 7% higher amount of TFAl and distorted TFAl species retained in the  $\text{P}_2\text{Cu-H}$  sample as compared to that in the  $\text{P}_1\text{Cu-H}$  sample according to the  $^{27}\text{Al}$  MAS NMR

results (Table 5). This indicates the distorted TFAl species protects other TFAl against dealumination during hydrothermal treatment, thus keeping the long-range order of structure stable, as confirmed with the XRD results in Fig. 2. This proposal was shown in Scheme 3.



**Scheme 3.** The possible mechanism of phosphorus protection effect on the structure of the phosphorus-doped samples; (a) the interlinkage of framework Si and Al in the framework; (b) the protection effect of the distorted TFAl on the network of the P<sub>x</sub>Cu-H catalysts; (c) the detachment of the framework Al in the sample without phosphorus.

### 4.3. Effect on the Cu species

#### 4.3.1. In the fresh samples

The isolated Cu<sup>2+</sup> ions amount decreased with increasing phosphate content, according to the EPR result in Fig. 8. No CuO<sub>x</sub> appeared in the P<sub>x</sub>Cu samples according to the H<sub>2</sub>-TPR results (Fig. 9a), ruling out the agglomeration of the isolated Cu<sup>2+</sup> ions to CuO<sub>x</sub> caused by dealumination [19]. Therefore, the decline of the isolated Cu<sup>2+</sup> ion content can be attributed to the formation of Cu-phosphates in the phosphorus-doped samples as shown in Fig. 9a, consistent with the previous work [65].

#### 4.3.2. In the aged samples

Only  $\text{Cu}^{2+}$  ions on  $\text{Al}_2\text{O}_3$  were observed in the Cu-H sample after the hydrothermal aging, according to the EPR results in Fig. 7. Nevertheless, no such species was detected with  $^{27}\text{Al}$  MAS NMR, as shown in Fig. 4b no signal at 0 ppm which represents octahedral Al. This is ascribed to the interaction of the paramagnetic  $\text{Cu}^{2+}$  ions with the quadrupolar  $^{27}\text{Al}$  nuclei which makes the octahedral aluminum “NMR invisible”, as discussed in section 4.2.1. [4, 24].

A large amount of isolated  $\text{Cu}^{2+}$  ions remained in the  $\text{P}_x\text{Cu-H}$  samples according to the EPR results in Fig. 8. Furthermore, both the content of the isolated  $\text{Cu}^{2+}$  ions as well as the TFAI increased with the increase of the phosphorus loading in the aged samples, according to Fig. 8 and Table 5. The cupric species have been known prefer to stay as isolated  $\text{Cu}^{2+}$  coordinating to the TFAI to maintain low free energy if the structure remains intact in the hydrothermal treatment [26, 28]. Therefore, the phosphorus protects the isolated  $\text{Cu}^{2+}$  ions by retaining the TFAI in the framework during the hydrothermal treatment.

#### 4.4. Effect on the SCR performance

##### 4.4.1. Before hydrothermal aging

The  $\text{P}_x\text{Cu}$  sample exhibited a decline of SCR activity below 250 °C, as compared to those of the Cu-SSZ-13, as shown in Fig. 1a. This is probably caused by the high redox barriers for the Cu-phosphate species according to  $\text{H}_2$ -TPR in Fig. 9, making it inactive for SCR reaction, which is known as highly dependent on the redox of cupric sites in Cu-SSZ-13 [66, 67].

The  $\text{NO}_x$  conversions with the  $\text{P}_x\text{Cu}$  samples are higher than the Cu-SSZ-13 with

reaction temperature higher than 450 °C, as shown in Fig. 1a. It is known that NH<sub>3</sub> oxidation rate increased at such high temperature, as a competitive reaction with NH<sub>3</sub>-SCR [68]. Fig. 7 shows lower isolated Cu<sup>2+</sup> content in the P<sub>x</sub>Cu samples than in the Cu-SSZ-13. Probably, NH<sub>3</sub> oxidation is dependent on the isolated Cu<sup>2+</sup> content than NH<sub>3</sub>-SCR, resulting in a decline of the reaction rate for NH<sub>3</sub> oxidation and less consumption of NH<sub>3</sub>, promoting the NH<sub>3</sub>-SCR reaction rate by more reactant [68, 69]. This agrees with the decline of NH<sub>3</sub> conversion with the phosphorus doped samples in NH<sub>3</sub> oxidation experiments, as shown in Fig. S7a in the *Supporting Information*.

#### 4.4.2. After hydrothermal aging

As shown in Fig. 1b, the NO<sub>x</sub> conversion with the non-phosphorus doped sample (Cu-H) decreased significantly after the hydrothermal aging at 750 °C, as compared with the Cu-SSZ-13 before hydrothermal aging in Fig. 1a. The phosphorus doping increased the NO<sub>x</sub> conversion significantly from 150 °C to 550 °C (P<sub>1</sub>Cu-H and P<sub>2</sub>Cu-H) as shown in Fig. 1b. This can be explained by the stabilization effect of the phosphate ions interacting with the framework, as well as the remaining of the isolated Cu<sup>2+</sup> ions, as discussed in Section 4.2 and 4.3. Notably, the catalyst with the high phosphorus content (P<sub>2</sub>Cu-H) shows the best activity. The excellent activity above 450 °C can be explained by less competition of NH<sub>3</sub> oxidation at the temperatures (Fig. S7b), similar to the sample before hydrothermal aging as discussed in Section 4.4.1.

## 5. Conclusion

Doping with P as phosphate acid detach a part of TFAI to EFAI in the Cu-SSZ-13. Nevertheless, the formation of a framework silicoaluminophosphate interface retards the further dealumination of the Cu-SSZ-13 sample with phosphorus doping, retaining

the CHA structure intact.

For the cupric sites, the isolated  $\text{Cu}^{2+}$  ions react partly with the phosphate, forming the Cu-phosphate species in the PxCu samples. The Cu-phosphate species may be inactive for  $\text{NH}_3$ -SCR reaction due to the very high redox barriers ( $\text{H}_2$ -reduction temperature at around 535 °C) of the cupric species. This reduces the SCR performance of PxCu samples at low temperatures, whereas enhancing their deNO<sub>x</sub> activity above 450 °C. After hydrothermal treatment, the isolated  $\text{Cu}^{2+}$  ions vanished due to the structural collapse. In contrast, the intact structure of the aged samples with P loading retains most of the isolated  $\text{Cu}^{2+}$  ions, maintaining their excellent SCR performance.

A small amount of P (around 1-2 wt.%) in the tail gas may be favorable for the hydrothermal stability of Cu-SSZ-13 with a low Si/Al ratio. However, the high P content (around 5 wt.%) seriously decreases the deNO<sub>x</sub> activity of the doped sample. Therefore, the amount of P in the vehicle exhaust should be precisely controlled.

#### Acknowledgments

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