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Enhanced hydrothermal stability of a Cu-SSZ-13 catalyst for the selective reduction of NO_x by NH₃ synthesized with SAPO-34 micro-crystallite as seed

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Abstract: The distribution of framework Si and Al in the Cu-SSZ-13 catalyst, for NH₃ selective catalytic reduction of NO_x, is manipulated via a new strategy, using SAPO-34 as a seed in hydrothermal synthesis instead of the conventional SSZ-13 micro-crystallite. The SAPO-34 seed has a strong impact on the hydrothermal stability of the catalyst, moderating the dealumination as well as the agglomeration of the active Cu²⁺ ions in the Cu-SSZ-13 with hydrothermal treatment at 800 °C.

Keywords: Selective reduction of NO_x with NH₃, Cu-SSZ-13, SAPO-34, hydrothermal stability, Al distribution

1. Introduction

In the past decade, Cu-SSZ-13 has been developed as a commercial catalyst for selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) in the exhaust gas of diesel vehicles, to meet the requirements of current emission regulation [1-4]. However, to keep the high activity of the Cu-SSZ-13 in the hydrothermal working condition is still a challenge, especially at high temperatures above 800 °C. The harsh conditions cause dealumination of the framework, as well as agglomeration of the active Cu²⁺ sites [5-7].

Substantial works have been done on optimizing the structural properties of SSZ-13, e.g., the compositional Si/Al ratio [6, 8], the size, shape, and the crystallinity of the zeolite crystallites [8-10], and the pore distribution etc. [11], to moderate the dealumination during hydrothermal treatment. Nevertheless, zeolite samples with

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similar macroscopic characteristics above mentioned may still show different stability [10, 12]. This is because the microscopic structure, such as the position and distribution of the framework Al sites (TFAl), also influences the stability of a given zeolite [12-14]. On the other hand, for Cu-SSZ-13, the isolated Cu^{2+} ions in different locations show different hydrothermal stability [4], and the location of the cupric ion sites is highly dependent on the distribution of TFAl in the framework [15, 16]. Accordingly, manipulating and optimizing the distribution of the TFAl may improve the stability of both TFAl and isolated Cu^{2+} ions in Cu-SSZ-13. Recently, a few rational approaches for controlling the TFAl distribution in SSZ-13 appeared in the literature [10, 17].

In this work, we demonstrate a novel and simple strategy to control the TFAl distribution in the framework of SSZ-13, by using a SAPO-34 seed in the hydrothermal synthesis. The effects of the SAPO-34 seeds on the structure, active sites and hydrothermal stability of Cu-SSZ-13 are examined. A scheme for the enhancing effect of the SAPO-34 seed on the performance of Cu-SSZ-13 catalyst is proposed.

2. Results and Discussion

2.1. Structure analysis

Sample notations, preparation procedures and amount of the seeds introduced during synthesis are listed in Table 1. The details of the catalyst preparation and characterization are given in *supporting information*. ICP measurements show that all the fresh and aged samples have a similar cupric content of *ca.* 2.5 wt.% and Si/Al ratio at around 8, regardless of the type and amount of the seeds. No phosphorus was detectable with XRF for all the samples, ruling out the presence of SAPO-34 phase in the prepared catalysts as well as any bulk effect of phosphorus bonded to the zeolite framework. This is also confirmed by no resonance of phosphorus species observed in ^{31}P MAS NMR in Fig. 1a. This is a surprise to us, because SAPO-34 seeds contain *ca.* 26 wt.% phosphorous, thus the P content is not negligible in the preparation slurry (0.37 - 2.6 g/L for P_1Cu - P_7Cu).

Table 1. Sample notations and details of preparation procedure

Samples	Preparation procedure
Cu-SSZ-13	SSZ-13 synthesized 1 wt.% SSZ-13 seed (SSZ-13 seed/SiO ₂), then Cu-exchanged
H-SSZ-13	NH ₄ ⁺ -exchanged SSZ-13, then calcinated at 600 °C for 6 h
P ₁ Cu	SSZ-13 synthesized 1 wt.% SAPO seed (SAPO seed/SiO ₂), then Cu-exchanged
P ₃ Cu	SSZ-13 synthesized 3 wt.% SAPO seed (SAPO seed/SiO ₂), then Cu-exchanged
P ₅ Cu	SSZ-13 synthesized 5 wt.% SAPO seed (SAPO seed/SiO ₂), then Cu-exchanged
P ₇ Cu	SSZ-13 synthesized 7 wt.% SAPO seed (SAPO seed/SiO ₂), then Cu-exchanged
Cu-H	Cu-SSZ-13 hydrothermal aged in 10% H ₂ O/air flow at 800 °C for 16 h
P ₁ Cu-H	P ₁ Cu hydrothermal aged in 10% H ₂ O/air flow at 800 °C for 16 h
P ₃ Cu-H	P ₃ Cu hydrothermal aged in 10% H ₂ O/air flow at 800 °C for 16 h
P ₅ Cu-H	P ₅ Cu hydrothermal aged in 10% H ₂ O/air flow at 800 °C for 16 h
P ₇ Cu-H	P ₇ Cu hydrothermal aged in 10% H ₂ O/air flow at 800 °C for 16 h

a. Note that the fresh and aged P₁Cu, P₃Cu, P₅Cu and P₇Cu samples are collectively named P_xCu and P_xCu-H, respectively.

Fig. 1. (a) Solid state ³¹P MAS NMR spectra of the fresh catalysts; XRD patterns of the (b) fresh and the (c) aged catalyst samples. The relative crystallinity is given above each pattern in Fig. 1c, which is calculated with crystallinity of aged sample relative to their that of fresh counterparts. The hydrothermal treatment was carried out in synthetic air containing 10% H₂O at 800 °C for 16 h.

As shown in Fig. 1b, all the catalyst samples exhibit typical CHA structure [18]. However, the relative intensity of peaks at 9.4° and 20.5° increase with increase of the amount of SAPO-34 seed when preparing the samples from P₁Cu to P₇Cu, indicating the SAPO-34 seed affects the growth of SSZ-13 crystal. After the hydrothermal treatment in air at 800 °C, the structure of the samples is still well retained (Fig. 1c), although the crystallinity decreased for all the samples as confirmed with the decline of the relative crystallinity shown above in each pattern.

Solid-state ²⁷Al MAS NMR spectra of the samples are put together in Fig. 2a and b to detect the local Al coordination. All the fresh and aged samples present a resonance at 56 ppm and a small peak at 0 ppm, assigned to the tetrahedral framework Al (TFAI) species [3], and the octahedral extra-framework Al (EFAI) [19],

respectively. The normalized TFAI signal area of samples are displayed above each spectrum. All the fresh samples contain similar TFAI content, indicating the addition of the SAPO-34 seed has almost no influence on the framework Al content. The TFAI in the aged samples decreased, as compared to the values in the fresh samples. However, the remained TFAI in the aged samples follow the order: $P_5\text{Cu-H} > P_3\text{Cu-H} > P_1\text{Cu-H} > P_7\text{Cu-H} > \text{Cu-H}$, as shown above each spectrum in Fig. 2b. It indicates that using SAPO-34 as seed moderates the delamination of samples during hydrothermal treatment.

Fig. 2. Solid state ^{27}Al MAS NMR spectra of the (a) fresh catalysts; (b) hydrothermal treated catalysts. Solid state ^{29}Si MAS NMR spectra of the (c) proportion of $\text{Si}_{4-n}\text{Al}_n$ of fresh samples; (d) fresh catalysts; (e) hydrothermal treated catalysts; (f) magnification of the ^{29}Si MAS NMR patterns in -105 - -90 ppm of the fresh catalysts. The original ^{27}Al and ^{29}Si MAS NMR profiles are represented with the solid lines with different colors. The deconvolution methods of the ^{27}Al and ^{29}Si NMR are Lorentzian/Gaussian and Gaussian fitting, respectively. The amounts of TFAI in the fresh and aged samples were normalized and shown above each spectrum, using the TFAI signal area of the H-SSZ-13 sample as a reference. Proportion of $\text{Si}_{4-n}\text{Al}_n$ of fresh samples according to the Fig. 2d (details shown in Table S4), $\text{Si}_{4-n}\text{Al}_n$ is the $\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ for short.

As shown in Fig. 2d, five resonance peaks can be fitted with the ^{29}Si solid-state NMR spectra, at -110, -105, -100, -98 and -94 ppm, respectively, assigned to Si centering tetrahedral coordinated with different amount of (-O-Si) and (-O-Al), *i.e.*, $\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ ($n = 0, 1, 2, 3$ and 4 , respectively) [5, 20-23]. This supplies a tool to determine the distribution of Al by comparing the Si/Al ratios in the moieties. Fig. 2c plots the ratio of the moieties with high Si/Al ratio, *i.e.*, $\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ ($n > 1$). The value first increases with the amount of SAPO-34 seeds used in hydrothermal synthesis (from Cu-SSZ-13 to P₅Cu), then decreases with the further increase of the amount of the SAPO-34 seeds (from P₅Cu to P₇Cu). Accordingly, the resonance peak at -94 ppm in ^{29}Si MAS NMR spectra, assigned to $\text{Si}(\text{OAl})_4$, appears exclusively in P₃Cu and P₅Cu, as shown in Fig. 2d and more clearly in Fig. 2f. This indicates that using SAPO-34 as the seed facilitates the coordination of Si with (-O-Al) to some extent, making Al distribution in the framework with a higher concentration.

The ^{29}Si solid-state NMR spectra of the aged samples are shown in Fig. 2e. After hydrothermal treatment, the integrated peak area of $\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ ($n \geq 1$) features (-94, -98, -100 and -105) decreased, as compared to $\text{Si}(\text{OSi})_4$ peak at -110 ppm. The decrease of (-O-Al) bonded to Si is probably caused by the dealumination during the hydrothermal treatment [5], consistent with the ^{27}Al MAS NMR results in Fig. 2b. Interestingly, the amount of $\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ ($n > 1$) in the fresh samples in Fig. 2c follow the order: P₅Cu > P₃Cu > P₁Cu > P₇Cu > Cu-SSZ-13, in the same sequence as remained TFAI in the aged samples in Fig. 2b. This indicates that the coordination of Si with high (-O-Al) likely protects the Al in the framework in the high-temperature hydrothermal treatment [14].

2.2. Cupric ion site

EPR results in Fig. 3a and b show the content of cupric species are mostly identical in all the fresh samples, irrespective to the amount of SAPO-34 used in the hydrothermal synthesis. After hydrothermal treatment, different isolated Cu^{2+} ions remained in the samples, as shown in Fig. 3c and d. P₅Cu-H sample remained much more isolated Cu^{2+} ions than other aged samples.

Fig. 3. Electron Paramagnetic Resonance (EPR) spectra and the normalized Cu^{2+} ions concentration of the fresh (a and b) and aged catalyst (c and b) samples. The normalized Cu^{2+} ions concentration was determined with double integrating the EPR spectra, using the isolated Cu^{2+} ions content in Cu-SSZ-13 as the reference. Spectra were collected at -150°C .

The TEM images of the Cu-SSZ-13 and P_5Cu samples are shown in Fig. 4a and 4b, respectively. No CuO nanoparticle was observed in the samples, indicating that the cupric ions are dispersed in an atomic/ionic level. After the hydrothermal treatment, CuO nanoparticles (lattice spacing with 0.27 nm, (110) face) formed in both Cu-H and $\text{P}_5\text{Cu-H}$, according to TEM in Fig. 4c and d [24]. Fig. 4e and f clearly show that the particle size distribution can be distinguished by two regions, peaking at around 1.5 nm and 3 nm, respectively. These nanoparticles must have been formed during the hydrothermal treatment, caused by the agglomeration of the isolated Cu^{2+} ions [5].

Fig. 4. The TEM images of the fresh and aged Cu-SSZ-13 (a and c) and P₅Cu (b and d) samples. The CuO size distribution of the aged Cu-SSZ-13 (e) and aged P₅Cu (f) samples based on 100 particles counted. H₂-TPR spectra of (g) fresh and (h) aged samples.

H₂-TPR in Fig. 4g and 4h show the reduction curves of the fresh and aged samples, respectively. The cupric species are reduced in two steps from Cu²⁺ to Cu⁺ (250 – 500 °C), and from Cu⁺ to Cu⁰ (600 – 800 °C), with the fresh samples. The peak below 500 °C in the H₂-TPR profiles in Fig. 4g can be divided into two peaks at around 330 °C (Peak I) and 415 °C (Peak II), respectively. According to literature [16, 25], the peak I is assigned to the

[Cu(OH)]⁺ near the eight-membered ring, whereas the peak II is assigned to the isolated Cu²⁺ ions bonded with the paired Al (Al-O-Si-O-Al or Al-(O-Si)₂-O-Al) in the six-member ring, denoted as Cu²⁺-2Al. In other words, the reduction temperature is dependent on the location of the cupric species on the framework. As shown in Fig. 4g, the intensity of Peak II is dependent on the amount of SAPO-34 seeds used in the preparation of the PxCu samples, first increasing from Cu-SSZ-13 to P₅Cu, then decreasing with the SAPO-34 seeds content increasing to 7 wt.% with P₇Cu. Clearly, the SAPO-34 seeds influence the location and the type of cupric ions dispersed on the SSZ-13 framework.

The change of cupric species can probably be explained by the change of distribution of the Al tetrahedron in the SSZ-13 framework. The content of the framework Al is very close in the Cu-SSZ-13 and PxCu samples according to ²⁷Al NMR in Fig. 2a. Nevertheless, Fig. 2c shows the distribution of the framework Al changes with different amount of SAPO-34 used in the samples. The content of Si(OSi)_{4-n}(OAl)_n (n > 1) first increases with the SAPO-34 seed adding from Cu-SSZ-13 to P₅Cu, then the content of Si(OSi)_{4-n}(OAl)_n (n > 1) decrease from P₅Cu to P₇Cu. This tendency is identical with the change of cupric type in Fig. 4g as discussed above. This agrees with the well-known dependency of the type of isolated Cu²⁺ ions on the distribution of framework Al [26]. It is plausible that the high content of Si(OSi)_{4-n}(OAl)_n (n > 1) increases the population of the paired neighboring Al sites in SSZ-13, facilitating the formation of the Cu²⁺-2Al. This hypothesis can be confirmed with the Co²⁺ titration results (Co²⁺ exchanged with NH₄⁺-SSZ-13 synthesized with different seeds), because Co²⁺ ions exclusively occupy Al pairs sites in SSZ-13 during ion-exchange [15, 17]. The Co content increasing tendency follows Cu-SSZ-13 (2.08 wt.%) < P₇Cu (2.21 wt.%) < P₁Cu (2.67 wt.%) < P₃Cu (3.06 wt.%) < P₅Cu (3.27 wt.%), well agreed with the changes of Si(OSi)_{4-n}(OAl)_n (n > 1) content in the samples (Fig. 2c).

As shown in Fig. 4h, the H₂-TPR peak area below 500 °C (peak III) is much higher than above 600 °C (peak IV) with all the hydrothermal treated samples. This is different from the fresh samples in Fig. 4g. Pike *et al.* [27] have reported different reductivity of the CuO nanoparticles with different size, but both types can be reduced completely below 500 °C. Therefore, the unequal H₂-TPR reduction area (peak III and peak IV) in the aged

samples can be explained by the reduction of the new CuO nanoparticles, formed via the agglomeration of the isolated Cu^{2+} ions. However, EPR results in Fig. 3d shows that higher Cu^{2+} ions content retained in P_5Cu samples than other samples after the hydrothermal treatment. It should be attributed to the higher content of $\text{Cu}^{2+}\text{-2Al}$, showing high stability during the aging process [5, 6], in P_5Cu than that in other samples (Fig. 4g).

2.3. Catalytic performance

The catalytic performance of the selected catalysts is shown in Fig. 5. The fresh Cu-SSZ-13 and P_5Cu exhibit quite identical NO_x conversion. After the hydrothermal treatment, all the catalysts exhibit lower activity. This is because of the agglomeration of isolated Cu^{2+} ions as the major active sites for $\text{NH}_3\text{-SCR}$ [15, 28, 29]. Meanwhile, the agglomerated CuO nanoparticles catalyze NH_3 oxidation by O_2 , diminishing the reactants for the $\text{NH}_3\text{-SCR}$. Nevertheless, $\text{P}_5\text{Cu-H}$ still shows 10 - 15% higher NO_x conversion than Cu-H in the whole temperature range. This is because using SAPO-34 seed during the hydrothermal synthesis of SSZ-13, enhancing the hydrothermal stability of the catalyst, remaining double amount of the isolated Cu^{2+} ions as active sites (Fig. 3d).

Fig. 5. NO_x conversion during standard $\text{NH}_3\text{-SCR}$ as a function of the temperature (150-550 °C) of the catalysts. Reaction conditions: 500 ppm NO , 500 ppm NH_3 , 5% O_2 , 5% H_2O , balanced with N_2 ; flow rate: 500 mL/min, GHSV: 150, 000 h^{-1} . Hydrothermal condition: 10% H_2O in air at 800 °C for 16 h, 500 mL/min.

3. Conclusion

This work provides a new strategy to improve the hydrothermal stability of Cu-SSZ-13, viz. SAPO-34 seed is used as the seed to grow the SSZ-13 crystal. It shows the introduction of SAPO-34 enhances the distribution of the Al tetrahedron in the CHA framework, as well as influences the type and stability of the isolated Cu^{2+} ions as the major active sites for NH_3 -SCR. With the proper amount of SAPO-34 seeds, the isolated Cu^{2+} can be largely prevented from agglomeration in the hydrothermal working condition, shedding substantial light on the next generation of NH_3 -SCR catalysts. Nevertheless, the mechanism of how the SAPO-34 seeds involved in the synthesis of SSZ-13 is still an open issue for further research.

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