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One-pot synthesis of high performance Cu-SAPO-18 catalyst for NO reduction by NH_3-SCR: Influence of silicon content on the catalytic properties of Cu-SAPO-18

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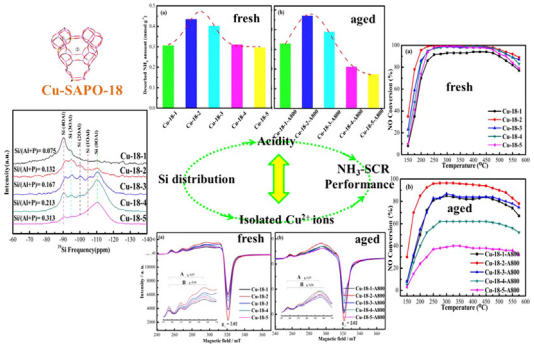
HIGHLIGHTS

- The influence of Si content on the NH_3-SCR performance over Cu-SAPO-18 is studied.
- The structure-performance relationship of Cu-SAPO-18 catalyst is well established.
- The Si(xOAl)(x = 1–3) structures are beneficial for hydrothermal stability of Cu-SAPO-18.
- A suitable Si content leads to a good SCR performance of Cu-SAPO-18.
- A high performance Cu-SAPO-18 catalyst for NH_3-SCR reaction is obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Five Cu-SAPO-18 (a silicoaluminophosphate molecular sieve) catalysts with different Si contents prepared by a one-pot method were used to investigate the effect of their Si content on the ammonia selective catalytic reduction (NH_3-SCR) performance. Although the as-prepared catalysts exhibited similar Cu loading, they showed quite different NO conversions from 150 °C to 575 °C before and after hydrothermal aging treatment at 800 °C for 12 h. The XRD, ^{29}Si MAS NMR, NH_3-TPD, H_2-TPR, EPR and kinetic tests were applied to characterize the various Si coordination structures in Cu-SAPO-18 samples and their roles on the NH_3-SCR performances. The ^{29}Si MAS NMR, NH_3-TPD and EPR results indicated that the varying proportion of Si could affect the Si coordination structures, and further affect the acid properties and Cu distributions in Cu-SAPO-18 catalysts. The amount of acid sites and isolated Cu^{2+} ions firstly increases and then decreases with increasing Si content. The NO conversion results indicated that catalytic activities are jointly decided by acidity and amount of isolated Cu^{2+} ions. On the other hand, the more Si (xOAl) (x = 1–3) structures, the more strong acid sites could be generated in Cu-SAPO-18 catalysts. Furthermore, these strong acid sites are beneficial for the stabilization of isolated Cu^{2+} ions, and thus the stabilities of isolated Cu^{2+} ions and zeolite framework are enhanced during the harsh hydrothermal aging treatment. Additionally, the kinetic result suggested that Si content does not influence the apparent activation energy (E_a) of NH_3-SCR over Cu-SAPO-18 catalyst at low temperatures.

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1. Introduction

Nowadays, selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) has been proven as the most efficient solution to eliminate NO_x from diesel exhaust treatment systems [1–3]. Cu-modified CHA zeolites (SSZ-13 and SAPO-34 (a silicoaluminophosphate molecular sieve)) have been described as excellent catalysts for NH_3-SCR reaction in exhaust emission control [4–7]. Cu-AEI catalysts (Cu-SSZ-39 and Cu-SAPO-18), which have a similar three-dimensional pore system and large cavities to the CHA zeolites, have also attracted increasing attention due to the superior catalytic activity and hydrothermal resistance ability in NH_3-SCR reaction [8–11].

Moliner et al. [8] first reported Cu-SSZ-39 catalyst for deNO_x by NH_3-SCR, which shows an extraordinary catalytic activity (NO_x conversion close to 100% at 250–450 °C) and hydrothermal stability, even better than Cu-SSZ-13 catalyst (NO_x conversion close to 100% at 350–420 °C) under the same test conditions (500 ppm NO, 500 ppm NH_3, and 7% O_2, GHSV = 27 000 mL h^{-1} g_{cat}^{-1}). Upon hydrothermal aging at 750 °C for 13 h, Cu-SSZ-13 almost lost its activity (NO conversion < 40%), while Cu-SSZ-39 maintained most of the activity in the whole temperature range. Yang et al. [12] found that Cu-SAPO-18 catalyst performed higher catalytic activities, better hydrocarbon coking resistance and hydrothermal stability as compared to Cu-ZSM-5. The NO conversion over Cu-ZSM-5 catalyst dramatically dropped by propene or hydrothermal aging treatment (at 800 °C for 12 h) below 400 °C. While the activities of Cu-SAPO-18 were almost not affected by the presence of propene or hydrothermal aging treatment below 250 °C or above 400 °C under the same reaction conditions (150 mg catalyst, 400 ppm NO, 400 ppm NH_3, 14% O_2, 2% H_2O and balance He with a total flow rate 300 mL/min). Martínez-Franco et al. [11] directly synthesized the highly active and hydrothermally stable Cu-SAPO-18 catalyst, which makes it a very promising SCR catalyst. Recently, Li et al. [13] prepared a series of CeO_2-protected Cu-SAPO-18 catalysts, which exhibited excellent catalytic activity, high stability, high H_2O and SO_2 resistance for NH_3-SCR reaction. Although Cu-AEI zeolites have proved to be excellent SCR catalysts, the relationship between the SCR performance and Cu-AEI structure is not understood thoroughly.

Silicon content is a vital parameter in aluminosilicophosphate molecular sieves since the incorporation of silicon into the neutral framework of AlPOs molecular sieves will generate protons and exchangeability [14–16]. Furthermore, different contents of Si incorporation into AlPOs inclined to generate various Si coordination structures [Si(xOAl) (x = 0–4)], and the different Si coordination structures further decided various acid properties in aluminosilicophosphate molecular sieves [17,18]. It is well known that the acidity of molecular sieves strongly affects the NH_3-SCR activity of Cu-based molecular sieves catalyst [15,19,20]. On the other hand, various Si coordination structures and acid sites have different stabilizing abilities to the extra-framework Cu^{2+} ions during harsh hydrothermal treatment [11,19]. For example, since Si islands cannot create negative charges and acid sites in the zeolitic crystal, therefore, Si islands (Si (0OAl) structure) will not be able to efficiently stabilize the extra-framework Cu^{2+} ions in Cu-based aluminosilicophosphate catalyst [11,21]. Valange et al. [22] suggested that the copper species are better stabilized in a strong acidic ZSM-5 zeolite. Although numerous works have been contributed to the effect of Si content on SCR performance of Cu-zeolite [14,15,19,23,24]. However, to the best of our knowledge, it is still a blank to investigate the relationships between Si content and Si coordination structures, and effect of various Si coordination structures on the SCR performance of Cu-SAPO-18 catalyst [11–13,25,26]. Therefore, it is very necessary to systematically investigate how the Si content affects the physicochemical properties such as Si coordination structure, acidity and Cu loading, which are closely related to the SCR performance of Cu-SAPO-18 catalyst.

In this report, five Cu-SAPO-18 catalysts with different Si contents and equivalent Cu loading were synthesized and characterized in detail to shed light on the structure–performance correlation. The ^{29}Si MAS NMR was applied to confirm the proportions of Si coordination structures in Cu-SAPO-18 catalysts and to explore the effect of Si content on Si coordination structures. The NH_3-TPD was used to research the effect of Si content on acid properties in Cu-SAPO-18 samples. The H_2-TPR and EPR were performed to evaluate the reducibility and distribution of Cu species in the catalysts with various Si content. The catalytic activities of Cu-SAPO-18 catalysts were conducted to evaluate the effect of Si content on SCR performance. The structure–performance relationship between Si coordination structure and SCR performance over Cu-SAPO-18 catalysts was well established. Additionally, the NH_3-SCR kinetic tests were performed to explore whether the Si content could directly affect the NH_3-SCR reaction mechanism over Cu-SAPO-18 catalyst.

2. Experimental

2.1. Materials

Cu source ($CuSO_4{\cdot}5H_2O$, 99%), triethylenetetramine (TETA, 99 wt %), phosphoric acid (H_3PO_4, 85% wt) were purchased from Sinopharm Chemical Reagent Co., Ltd. N,N-diisopropylethylamine (DIPEA, 99 wt %) was purchased from Adamas Reagent, Ltd. Aluminium source (pseudo boehmite, 72 wt% Al_2O_3) was purchased from Zibo Baida Chem. ind. Co., Ltd. Silica source (silica sol, 30 wt%) was purchased from Qingdao Haiyang Chem. Co., Ltd. All chemicals were used as received.

2.2. Catalysts preparation

The Cu-SAPO-18 powders with various Si contents were directly synthesized with the mole composition of Al_2O_3: 0.9 P_2O_5: (0.2/0.4/0.6/0.8/1.2) SiO_2: 1.55 DIPEA: 0.1 Cu-TETA: 45 H_2O. The detailed preparation process is shown in the Supporting Information. The fresh sample was named as Cu-18-X, where “Cu-18” stands for Cu-SAPO-18 catalyst and “X” stands for the number of catalyst. The H-SAPO-18 powders with various Si contents were synthesized with the mole composition of Al_2O_3: 0.9 P_2O_5: (0.2/0.4/0.6/0.8/1.2) SiO_2: 1.65 DIPEA: 45 H_2O. The preparation process is also shown in the Supporting Information.

The monolith catalyst was prepared as follows: certain amounts of water were added to the as-prepared powders to form well-proportioned slurries. A cordierite (cylinder, diameter: 11 mm, length: 22 mm, bulk: 2.1 cm^3, 400 cell cm^{-2}) was coated by dipping it into the slurries. In order to control the similar loading and achieve a homogeneous coating on the cordierite support, the excess slurry was carefully removed by blowing air through the channels and the catalyst was dried at 110 °C for 2 h and then weighed after each immersion. Successive immersions (about 3–4 times) of the cordierite in the suspension were performed to achieve the expected loading of about 250 g·L^{-1} [27].

2.3. Hydrothermal aging treatment

To investigate the hydrothermal stability of catalyst, the monolithic SCR catalyst was hydrothermal aged in a quartz tube reactor, containing 10% H_2O and 90% air flowing at the rate of 2000 $cm^3{\cdot}min^{-1}$ for 12 h at 800 °C. The hydrothermal aged sample was named as Cu-18-X-A800, “X” stands for the number of catalyst and “A800” stands for hydrothermal aging treatment at 800 °C for 12 h.

2.4. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X’Pert Pro X-ray diffractometer over a 2θ range of 5° − 40° with the step size of 0.01° using Cu Kα irradiation. The Cu loading was carried out by ICP-AES (prodigy 7, Teledyne Leeman labs), after solid dissolution in