Applied Catalysis B: Environmental 220 (2018) 161–170

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Research Paper

New insight into Cu/SAPO-34 preparation procedure: Impact of NH_4-SAPO-34 on the structure and Cu distribution in Cu-SAPO-34 NH_3-SCR catalysts

Minhong Xu[a], Jun Wang[a], Tie Yu[d,**], Jianqiang Wang[a], Meiqing Shen[a,b,c,*]

[a] Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P.R. China
[b] State Key Laboratory of Engines, Tianjin University, Tianjin 300072, P.R. China
[c] Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, P.R. China
[d] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P.R. China

ARTICLE INFO

Article history:
Received 11 March 2017
Received in revised form 7 August 2017
Accepted 9 August 2017
Available online 12 August 2017

Keywords:
NH_4-SAPO-34
Cu-SAPO-34
Liquid ion exchange
NH_3-SCR
Si—(OH)—Al

ABSTRACT

Cu/SAPO-34 is a promising NH_3-SCR catalyst and its precise preparations involving ammonia exchange, copper loading and copper distribution are still the challenges in exchange procedure of SAPO-34 support. In the present work, a new series of x-NH_4-SAPO samples prepared by controlling NH_3 adsorption temperature (x standed for NH_3 adsorption temperature) were used to examine their impacts on the following Cu exchange compared with NH_4-SAPO-34 by traditional liquid exchange. The TPD and DRIFTS experiments revealed that the NH_4^+ amounts on x-NH_4-SAPO samples increased with the NH_3 adsorption temperature decreasing. And 200-NH_4-SAPO prepared by gas NH_3 adsorption (GA) under 200 °C contained the similar NH_4^+ loading with L-NH_4-SAPO prepared by the liquid ion exchange (LIE) method, but they presented different coordinations between NH_4^+ species and Si—(OH)—Al. After copper exchange, the H_2-TPR and EPR results unveiled monodentate NH_4^+ on Si—(OH)—Al structure would facilitate isolated Cu^{2+} generation in Cu/SAPO-34, while the polydentate NH_4^+ would promote CuO formation *via* liquid Cu ion exchange. Therefore, it was found that the isolated Cu^{2+} content in 200-Cu-SAPO was lower than L-Cu-SAPO even under the same copper exchange condition for different NH_4^+ coordinations. In addition, the *ex-situ* IR and NMR results demonstrated that the Si—O—Al bonds without NH_4^+ protections unveiled bond breakage during the liquid Cu exchange. Finally, our study proposed NH_4^+ exchange mechanism on Brønsted acid sites in NH_4-SAPO-34 and indicated their influences on the copper distribution and the support integrity for x-Cu-SAPO catalysts.

1. Introduction

Selective catalytic reduction of NO_x using ammonia (NH_3-SCR) has drawn wide attention as an advanced process for the catalytic removal of NO_x in the exhaust gas of diesel or lean-burn engines [1–8]. As early as 1992, Ishihara et al. [9] reported that copper-exchanged SAPO-34 exhibited superior high-temperature hydrothermal stability and excellent catalytic activity for the selective catalytic reduction of NO_x with propene (HC-SCR), compared to Cu-exchanged beta, USY and ZSM-5. Subsequent NH_3-SCR studies mostly focused on Cu-ZSM-5 and Cu-Beta for nearly 20 years. The research about Cu-SAPO-34 had not achieved progress for a long time until recent years. Since 2010, there have been dozens of literatures about Cu-SAPO-34 as NH_3-SCR catalysts due to the modification of the preparation procedure. In previous studies of Cu-SAPO-34 catalyst, Frache [10] reported that the total surface area and micropore volume of SAPO-34 dropped severely *via* the liquid ion exchange, when H-SAPO-34 was directly exchanged in Cu liquid solution. Akolekar et al. [11,12] also discovered the same phenomenon that SAPO-34 would undergo an extensive crystallinity loss upon direct copper ion exchange. Unlike the direct ion exchange process, H-SAPO-34 experienced two-step liquid ion exchange (TLIE) process could generate desired Cu-SAPO-34 right now [13–15]. First, H-SAPO-34 support was stirred in NH_4NO_3

---

* Corresponding authors at: School of Chemical Engineering and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, China. Tel./ Fax: (+86) 22-27892301.
** Corresponding author at: Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, China.
E-mail addresses: yutie043116@tju.edu.cn (T. Yu), mqshen@tju.edu.cn (M. Shen).

http://dx.doi.org/10.1016/j.apcatb.2017.08.031
0926-3373/

solution at a certain temperature to prepare NH_4-SAPO-34. Second, NH_4-SAPO-34 was exchanged in a copper solution to generate Cu-SAPO-34. Until now, several research groups have studied the catalytic performance and the nature of Cu species in homemade Cu-SAPO-34 catalysts, but still displaying different results after the liquid ion exchange process. In Gao's study [15], H-SAPO-34 was exchanged with 0.1 M NH_4NO_3 at 50 °C for 1 h to prepare NH_4-SAPO-34, and they pointed out that some ion exchanged Cu-SAPO-34 catalysts presented low specific surface areas, micropore volumes and poor crystallinity. In our previous studies [8,14], however, Cu-SAPO-34, with fairly good performances in many aspects, could be prepared by a mature ammonium exchange process. Therefore, it is seen that NH_4-SAPO-34 preparation step plays a significant role in protecting the structure of final Cu-SAPO-34. It is meaningful to find a systematic method to investigate the SAPO-34 behavior during the ion exchange process.

For H-SAPO-34 supports, hydrogen ions provide charge compensation of the Si-O-Al bonds and coordinate with ammonia species to form NH_4-SAPO-34 sample. In previous reports, NH_4-SAPO-34 could be synthesized through the ion exchange method by ammonia nitrates and ammonia adsorption on Si—(OH)—Al Brønsted acid sites [16,17]. The generated NH_4^+ was the dominant species for Cu substitution to prepare final Cu-SAPO-34 [14,15], but no literature explored the process of NH_4^+ replacement by copper ion during the Cu-exchanged process. Meanwhile, the precise copper loading and Cu^{2+} regulation and the relative exchange rates between H^+ and NH_4^+ with Cu^{2+} during liquid the ion exchange process have not been reported for the Cu-SAPO-34 system yet. In this research, we introduce the gaseous ammonia adsorption method (GA) to substitute liquid NH_4^+ ion-exchanged (LIE) method, which thereby preclude the influence of water upon the structural damage during the liquid ammonium ion exchange process. And the gaseous ammonia adsorption process is easily controllable, therefore, it is worthy to be examined for industrialized application.

In this study, we prepared a series of Cu-SAPO-34 catalysts through various NH_4-SAPO-34 samples by GA and LIE methods. The states of ammonium species in the NH_4-SAPO-34 samples were characterized by TPD, DRIFTS and NMR. The ICP, H_2-TPR and EPR results were used to determine the Cu species distribution. A combination of XRD, BET, *ex-situ* IR and NMR was applied to reveal the structural variation during copper exchange process. Furthermore, the NH_4-SAPO-34's impact on Cu species and catalyst structures was analyzed to explain the NH_3-SCR activities. Finally, we elucidated the unique characteristics of the gaseous ammonia adsorption samples during the liquid Cu ion exchange process.

2. Experiment

2.1. Catalyst synthesis

H-SAPO-34 support was synthesized by the hydrothermal method from a gel with a mole composition of 1.0 Al_2O_3: 0.8 SiO_2: 1.0 P_2O_5: 2.0 morpholine: 60 H_2O. The sources of aluminium, silicon and phosphorus were pseudoboehmite (70 wt% Al_2O_3), silica sol (25 wt% SiO_2) and orthophosphoric acid (85 wt% H_3PO_4) respectively and the detailed synthesis procedure was presented in our previous work [18].

For the gaseous ammonia adsorption procedure (GA), H-SAPO-34 firstly adsorbed NH_3 at different temperature (100, 200, 250 and 300 °C), and purged with N_2 to remove weakly adsorbed NH_3 at the adsorption temperature. These samples were named as "x-NH_4-SAPO", where x standed for NH_3 adsorption temperature.

However, for liquid NH_4^+ ion exchange procedure (LIE), ion exchange was conducted with H-SAPO-34 twice in 1.0 M ammonium nitrate solution at 80 °C for 1 h, and the pH was buffered during the process between 3.0 and 3.5. Then, the solid was filtered and washed with deionized water. The NH_4-SAPO-34 sample was dried at 100 °C for 12 h at least. The sample was named as "L-NH_4-SAPO".

Table 1
The composition of the Cu (H)-SAPO-34 catalysts.

Samples	Molar composition	Cu loading (wt%)
H-SAPO	$Si_{0.113}Al_{0.484}P_{0.403}O_2$	0
100-Cu-SAPO	$Si_{0.113}Al_{0.484}P_{0.403}O_2$	2.51
200-Cu-SAPO	$Si_{0.113}Al_{0.484}P_{0.403}O_2$	1.72
250-Cu-SAPO	$Si_{0.113}Al_{0.484}P_{0.403}O_2$	1.10
300-Cu-SAPO	$Si_{0.112}Al_{0.484}P_{0.404}O_2$	0.43
L-Cu-SAPO	$Si_{0.113}Al_{0.484}P_{0.403}O_2$	1.56

Then, all the NH_4-SAPO-34 samples were undergone the same liquid Cu ion exchange. The NH_4-SAPO-34 was added into copper (II) sulfate (98 w%, $CuSO_4{\cdot}5H_2O$, Tianjin Kewei Chemical Co., China) solution (0.35 M) according to BASF patent [19]. Then, the slurry was vigorously mixed at 70 °C for 2 h and then thoroughly filtered and washed with deionized water until a value of pH = 7 in filtrate was reached. Finally, the powder was dried for at least 12 h and calcined in a muffle furnace with air at 550 °C for 5 h. For the NH_4-SAPO-34 prepared by GA method, the corresponding Cu-SAPO-34 sample was named "x-Cu-SAPO", where x standed for NH_3 adsorption temperature. For the NH_4-SAPO-34 prepared by LIE method, the Cu-SAPO-34 sample was named as "L-Cu-SAPO".

2.2. Characterizations

Temperature-programmed desorption over NH_4-SAPO-34 samples (TPD) was carried out to evaluate the NH_3 loadings. The samples were elevated from 100 °C to 600 °C at a ramping rate of 10 °C min^{-1} in the N_2. A Fourier transform infrared (FTIR) spectrometer (MKS-2030) equipped with a 5.11 m gas cell was used to analyze the reactor outlet concentration.

The chemical compositions of the Cu (H)-SAPO-34 samples were tested by X-ray fluorescence (XRF) spectrometer (S4 Pioneer). Cu contents in Cu-SAPO-34 samples were determined by inductively coupled plasma and atomic emission spectrometry (ICP-AES), and the results were listed in Table 1.

The powder X-ray diffraction (XRD) measurements were carried out on Bruker D8 Advance TXS with nickel-filtered CuKα radiation (λ = 1.5418 Å), in the range from 10° to 45°, and with a step size of 0.02°. The specific surface areas (SSAs) of the samples were measured by a micropore physisorption analyzer (F-Sorb 3400) and calculated from the linear portion of the BET plot by measuring the N_2 isotherm of the samples at −196 °C. Before the measurements, the zeolites were degassed at 150 °C for 3 h under vacuum.

Temperature-programmed reduction by H_2 (H_2-TPR) experiments were carried out in a U-shaped tubular quartz reactor. Before the experiments, the samples were firstly pretreated in 5% O_2/N_2 at 500 °C for 30 min. Then, the samples were cooled down to room temperature in a flow of pure N_2 (30 mL min^{-1}) to purge the residual gaseous and weakly adsorbed oxygen. In the H_2-TPR process, the samples were elevated from room temperature to 900 °C at a ramping rate of 10 °C min^{-1} in a flow of 5% H_2/N_2 (15 mL min^{-1}). The consumption of hydrogen was monitored by a PX200 thermal conductivity detector (TCD), and the baseline offset was subtracted based on the H_2 consumption of the H-SAPO-34 sample.

Electron Paramagnetic Resonance (EPR) spectra were recorded on Bruker A300 at room temperature and atmospheric pressure. Prior to the EPR analyses, Cu-SAPO-34 samples were pretreated in 20% O_2/N_2 at 500 °C for 2 h. Bruker A300 software was used for subsequent data analysis.

Diffuse reflectance infrared Fourier-transform spectra (DRIFTS) were obtained on a Nicolet 6700 FTIR equipped with a MCT detector