NH_3-SCR activity and hydrothermal stability of one-step hydrothermally synthesized Cu-SAPO-34 catalysts

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Introduction

The selective catalytic reduction of NO_x by NH_3 (NH_3-SCR) is one of the most promising technologies for NO_x emission control for diesel engines. Cu-chabazite (CHA) catalysts show higher activity and better hydrothermal stability compared to other Cu-based zeolites, such as Cu-ZSM-5 and Cu-beta [1-3]. The reported one-step hydrothermal synthesis method was designed to obtain the Cu-SAPO-34 catalyst using low-cost copper-tetraethylenepentamine (Cu-TEPA) as a novel template, which is beneficial for the wide use of Cu-SAPO-34 catalyst. Compared with the conventional ion exchange method, the direct route introducing high Cu loading achieves high dispersion of Cu species. The SCR catalytic performance and hydrothermal stability of this zeolite with different Cu loadings and catalyst composition were investigated in detail.

Materials and Methods

A series of Cu-SAPO-34 catalysts were prepared by one-step synthesis using copper-containing templates. First, distilled water, pseudoboehmite, phosphoric acid and fumed silica were mixed and stirred until a gel mixture was formed. Then, copper sulfate and tetraethylenepentamine (TEPA) were added to the mixture. Finally, propylamine (PA) was added as co-template to adjust the Cu loading. The resulting gel was transferred to an autoclave with a Teflon liner, and heated at 180 °C under static conditions for 48 hours. The crystalline products were filtered and washed with abundant water and dried at 100 °C overnight. The samples were calcined at 700 °C in air to remove the organic templates. All the SCR activity tests for the catalysts were carried out in a fixed-bed quartz tube flow reactor at atmospheric pressure. The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, balance N_2 and 500 ml/min total flow rate. During the performance tests, about 60 mg catalyst was used, yielding a rather high GHSV of 400,000 h^{-1}. The hydrothermal treatment was carried out with a gas condition of air and 10% H_2O at 750 °C for 16 h to obtain the aged catalysts.

Results and Discussion

Through adjusting the amount of Cu-TEPA and PA, Cu-SAPO-34 catalysts with different Cu loadings were obtained. **Table 1** summarizes the chemical composition of all samples, with Cu loadings varying from 2-6%. The contents of other elements such as Al, Si, P were basically the same, and Si/Al ratios were 0.28-0.41. The NO_x conversion as a function of reaction temperature between 150 and 550 °C over Cu-SAPO-34 catalysts with different Cu loadings is shown in **Figure 1 a**. The $Cu_{2.95}$-SAPO-34 catalyst with the lowest Cu loading exhibited the lowest performance at 150-400 °C compared with the others. With increased Cu loading, the NO_x conversion at 150-350 °C improved. For the $Cu_{3.27}$-SAPO-34 catalyst, the NO_x conversion reached *ca.* 98% at 250 °C and maintained a level above 80% until 500 °C. After hydrothermal treatment of the $Cu_{3.27}$-SAPO-34 catalyst at 750 °C for 16 hours , a slight improvement was observed in the SCR performance at 150-300 °C. The NO_x conversion remained higher than 80% from 225 to 400 °C, indicating good hydrothermal stability (**Figure 1 b**).

Table 1. Chemical composition of catalysts

Catalysts	Concentration (wt. %)[a]				
	Cu	Al	Si	P	Si/Al
$Cu_{2.95}$-SAPO-34	2.95	17.96	5.00	14.56	0.28
$Cu_{3.27}$-SAPO-34	3.27	17.77	7.14	14.08	0.40
$Cu_{4.56}$-SAPO-34	4.56	17.44	7.07	14.27	0.41
$Cu_{5.28\%}$-SAPO-34	5.28	16.76	5.00	14.28	0.30

[a] Obtained by ICP

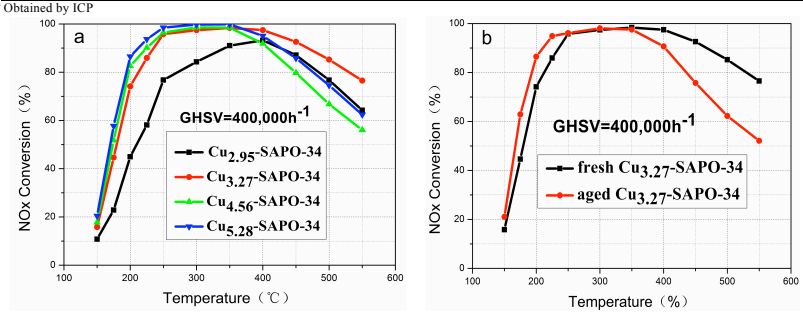

Figure 1 a. NO_x conversion over catalysts with different Cu loadings
b. NO_x conversion over fresh and aged $Cu_{3.27}$-SAPO-34

Significance

The reported one-step hydrothermal synthesis method can save production cost. More importantly, the obtained catalyst exhibits good NH_3 SCR activity and hydrothermal stability.

References

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