Tuning the low temperature catalytic activity of Cu-SSZ-13 over NO SCR: Control of Al content and acidity

Soon Hee Park,[a] Ha Na Jeong,[b] Kwan-Young Lee,[c] Yun Sung Lee,[b] Young Jin Kim,[d] Chang Hwan Kim,[d] Sung June Cho[b,*]

[a]*Ultra Low Energy & Emission Vehicle Center, Korea University, Seoul, 02841, Republic of Korea*
[b]*Department of Chemical Engineering, Chonnam National University, Gwangju, 61186, Republic of Korea*
[c]*Department of Chemical and Biological Engineering, Korea University, Seoul, 02841, Republic of Korea*
[d]*Advanced Catalysts and Emission-Control Research Laboratory, R & D Division, Hyundai Motor Group, Hwaseong 18280, Republic of Korea*
**Corresponding author: +82-62-530-1909, sjcho@chonnam.ac.kr*

Abstract: Low temperature activity of Cu-SSZ-13 over NO selective catalytic reduction (SCR) using NH_3 has been investigated by the control over the Al content, thereby changing the acidity and the Cu content. The Si/Al_2 ratio in SSZ-13 was controllable in the range of 8 – 40 through adjusting synthesis condition. The size of SSZ-13 particle has been varied from 500 nm to 3 μm with the Al content. The low temperature activity of NO SCR below 473 K has been improved through the control of Cu content while the high temperature activity above 673 K has also been deteriorated.
Keywords: NO SCR, Cu-SSZ-13, Low temperature activity.

1. Introduction

Copper ion exchanged chabazite (CHA) zeolite of high silica (Cu-SSZ-13) has been utilized extensively for selective catalytic reduction of NOx using ammonia.[1] The content of copper and the corresponding location affected the catalytic performance critically and also hydrothermal stability. The ion exchange level of Cu^{2+} in CHA can be determined with the Si/Al_2 ratio which has been difficult to control because the direct conversion of Y zeolite resulted in the overall Si/Al_2 in addition to the zeolite product yield.[2]

In this work, the Si/Al_2 in the CHA zeolite was controlled readily to the range of 8 - 40 while the hydrothermal synthesis condition was varied. The CHA zeolite was synthesized employing trimethyl adamantylammonium ion or benzyltrimethyl ammonium ion as a structure directing agent at 413 K for 4 days under rotation at 40 rpm in the presence or absence of seed zeolite crystals, NH_4^+-exchanged Y. The CHA zeolite of different Si/Al_2 was also subjected to the Cu ion exchange for further study on the location of Cu, its hydrothermal stability and finally the catalytic performance at low temperature in selective catalytic reduction of NO.

2. Experimental

Briefly, SSZ-13 was prepared using the following gel composition: SiO_2 : xNaOH : ySDA : zH_2O where x, y and z can be varied in the range 0.1 to 0.3, 0.1 to 0.4 and 20 to 30, respectively. As SiO_2 and SDA source, the ultrastable Y zeolite or sodium silicate and trimethyl adamantylammonium ion or benzyltrimethyl ammonium ion were employed respectively to control the Al content. The hydrothermal synthesis was performed at 400 ~ 423 K for no less than 4 day. The obtained samples were calcined at 823 K and subsequently ion exchanged with copper salts. The copper containing chabazite (Cu-SSZ-13) was subjected to the catalytic reaction in which the NO and NH_3 were 350 ppm, respectively with 5% oxygen, 3% water and nitrogen balance.

3. Results and discussion

Figure 1 shows the morphology of the SSZ-13 with different Si/Al_2 ratio which was determined by the elemental analysis and ^{29}Si MAS NMR. The particle size at low Si/Al_2 was 3 μm while the corresponding size was decreased to 500 nm only with the increasing Si/Al_2.

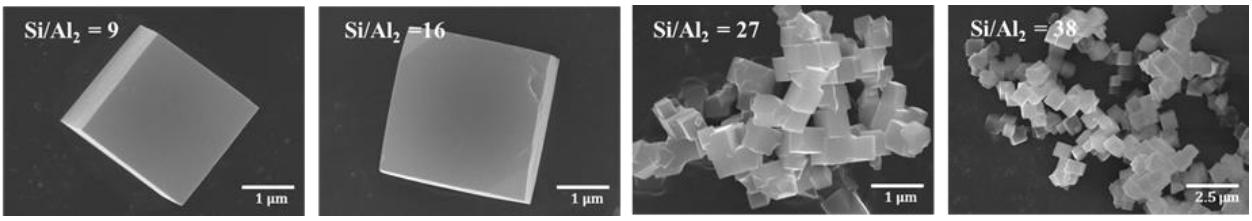

Figure 1. Scanning electron micrograph of SSZ-13 with different Si/Al_2 ratio.

The copper content in SSZ-13 with Si/Al_2 ratio of 16 was controlled to 2.1, 3.5 and 5.0 wt%, respectively in order to investigate the effect of Cu loading on low temperature activity over NO SCR. Figure 2 shows the catalytic conversion as a function of temperature. The low temperature activity was found to be improved with the increase of Cu content while the high temperature activity was decreased significantly, which can be probably due to NH_3 oxidation. The hydrothermal aging of the Cu-SSZ-13 catalyst at 1023 K for 12 h did not affect the initial activity at all.

In the meantime, NH_3 storage capacity was increased to ~ 1 mmol per gram catalyst containing higher Al content without deterioration of catalytic activity. Also, the NO adsorption as NO_2 on Cu was doubled because of large Cu content, 5 wt%.

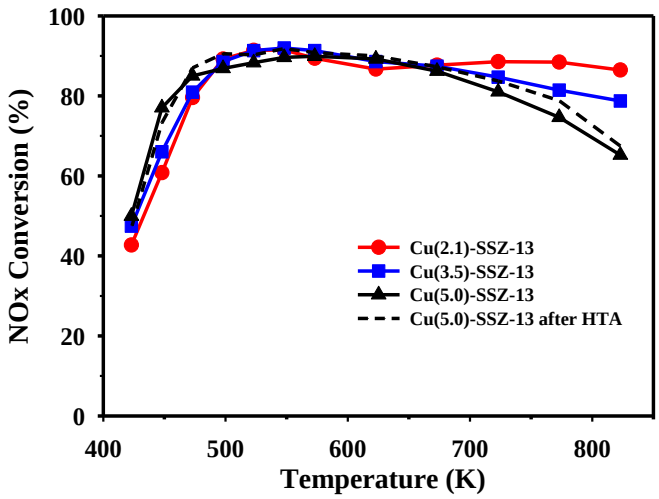

Figure 2. NO SCR activity for Cu-SSZ-13 catalyst. The number in the parenthesis is Cu loading. The reaction condition was [NO] = $[NH_3]$ = 350 ppm, $[O_2]$ = 5%, $[H_2O]$ = 3% and N_2 balance at GHSV ≈ 50,000 h^{-1}

4. Conclusions

In the present work, the low temperature catalytic activity of Cu-SSZ-13 catalyst over NO SCR was tuned by changing the Al content and consequently Cu content and acidity. The low temperature activity can be increased at the expense of high temperature activity when Cu content was increased. In the meantime, the resulting NH_3 and NO storage capacity can also be controllable, which can be beneficial for the improvement of low temperature activity.

This work was supported by the Korea Research Foundation funded by the Korea government (Ministry of Science, ICT & Future Planning) (NRF-2016R1A5A1009592).

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