Applied Catalysis B: Environmental 200 (2017) 428–438

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Synthesis of zeolite UZM-35 and catalytic properties of copper-exchanged UZM-35 for ammonia selective catalytic reduction

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ARTICLE INFO

Article history:
Received 11 June 2016
Received in revised form 19 July 2016
Accepted 20 July 2016
Available online 20 July 2016

Keywords:
UZM-35 and Cu-UZM-35
Synthesis
Characterization
NH_3-SCR
Hydrothermal stability

ABSTRACT

The synthesis of zeolite UZM-35 with the MSE topology and the catalytic properties of copper-exchanged UZM-35 (Cu-UZM-35) for the selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) are presented. When the simple dimethyldipropylammonium cation is used as an organic structure-directing agent together with Na^+ and K^+, crystallization of pure UZM-35 is very sensitive not only to the types of Al and Si sources employed, but also to the SiO_2/Al_2O_3 and $K_2O/(Na_2O+K_2O)$ ratios in the synthesis mixture. In the temperature range studied, fresh Cu-UZM-35 shows comparable deNOx performance to fresh Cu-SSZ-13, the best NH_3-SCR catalyst known to date. When hydrothermally aged at 750 °C, although the latter catalyst outperforms the former one, the operating temperature window of Cu-UZM-35 is considerably wider than that of Cu-SSZ-13. Like Cu-beta, Cu-UZM-35 also produces a higher amount of N_2O during SCR than Cu-SSZ-13 and Cu-ZSM-5. However, it shows a significantly lower NH_3 oxidation activity than Cu-SSZ-13 and Cu-ZSM-5. The overall characterization results of this study demonstrate the highly stable nature of framework Al atoms in the large-pore zeolite UZM-35 and their strong interactions with Cu^{2+} ions. This may lead to a moderate alteration of exchanged Cu^{2+} ions to CuO_x and $CuAl_2O_4$ phases at high temperatures, thus rendering Cu-UZM-35 hydrothermally stable during NH_3-SCR.

1. Introduction

Nitrogen oxides (NO_x) are the major source of acid rain and photochemical smog, continuously threatening the health of mankind [1]. With the popularization of high fuel-efficient diesel vehicles, their emission has become a primary environmental concern. Consequently, ever-tightening emission standards have been issued worldwide to improve air quality [2]. Among the deNOx technologies currently available, selective catalytic reduction of NO_x with urea (urea-SCR) is recognized as the most effective and promising technology to meet the strict upcoming emission regulations such as Euro VI and EPA Tier 3 [3,4].

In general, the diesel exhaust temperature ranges from 150 to 350 °C. Hence, much attention has been focused on transition metal-exchanged zeolites with an excellent low-temperature SCR activity, primarily copper-exchanged ZSM-5 (framework type MFI) with two intersecting 10-ring channels [5,6]. However, their low hydrothermal stability has placed an obstacle in the way of commercial success, because the diesel exhaust temperature can rise periodically to above 700 °C during the regeneration of diesel particulate filters installed before or after the SCR reactor [7,8]. In this regard, the discovery by BASF researchers in 2009 [9] that especially after being hydrothermally aged at 750 °C, Cu-SSZ-13 (CHA) with large 20-hedral ($[4^{12}6^28^6]$) *cha*-cages connected by small 8-ring windows, becomes much more active for reducing NO_x than Cu-ZSM-5, the best low-temperature NH_3-SCR catalyst up to that time [10,11], offered a major breakthrough in the urea-SCR technology. Since then, considerable efforts have been devoted not only to the elucidation of the nature of active sites in Cu-SSZ-13 [12–15], but also to the search for other copper-exchanged zeolites that could be hydrothermally more stable during NH_3-SCR than Cu-SSZ-13.

Zeolite MCM-68 (MSE) was first discovered in 1997 by Weston and Dhingra of Mobil, with the patent being released a few years later [16]. As shown in Fig. 1, MCM-68 contains a three-dimensional pore system consisting of one type of straight 12-ring (6.4 × 6.8 Å) channels and two types of tortuous 10-ring (5.2 × 5.8 and 5.2 × 5.2 Å) channels. The two 10-ring channels intersect with each other, forming a large cylindrical cage circumscribed by 12-

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http://dx.doi.org/10.1016/j.apcatb.2016.07.040
0926-3373/