Catalysis Communications 11 (2010) 955–959

Contents lists available at ScienceDirect

Catalysis Communications

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

The promotional effect of Cr on catalytic activity of Pt/ZSM-35 for H_2-SCR in excess oxygen

Qing Yu [a], Manfred Richter [b], Landong Li [a], Fanxiao Kong [a], Guangjun Wu [a], Naijia Guan [a,*]

[a] Key Lab of Functional Polymer Materials (Nankai University, Ministry of Education), College of Chemistry, Nankai University, Tianjin, 300071, PR China
[b] Leibniz Institute for Catalysis, University of Rostock, Albert-Einstein-Str. 29A, Rostock, Germany

ARTICLE INFO

Article history:
Received 7 January 2010
Received in revised form 10 March 2010
Accepted 30 March 2010
Available online 8 April 2010

Keywords:
Chromium
Pt/ZSM-35
H_2-SCR
NH_4^+

ABSTRACT

Selective catalytic reduction of NO by hydrogen was studied over Cr modified Pt/ZSM-35 catalysts. The preparation process greatly influenced catalytic activity and sample prepared by co-impregnation method exhibits the best activity. In situ DRIFT studies revealed that on Pt–Cr/ZSM-35, (1) new Pt-$NO^{\delta+}$ and NO species adsorbed on Pt were detected upon $NO + O_2$ adsorption; (2) much more ammonia species were formed under reaction condition. Cr addition not only enhanced the adsorption of NO_x but also promoted the formation of surface NH_4^+ species, which should be the origin of promotional effect of Cr on Pt/ZSM-35 for H_2-SCR reaction.

1. Introduction

Selective catalytic reduction (SCR) is one of the most effective and practical method of NO_x abatement in excess oxygen. In the past decades, hydrocarbon [1–4], ammonia [5,6] and hydrogen [7–11] were reported to be active reductants in SCR reaction. Among the reductants mentioned, less processed and less expensive nontoxic hydrogen is particularly attractive because of the high activity of H_2-SCR at low temperatures of <200 °C.

Platinum catalysts [12,13] and palladium catalysts [14,15] have been shown to be active for H_2-SCR reaction. For these catalysts, high activity and selectivity at relatively low temperature is of great challenge. Different modifiers have been employed to improve the activity and selectivity for certain H_2-SCR catalyst. Yokota et al. reported that addition of Mo and Na [16], which reduced the oxidation efficiency of Pt, enhanced the NO conversion and N_2 selectivity of Pt/SiO_2. Burch and Machida also studied the effect of Na addition on the performance of Pt/Al_2O_3 [17] and Pt–ZSM-5 [18], respectively. However, the effect of Na addition is very much dependent on the types of catalyst supports. Kureti et al. [19] claimed that the introduction of tungsten to Pt/ZrO_2 increased the electron density on Pt and thus activated the catalyst for H_2-SCR. The addition of Ti species also enhanced the activity and selectivity of Pt/Si-MCM-41 in H_2-SCR by changing existence state and dispersion of platinum [20].

ZSM-35 with two-dimensional channel system (10 MR of 4.2*5.4 Å and 8 MR of 3.5*4.8 Å) belongs to FER family. In our previous work [21], the performance of several Pt based zeolites for H_2-SCR reaction was investigated. Among all catalysts, Pt/ZSM-35 exhibited the most attractive activity (120 °C NO conversion of 80.8%, S_{N2} of 68.5%), which is better than Pt/ZSM-5 (120 °C NO conversion of 65.3%, S_{N2} of 42.7%). In the present work, ZSM-35 zeolite is still of our most concern. Chromium is selected and used as promoter to improve the performance of Pt/ZSM-35 in H_2-SCR. In situ DRIFT study together with H_2-TPR is employed to get insight into the origin of the promotional effect of Cr.

2. Experimental

2.1. Catalysts preparation

Parent NaZSM-35 zeolite ($SiO_2/Al_2O_3 = 30$) were kindly provided by Prof. Yuan's group of Nankai University. The hydrogen form zeolite was obtained by ion exchange of calcined NaZSM-35 with aqueous solution of ammonium nitrate three times at 80 °C for 10 h, followed by drying at 70 °C overnight and calcined at 550 °C for 6 h.

0.5%Pt/ZSM-35 catalyst was prepared by wet incipient impregnation using K_2PtCl_6 as precursor. For modification, the HZSM-35 powders were suspended in an aqueous solution of $Cr(NO_3)_3$ and K_2PtCl_6. For comparison, the impregnation order of Cr and Pt was also changed: xPt/yCr/ZSM-35 catalysts were obtained by depositing K_2PtCl_6 onto y%Cr/ZSM-35 sample while yCr/xPt/ZSM-35 catalysts were obtained by depositing $Cr(NO_3)_3$ onto x%Pt/ZSM-35. After impregnation, all samples were dried at 70 °C overnight and calcined at 550 °C in air for 3 h.

* Corresponding author. Tel.: +86 22 23509140; fax: +86 22 23500319.
E-mail address: guannj@nankai.edu.cn (N. Guan).

1566-7367/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2010.03.021

2.2. Catalysts characterization

Temperature programmed reduction by hydrogen (H_2-TPR) was carried out in a quartz U-shaped reactor and H_2 consumption was monitored by a calibrated thermal conductivity detector (GOW-MAC Instruments). 0.2 g of the sample was pretreated at 400 °C for 30 min in air flow at 50 ml/min, followed by cooling down to 25 °C in N_2 flow. Then H_2-TPR of the samples was started by exposure to 5%H_2/Ar and elevating the temperature to 550 °C at a heating rate of 10 °C/min.

2.3. Activity test

The selective catalytic reduction of NO by hydrogen at atmospheric pressure was carried out in a fixed-bed flow microreactor. The typical reactant gas composition was NO (1000 ppm), H_2 (5000 ppm), O_2 (6.7%), and the balance He. The total flow of the inlet gas was set at 100 ml/min. A sample weight of 50 mg was employed, corresponding to the gas hourly space velocity (GHSV) of 80000/h. Prior to testing, the samples were activated in He (100 ml/min) at 500 °C for 30 min. The products were analyzed on-line using a gas chromatograph (HP 6890 series) equipped with a TCD detector. A molecular sieve 5A column served for the separation of H_2, N_2, O_2, and a porapak Q column for the separation of N_2O and NO. Simultaneous analysis of NO, NO_2 and NH_3 was accomplished by a three-channel multigas sensor (Limas 11HW, ABB, Germany). The results are described in terms of NO conversion, N_2 selectivity (S_{N_2}) and H_2 conversion, which are calculated on the basis of Eqs. (1)–(3):

$$NO\ \ conv.=\frac{[NO]_0-[NO]}{[NO]_0}\times 100\% \tag{1}$$

$$N_2\ \ conv.=\frac{[H_2]_0-[H_2]}{[H_2]_0}\times 100\% \tag{2}$$

$$S_{N_2}=\frac{2[N_2]}{1000\times(NO\ \ conv.)}\times 100\% \tag{3}$$

$[NO]_0$ represents the inlet concentration of NO, [NO] represents the outlet concentration of NO, $[H_2]_0$ represents the inlet concentration of H_2, $[H_2]$ represents the outlet concentration of H_2 and $[N_2]$ represents the outlet concentration of N_2.

2.4. In situ DRIFT studies

The in situ DRIFT studies were carried out using a Bruker Tensor 27 spectrometer equipped with a heatable and evacuable IR cell with ZnSe windows, connected to a gas dosing system. For each experiment, the catalyst was activated at 400 °C under helium for 1 h, and then its absorption was measured at each desired temperature (coded as S_c). The IR spectra of surface species shown

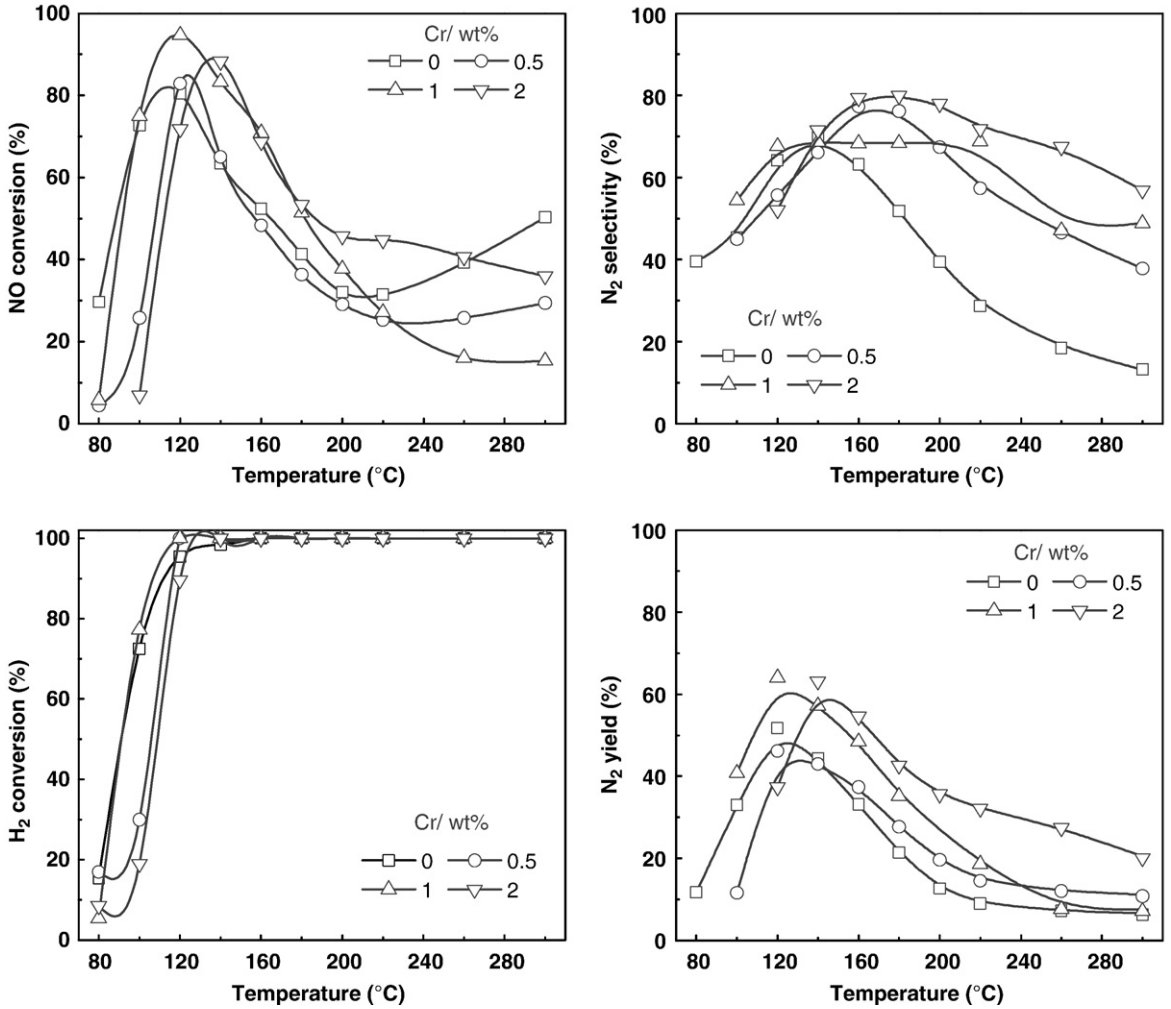

Fig. 1. Catalytic performance of 0.5%Pt–x%Cr/ZSM-35 in H_2-SCR. Reaction conditions: 0.1% NO, 0.5% H_2, 6.7% O_2 and He balance, GHSV = 80000 h^{-1}.