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Catalytic reduction of NO by NH_3 over Fe–Cu–O_X/CNTs-TiO_2 composites at low temperature

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ABSTRACT

Activity of iron–copper oxides supported on TiO_2 and carbon nanotubes (CNTs) for low-temperature selective catalytic reduction of NO by NH_3 in the presence of oxygen was investigated. The addition of FeO_X and CNTs synergistically promoted the NO conversion through the adsorption of NO and NH_3 and the catalytic oxidation of NO to NO_2. NO_2 adsorbed on the surface of the catalysts was found to be essential for NO reduction at low temperature, and approximately 90% NO conversion could be achieved at reaction temperature as low as 150 °C. Moreover, it was found that the deactivation caused by H_2O could be recovered after H_2O was switched off, while the deactivation caused by SO_2 was dependent on the reaction temperature.

1. Introduction

Nitrogen oxides (NO_X), which induce the formation of acid rain and ground-level ozone and cause respiratory problems, are therefore harmful for the ecosystem and humanity. Selective catalytic reduction (SCR) of NO_X by NH_3 in the presence of oxygen is one of the most effective methods to decrease the NO_X levels in gaseous emissions [1]. In recent decades, a variety of SCR catalysts have been developed for possible application, which can be divided into three groups, namely, noble metals, ion-exchanged zeolites, and metal oxides. Among them, V_2O_5-WO_3/TiO_2 has been widely accepted as an industrial catalyst despite the fact that vanadium protoxide is toxic and V_2O_5-WO_3/TiO_2 is only active within a narrow and high temperature window (300–400 °C) [2–5]. So it is necessary to develop novel catalysts to reduce the vanadium loadings or replace the vanadium with other metal elements. For this reason, many researchers continue to modify current catalysts. Moreno-Tost et al. [6] investigated cobalt–iridium supported on zirconium-doped mesoporous silica as catalysts for NH_3-SCR and found out Co–Ir supported catalysts showed higher NO conversion than Co supported catalyst. Wu et al. [7] reported a MnO_X–CeO_2 catalyst which has a high NO_X conversion within a low temperature range (80–220 °C). Lu et al. [8] reported that CeO_2 supported on ACF obtained 70% NO conversion at 150 °C.

Cu and Fe are two of the typically studied transition metals in SCR catalysts. Catalytic behaviors of Cu and Fe zeolites in the NH_3-SCR of NO [9,10] as well as in the HC-SCR of NO_X have been studied systematically [11,12]. Also, copper oxides and iron oxides, supported on Al_2O_3 [13], TiO_2 [14], SiO_2 [15], ZrO_2 [16], and carbonaceous material [17,18], are found to be active in medium temperature SCR of NO. However, exhaust gases usually contain a large amount of fly ash and SO_2, which severely deactivate the catalysts. Thus, further lowering the de-NO_X temperature is necessary so that SCR systems can be installed downstream of the desulfurizer and the electrostatic precipitator.

Recently, it was reported that carbon nanotubes (CNTs) are good adsorbents of NO_2, O_2, VOCs and NH_3 [19]. We also found that the addition of CNTs was beneficial for the SCR of de-NO_X and De-VOCs over a variety of metal oxide catalysts [20–22]. Based on our foregoing research, we prepared CNTs and TiO_2-supported iron and copper oxides by sol–gel method and studied their performance for NO reduction at low temperatures in the present study.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by a sol–gel method. The purified CNTs [23] were first sonicated in ethanol for 30 min for good dispersion. Tetrabutyl titanate was then added, and the solution was sonicated for another 30 min. Copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$], ferric nitrate [$Fe(NO_3)_3{\cdot}9H_2O$], and acetic acid were dissolved in distilled water and ethanol and added into the above solution. The resulting solution was sonicated until sols were formed. The sols were aged at ambient conditions to obtain good gels, which were air-dried at 100 °C overnight and then calcined at 500 °C for 4 h in

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