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Article

Mn/beta and Mn/ZSM-5 for the low-temperature selective catalytic reduction of NO with ammonia: Effect of manganese precursors

Wenjin Xu [a], Guangxu Zhang [a,*], Hanwei Chen [a], Guomeng Zhang [b], Yang Han [a], Yichuan Chang [a], Peng Gong [a]

[a] *School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, Wuhan 430070, Hubei, China*
[b] *Shanghai Hengyuan Marine Equipment Co., Ltd., Shanghai 201709, China*

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ABSTRACT

Two series of Mn/beta and Mn/ZSM-5 catalysts were prepared to study the influence of how different Mn precursors, introduced to the respective parent zeolites by wet impregnation, affected the selective catalytic reduction (SCR) of NO by NH_3 across a low reaction temperature window of 50–350 °C. In this study, the catalysts were characterized using N_2 adsorption/desorption, X-ray diffraction, X-ray fluorescence, H_2 temperature-programmed reduction, NH_3 temperature-programmed desorption and X-ray photoelectron spectroscopy. As the manganese chloride precursor only partially decomposed this primarily resulted in the formation of $MnCl_2$ in addition to the presence of low levels of crystalline Mn_3O_4, which resulted in poor catalytic performance. However, the manganese nitrate precursor formed crystalline MnO_2 as the major phase in addition to a minor presence of unconverted Mn-nitrate. Furthermore, manganese acetate resulted principally in a mixture of amorphous Mn_2O_3 and MnO_2, and crystalline Mn_3O_4. From all the catalysts screened, the test performance data showed Mn/beta-Ac to exhibit the highest NO conversion (97.5%) at 240 °C, which remained >90% across a temperature window of 220–350 °C. The excellent catalytic performance was ascribed to the enrichment of highly dispersed MnO_x (Mn_2O_3 and MnO_2) species that act as the active phase in the NH_3-SCR process. Furthermore, together with a suitable amount of weakly acidic centers, higher concentration of surface manganese and a greater presence of surface labile oxygen groups, SCR performance was collectively enhanced at low temperature.

1. Introduction

Nitrogen oxides (NO_x) are significant atmospheric pollutants that have significant impact on both air quality and human health and that result from the burning of fossil fuels such as refined crude oil products (petrol and diesel) or solid coal, from cars, ships and industrial processes [1–3]. Selective catalytic reduction (SCR) of NO_x is reported to be an already feasible and mature process, which is widely applied to flue gas denitrification [4,5]. The SCR denitration catalyst is one of the key components in a SCR system, with typical commercial catalysts such as V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 being employed as the active components in this system [6]. There are, however, some shortcomings related the aforementioned catalysts, for example, the narrow working temperature window (300–400 °C) and the toxic effect of V_2O_5. Hence, there has been a wealth of interdependent research focusing on developing new highly effective and environmentally friendly SCR catalysts

* Corresponding author. Tel: +86-13871467069; E-mail: zhanggx2002@163.com
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[7,8].

Over the past few years, researchers have developed increasingly attractive and efficient SCR catalysts. Owing to the particular features, various transition metals (Cr, Mn, Fe, Cu and Ce) have been studied as the active components for SCR catalysts [9,10]. In particular, manganese-based catalysts are a current hot topic of interest because of the multiple valences, labile oxygen and diversiform oxidation states of manganese (Mn_3O_4, Mn_2O_3, MnO_2, MnO) [11,12]. Mn-based supported catalysts have attracted significant attention with respect to the manganese precursor used. Hwang *et al.* [13] used manganese(II) nitrate, manganese(II) acetate and manganese(III) acetate to prepare MnO_x/TiO_2 catalysts through a sol-gel method, concluding that the catalysts synthesized with manganese acetate showed higher catalytic performance as a result of abundant MnO_2 species and strong acid sites. Fang *et al.* [14] claimed that catalysts prepared from manganese acetate and manganese carbonate, containing Mn_2O_3 and Mn_3O_4, resulted in superior catalytic performance when compared with the corresponding catalysts prepared by manganese nitrate and manganese sulfate. However, Pena *et al.* [15] observed that catalysts prepared using manganese nitrate yielded MnO_2 and displayed enhanced catalytic performance than the corresponding catalyst prepared with manganese acetate. There remains on-going debate over how catalytic activity is influenced by the active phase of Mn-based catalysts prepared with different precursors. Therefore, to elucidate the influence of Mn precursors it is of interest to further investigate SCR performance and surface MnO_x species over Mn-based catalysts.

Furthermore, TiO_2 exhibits poor specific surface areas, which is thought to hinder the performance of Mn-based supported catalysts [16]. However, other supports that include transition metal oxides [17], carbon materials [18] and zeolites [19] have been widely used for the preparation of Mn-containing catalysts. Zeolites possess several advantageous characteristics such as large specific surface areas, unique pore structures and abundant acid sites, and are reported to be excellent catalyst supports [2,20]. Recent trends in zeolite-based catalysts have led to a proliferation of studies, such as MnO_x/ZSM-5 [21], MnO_x/beta [22], MnO_x/USY [23] and MnO_x/SAPO-34 [24]. Among these catalysts, the ZSM-5 series of catalysts [25,26] have attracted significant attention as alternative SCR catalysts. Additionally, there is significant research focus on metal-modified beta zeolite because of the superior hydrothermal stability reported in recent years. For example, Frey *et al.* [27] demonstrated that Fe/beta exhibited higher activity than Fe/ZSM-5 and Fe/ZSM-12 across a broad temperature window. Additionally, Corma *et al.* [28] reported a stable Cu-beta catalyst having SCR activity as high as that of Cu/ZSM-5. These studies suggest that beta zeolite has been regarded as a promising SCR catalyst support. Hitherto, significant efforts have focused on Mn/ZSM-5 in terms of preparation methods, calcination temperature and catalytic behavior [16,29]. Nevertheless, there are few reports offering insight into the SCR performance and physicochemical properties of Mn/beta; while, in addition, the influence of manganese precursors on NH_3-SCR performance of Mn/ZSM-5 and Mn/beta remains unclear. Accordingly, further studies are required to conduct systematic research on manganese-modified beta zeolite.

In this paper, different Mn precursors such as manganese nitrate, manganese acetate and manganese chloride were employed to prepare Mn/ZSM-5 and Mn/beta catalysts *via* wet impregnation, and the catalytic performance compared at 50–350 °C. Characterization methods including N_2 adsorption/desorption, X-ray diffraction (XRD), X-ray fluorescence (XRF), H_2 temperature-programmed reduction (H_2-TPR), NH_3 temperature-programmed desorption (NH_3-TPD) and X-ray photoelectron spectroscopy (XPS) were used to identify the surface active MnO_x species over the catalysts and to investigate the influence of the manganese precursors on SCR performance.

2. Experimental

2.1. Catalyst preparation

Commercial H/beta and H/ZSM-5 (Si/Al = 25, Nankai University, China) served as the supports, and different Mn precursors such as manganese nitrate ($Mn(NO_3)_2$, 50% solution, Aladdin, China), manganese acetate ($Mn(CH_3COO)_2•4H_2O$, Aladdin, China) and manganese chloride ($MnCl_2•4H_2O$, Aladdin, China) were employed as the source of Mn to fabricate Mn/beta and Mn/ZSM-5 catalysts *via* wet impregnation. A desired quantity of manganese precursors and 50 mL distilled water formed the required solution to which 10 g of zeolite support (H/beta or H/ZSM-5) was added. The mixtures were constantly stirred at 30 °C for 5 h, before heating in a water bath at 80 °C to remove the excessive moisture. Thereafter, the samples were dried at 100 °C overnight and then calcined at 400 °C for 5 h in air. The obtained catalyst powders were ground to 100–200 mesh, pressed to form tablets using a tableting press, and crushed to 20–40 mesh. The catalysts were denoted as Mn/beta-*x* or Mn/Z-*x*, where *x* represents Ac (manganese acetate), NO_3 (manganese nitrate) and Cl (manganese chloride). For example, Mn/beta-Ac or Mn/Z-Ac corresponds to Mn/beta or Mn/ZSM-5, respectively, prepared from the manganese acetate precursor. In this study, Mn loading was fixed at 20 wt% (based on the support) for all catalysts.

2.2. Catalyst activity test

For all prepared catalysts, SCR performance was evaluated using a fixed-bed quartz reactor (inner diameter 13 mm) at a reaction temperature of 50–350 °C under atmospheric pressure. The reactor was equipped with a temperature-programming controller. Catalyst (1.5 cm^3) was used for the catalytic assessment with a gas hourly space velocity (GHSV) of 50000 h^{-1}, with the simulated flue gas (total flow rate of 1250 mL/min) comprising 0.1% NO, 0.11% NH_3, 5% O_2, and N_2 as the balance gas. An online flue gas analyzer (Gasboard 3000) was employed to record the concentration of NO.

NO conversion was determined by the following equation:

$$X_{ON}\% = \frac{[NO]_{inlet} - [NO]_{outlet}}{[NO]_{inlet}} \times 100$$