Research article

Promotional effect of iron modification on the catalytic properties of Mn-Fe/ZSM-5 catalysts in the Fast SCR reaction

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ABSTRACT

A series of Mn-Fe/ZSM-5 catalysts with varying amounts of iron doping were prepared via the impregnation method and their catalytic activities in Fast SCR and NO oxidation evaluated. It was found that NOx (NO + NO$_2$) conversion using the iron-modified catalysts was obviously improved, probably due to the interaction between manganese and iron. Mn-Fe/ZSM-5 with a molar ratio of Fe/Mn = 0.49 exhibited the highest activity, achieving > 96.15% NOx conversion at 100 °C and stabilizing at about 100% conversion at between 150 and 250 °C. The properties of the catalysts were characterized using ICP, BET, XRD, H$_2$-TPR, NH$_3$-TPD and XPS techniques. XRD analysis revealed that the coexistence of manganese and iron oxides promoted the dispersion of active components and lowered the crystallinity, while the XPS results showed that iron doping increased the ratio of Mn^{4+}, increasing levels of oxygen vacancy and lattice oxygen, thereby facilitating the oxidation of NO to NO$_2$ and ultimately accelerating the Fast SCR process. However, excessive iron loading can lead to the agglomeration of active components. Furthermore, Mn-Fe$_{(0.490)}$/ZSM-5 also exhibited superior performance in terms of NO oxidation, with the maximum NO oxidation rate of 55.88% recorded at 300 °C, indicating the former's potential as a pre-oxidation catalyst for the Fast SCR reaction.

1. Introduction

Nitrogen oxides (NOx) emitted from car engines and fossil fuel combustion have become one of the primary air pollutants worldwide, leading to photochemical oxidant and acid rain, and further contributing to ozone depletion and global warming [1,2].

In recent years there has been great interest in developing selective catalytic reduction (SCR) technology for the removal of NO$_X$ utilizing NH$_3$ or urea as a reductant, typically involving the reaction between NO and NH$_3$ known as Standard SCR: $4NH_3 + 4NO + O_2 \rightarrow 4 N_2 + 6H_2O$ (1). By improving the NO$_2$/NO molar ratio, an equimolar NO-NO$_2$ reaction known as 'Fast SCR' occurs: $2NH_3 + NO + NO_2 \rightarrow 2 N_2 + 3H_2O$ (2). Koebel et al. [3] conducted systemic research into the reaction characteristics of Fast SCR and found that when temperatures were below 200 °C, the reaction rate of Fast SCR was > 10 times that of Standard SCR. However, NOx emission from vehicle engines contains 95% of NO and 5% of NO$_2$ [4], and thus an NO pre-oxidation step prior to the SCR reaction is necessary in order to fix the NO$_2$/NO molar ratio to 1:1 artificially.

The catalyst selected is momentous to the NO$_X$ removal with NH$_3$ in the SCR process. Nowadays, the commercial catalyst most commonly used in industry is TiO$_2$-supported V$_2$O$_5$, promoted with WO$_3$ [5].

However, this kind of commercial catalyst is not sufficiently active to completely remove NO$_X$ when the reaction temperature is around 250 °C or below. As a result, many researchers are currently making efforts to utilize new active components and supports with which to develop low-temperature SCR catalysts offering great activity, high stability and a broad reaction temperature window. In the past few decades, plenty of catalysts consisting of transition metal (Mn, Fe, Cu, Co, Ni) oxides on various supports have been investigated for use as low-temperature SCR catalysts. Manganese oxides in particular, containing a variety of types of labile oxygen, are reported to exhibit higher SCR activity at lower temperatures compared with other metal oxides [6–8]. Recent researches also focused on the various supports during NH$_3$-SCR, for, such as TiO$_2$ [9], Al$_2$O$_3$ [10], activated carbon (AC) [11], carbon nanotubes (CNTs) [12] exhibit excellent SCR activity, while ZSM-5 zeolite has obtained attention during SCR research due to its high acidity, absence of corrosive substances, possibility for regeneration and easy separation from reaction products [13–16]. Furthermore, whereas bimetallic Mn-based catalysts show better catalytic performance compared with single-metal catalysts, Fe oxides have proven to be one of the most suitable promoters due to their high levels of activity and thermal stability. For instance, when Fe was added to a Mn/TiO$_2$ catalyst, the dispersion of the MnOx increased greatly and led to
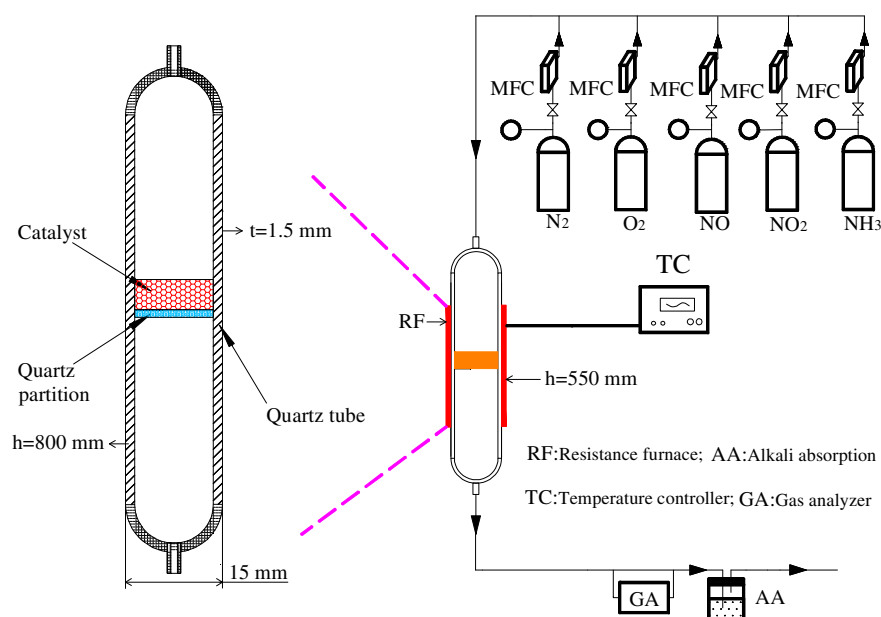

Fig. 1. The schematic diagram of experimental apparatus.

Table 1
Contents of Mn, Fe on Mn-Fe/Z catalysts samples.

Samples	The mass fraction of Mn	The mass fraction of Fe	The actual molar ratio of Fe/Mn	The designed molar ratio of Fe/Mn
Mn/ZSM-5	12.30%	0%	0	0
Mn-Fe$_{(0.122)}$/Z	11.93%	1.49%	0.12	0.13
Mn-Fe$_{(0.246)}$/Z	11.86%	2.97%	0.25	0.25
Mn-Fe$_{(0.490)}$/Z	11.88%	5.92%	0.49	0.50
Mn-Fe$_{(0.738)}$/Z	11.85%	8.90%	0.74	0.75

Table 2
Physical properties of the catalysts with different Fe loadings.

Samples	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
H-ZSM-5	366.28	0.05	2.10
Mn/ZSM-5	303.79	0.14	1.86
Mn-Fe$_{(0.122)}$/Z	295.08	0.15	2.06
Mn-Fe$_{(0.246)}$/Z	282.53	0.15	2.19
Mn-Fe$_{(0.490)}$/Z	266.28	0.15	2.16
Mn-Fe$_{(0.738)}$/Z	255.56	0.15	2.26

preferable NO$_X$ conversion [17]. Saeidi [18] also discovered that co-doped Mn-Fe/ZSM-5 catalysts exhibited approximately 100% NOx conversion rate between 200 and 360 °C.

In the present work, we used the impregnation method to prepare Mn-Fe/ZSM-5 catalysts with different levels of iron loading, with their catalytic activities in Fast SCR investigated in order to explore the interrelation between their physicochemical characteristics and catalytic performance. Furthermore, the catalytic oxidation of NO to NO$_2$ over these prepared catalysts was also studied with the purpose of examining the possibility of producing a superior catalyst offering great performance in catalyzing both Fast SCR and NO pre-oxidation.

2. Experimental

2.1. Preparation of catalysts

Mn-Fe/ZSM-5 samples with manganese loading of 12.00 wt% were prepared via the impregnation method. H-ZSM-5 zeolite (Si/Al = 25, the catalyst factory of Nankai University) was used as support material, with manganese nitrate (Mn(NO$_3$)$_2$, 50%, Sinopharm) and iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, 99.9%, Sinopharm) as the precursors of the manganese oxides and iron oxides, respectively. H-ZSM-5 powder and manganese nitrate, iron nitrate nonahydrate solution was placed in a beaker and dissolved in deionized water with continuous stirring. The mixture obtained was then stirred for 1 h and further dried overnight at 105 °C, followed by calcination in air for 2 h at 450 °C. Finally, the obtained samples were crushed and sieved to 40–60 mesh. The designed molar ratios of Fe/Mn were 1:8, 1:4, 2:4 and 3:4, with the resulting catalysts denoted as Mn-Fe$_{(x)}$/Z for short, where x represents the actual molar ratio of Fe/Mn, and Mn/ZSM-5 refers to the sample

without Fe.

2.2. Characterization

Inductively coupled plasma (ICP) was used for the quantitative analysis of the element content of the prepared samples, using a Varian Vista AX spectrometer. The specific surface area, pore volume and pore diameter (BET) of these catalysts were measured via N$_2$ adsorption in a Micromeritics ASAP 2460 instrument at − 196 °C. Powder X-ray diffraction (XRD) patterns were produced in a Bruker D8 Advance in order to analyze the crystal structure of the catalysts, using Ni-filtered CuK$_\alpha$ radiation in the range of 10°–80°. Temperature programmed reduction with hydrogen (H$_2$-TPR) and temperature programmed desorption with ammonia (NH$_3$-TPD) of all catalysts were operated using the same Tianjin Xian Quan TP-5076 chemical adsorption instrument with a thermal conductivity detector (TCD), with 50 mg catalyst for H$_2$-TPR and 100 mg catalyst for NH$_3$-TPD. The TPR experiment started with pretreatment in a N$_2$ (99.99%) stream at 500 °C for 1 h. Subsequently, the catalysts were cooled to room temperature and a H$_2$-N$_2$ (5 vol% H$_2$) mixture with a flow rate of 30 mL/min then used as a reductant. TPR commenced from 50 °C up to 800 °C at a heating rate of 10 °C/min, with H$_2$ consumption recorded continuously. In the TPD experiment, 100 mg catalyst samples were pre-treated in N$_2$ (99.999%) at 500 °C for 1 h. The catalysts were then saturated with NH$_3$ (10%, He as the balance gas) at 100 °C for 1 h, followed by He (99.999%) at 100 °C for 1 h to remove the physically adsorbed NH$_3$. Then the samples were heated to 800 °C at a rate of 10 °C/min in high purity He (99.999%), with NH$_3$ consumption recorded continuously. X-ray photoelectron spectroscopy (XPS) measurements were conducted at room temperature on a PHI Quantera SXM spectrometer (ULVAC-PHI Corporation, Japan)