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Short communication

Fe and/or Mn oxides supported on fly ash-derived SBA-15 for low-temperature NH_3-SCR

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ABSTRACT

Fe and/or Mn/SBA-15 catalysts were prepared by the impregnation method using low-cost fly ash-derived SBA-15 molecular sieve as support and tested towards NH_3-SCR. Powder XRD, N_2 adsorption, XPS, H_2-TPR and SEM techniques were used for catalyst characterization and investigation of relationships with the catalytic activity. The Fe-Mn/SBA-15 catalyst exhibited significantly higher NH_3-SCR activities than Mn/SBA-15 or Fe/SBA-15 in the 150–250 °C range owing to some developed synergistic effects between Mn and Fe. In particular, the addition of Mn improved the dispersion of Fe_2O_3 on the catalyst surface, while the addition of Fe promoted the formation of single β-MnO_2 phase. The high dispersion of Fe_2O_3, the appropriate Mn^{4+}/Mn^{3+} ratio, the concentration of adsorbed oxygen and the low-T enhanced redox activity of the Fe-Mn/SBA-15 improved its NH_3-SCR activity. This work opens new avenues of recycling fly ash formed in coal-fired power plants (reducing environmental pollution) and developing low-cost SCR catalysts for NO_x pollution control.

1. Introduction

Coal as a fossil fuel has played a pivotal role in the development of China's economy. Coal fly ash emissions as a result of coal burning reached 620 million tons in 2015, and total fly ash accumulation will exceed 3 billion tons by 2020 [1]. This large volume of waste poses serious hazards to the environment and human health. Instead, fly ash could be used as a raw material towards the removal of gas pollutants generated from coal burning, such as NO_x, which contributes to the photochemical smog and acid rain. Such a process would not only reduce the extent of pollution associated with fly ash production itself but also contribute to the reduction of gas pollution generated as a result of coal burning.

The selective catalytic reduction (SCR) of NO_x with ammonia (NH_3-SCR) is one of the most efficient technologies for NO_x removal from the flue gas of stationary and mobile sources. NH_3-SCR is nowadays a mature technology and largely employs V_2O_5/TiO_2 SCR catalysts [2,3]. The optimum reported temperature range of operation is 320–450 °C. However, in the past decades, low-temperature NH_3-SCR (< 300 °C), which can be placed downstream of the electrostatic precipitator and the desulfurizer and where most of SO_2 and dust are removed, has received great attention and is considered as an important energy efficient SCR process development.

In recent years, Mn-based, Ce-based and Co-based vanadium-free molecular sieve catalysts have been widely studied for low-temperature NH_3-SCR [4–13]. They display high catalytic activities and wide temperature window of operation. Many research studies have focused on using low-cost fly ash to prepare molecular sieves, such as A, X, Y, P, ZSM-5, β, MCM-41 and SBA-15 [14–16]. Traditionally, SBA-15 molecular sieves are synthesized from tetraethyl orthosilicate (TEOS) using P123 as templates, which are easy to remove, biodegradable, inexpensive and relatively non-toxic [17,18]. However, pure SBA-15, which is composed of amorphous SiO_2, is electrically neutral and lacks of acid sites and redox capabilities, which limit its use in the field of catalysis. Loading metals (Cu, Fe, Mn, Cr, Co, Ce, Ni, Mo, etc.) on SBA-15 molecular sieves can increase their catalytic activity. However, most studies have focused on the loading of metal ions onto SBA-15 which were synthesized using pure Si sources, i.e. TEOS [9–12]. In contrast, no studies on the use of fly ash-derived molecular sieves towards NH_3-SCR have been reported so far to the best of our knowledge.

The present work is aimed at recycling fly ash as a raw material for synthesizing promising vanadium-free molecular sieves towards the development of low-cost commercial NH_3-SCR catalysts. The use of fly ash as a raw material to synthesize high-value SBA-15 mesoporous molecular sieves was reported by us earlier [19]. Herein, a series of transition metal (Fe/Mn)-loaded fly ash-derived SBA-15 mesoporous

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molecular sieves were prepared via the wet impregnation method and characterized by X-ray diffraction, N_2 adsorption–desorption isotherms, H_2-temerature-programmed reduction, X-ray photoelectron spectroscopy and scanning electron microscopy. The catalytic activity towards NH_3-SCR ($NO/NH_3/O_2$) of such Fe and/or Mn-loaded SBA-15 solids was assessed.

2. Experimental

2.1. Raw materials and chemicals

A high-alumina fly ash formed in the thermal power plant of Inner Mongolia (China) was used as the raw material for SBA-15 and had the following chemical composition: 53.17% SiO_2, 36.86% Al_2O_3, 2.58% Fe_2O_3, 2.48% TiO_2, and 2.27% CaO. Details of the preparation of fly ash-derived SBA-15 mesoporous molecular sieve were previously reported [19]. The fly ash-derived SBA-15 had the following final chemical composition: 99.34% SiO_2, 0.625% Fe, 0.014% Ca and 0.051% Ti.

The chemical reagents of iron nitrate and manganese nitrate (analytical grade) used for the deposition of Fe and Mn, respectively, in SBA-15 were supplied by Sinopharm Chemical Reagent Co., Ltd. (Beijing, China), where that of ethanol (analytical grade) was provided by Beijing Enoch Technology Co., Ltd. (China).

2.2. Catalyst preparation

A series of bimetallic Fe-Mn/SBA-15 catalysts of varying Fe/Mn molar ratio were prepared via the one-step incipient wetness impregnation method using $Mn(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ as the metal precursors of Mn and Fe, respectively, and fly ash-derived SBA-15 as the porous support. Appropriate amounts of $Mn(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in distilled water under vigorous stirring. The suspension was then mixed with 1 g of fly ash-derived SBA-15 and stirred for 24 h at 60 °C. The impregnated solids were dried at 100 °C for 10 h and then calcined in air at 550 °C for 5 h at 5 °C/min. The resulting catalysts are denoted as *m*Fe-*n*Mn/SBA-15, where *m* and *n* represent the Fe and Mn loading (wt%), respectively. For comparison, Fe/SBA-15 and Mn/SBA-15 monometallic supported catalysts were also prepared after following the same synthesis procedure used for preparing the Fe-Mn/SBA-15 catalyst.

2.3. Catalysts characterization

Powder X-ray diffraction, Scanning Election Microscopy, N_2 adsorption-desorption measurements, XPS and H_2-TPR techniques were used to investigate the morphology and bulk/surface crystal structure and chemical composition of Fe-Mn/SBA-15. Details of all the above mentioned characterization methods are provided in Supporting information.

2.4. NH_3-SCR activity measurements

The NH_3-SCR reaction was evaluated in a typical fixed-bed microreactor. An amount of 0.3 g catalyst was introduced into the microreactor and then treated for 2 h in a simulated flue gas composed of 300 ppm NO, 300 ppm NH_3, 3 vol% O_2, and N_2 as balance gas using a GHSV of ~120,000 h^{-1}. The catalyst's activity (in terms of NO_x conversion) was evaluated at a given temperature (100–350 °C) after 60 min on reaction stream by measuring the NO_x composition of the inlet and outlet gas using a flue gas analyzer (MultiGas™ 6030, MKS). The conversion was estimated according to the following relationship:

$$NO_{x\,conversion} = [([NO_x]_{in} - [NO_x]_{out})/[NO_x]_{in}] \times 100\% \quad (1)$$

where $[NO_x]_{in}$ and $[NO_x]_{out}$ are the concentrations of NO_x in the inlet and outlet gas streams, respectively.

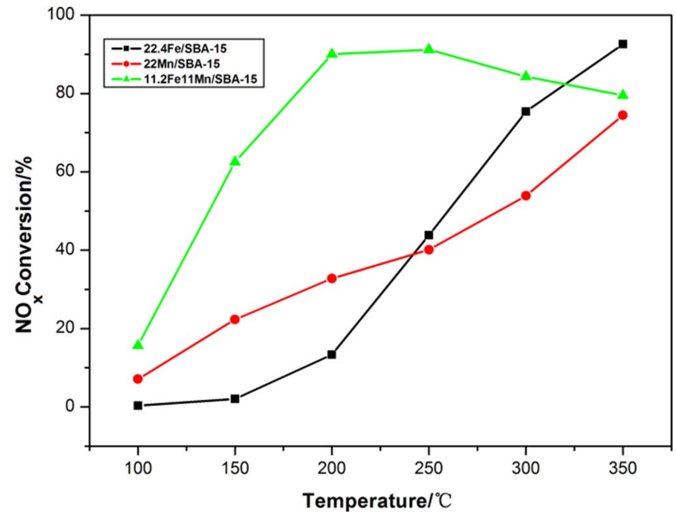

Fig. 1. NH_3-SCR performance (NO conversion) of the Fe and/or Mn/SBA-15 catalysts as a function of (a) various Mn/Fe molar ratios (Fe wt% loading of 4.48) and (b) various total metal content; (c) Synergistic effect between Mn and Fe.

3. Results and discussion

3.1. NH_3-SCR performance of Fe and/or Mn/SBA-15

The NH_3-SCR activity results of all the studied catalysts are presented in Fig. 1. When the Mn/Fe molar ratio increases from 1.0 to 5.0, the conversion of NO_x increases at all studied reaction temperatures (Fig. 1a). When the Mn/Fe molar ratio is 1.0, in general the conversion of NO_x increases with increasing total loading of the transition metals (Fig. 1b) except in the case of 13.44Fe13.2Mn/SBA-15, where the conversion of NO_x largely decreases. The latter is suggested to be due to the presence of a large number of Mn and Fe metal oxide crystal particles that block molecular sieve channels, thus preventing gas reactants diffusion.

To understand possible synergistic effects between Fe and Mn, the NH_3-SCR activities of Mn/SBA-15 and Fe/SBA-15 were also assessed for comparison (Fig. 1c). In the low-temperature region of 100–350 °C, the NO_x conversion of Fe-Mn/SBA-15 is considerably higher than that of Mn/SBA-15 and Fe/SBA-15, indicating a strong synergistic effect between Fe and Mn on the catalytic performance of Fe-Mn/SBA-15. When the temperature becomes < 250 °C, the NO conversion of Mn/SBA-15 is higher than that of Fe/SBA-15. However, the opposite trend is observed at temperatures higher than 250 °C. These results indicate that MnO_x plays a major role in NO_x conversion at low temperatures (100–250 °C), whereas Fe_xO_y plays a more important role at high temperatures (> 250 °C), results which are consistent with previous works [20–23]. Furthermore, Fig. 1c indicates that the synergistic effect between Fe and Mn is only optimum (> 90% NO_x conversion) in the temperature range of 200–250 °C.

The NH_3-SCR performance of various deNO_x catalysts reported [6,20–23,28,31,32] is summarized in Table S1. It is clearly seen that the prepared FeMn-fly-ash-derived SBA-15 of this work shows little difference in deNO_x performance compared with the other low-temperature NH_3-SCR catalysts. In the present work, it should be noted that similar performance is obtained but using larger GHSV (h^{-1}) and lower NO_x feed gas concentration compared to the other works. Moreover, the developed catalysts of this work are considered less costly, free of V, thus more suitable for industrial applications.

Examination of the long-term stability of Fe-Mn/SBA-15 in the presence of water was also performed (Fig. 2). It can be seen that the Fe-Mn/SBA-15 catalyst still exhibits significant NO_x conversion (80%) upon addition of 5 vol% H_2O in the feed gas stream at 200 °C after 6 h on stream. The catalyst shows significant recovery characteristics after

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