Chemical Engineering Journal 286 (2016) 291–299

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Effect of MnO_2 polymorphs structure on the selective catalytic reduction of NO_x with NH_3 over TiO_2–Palygorskite

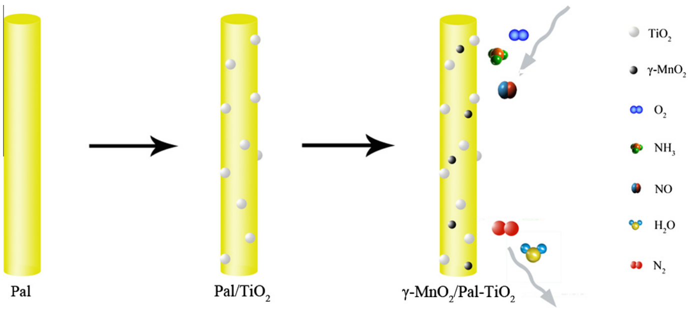
Shiping Luo [a,b], Wenting Zhou [a], Aijuan Xie [a,*], Fenqin Wu [a], Chao Yao [a,b], Xiazhang Li [b], Shixiang Zuo [a], Tianhua Liu [a]

[a] School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China
[b] R&D Center of Xuyi Attapulgite Applied Technology of Changzhou University, Xuyi 211700, China

HIGHLIGHTS

- $m(\text{Pal}):m(TiO_2) = 2:1$ is the best ratio as a carrier of γ-MnO_2.
- Different calcination temperatures have effect on the crystal structure of γ-MnO_2.
- γ-MnO_2 catalysts presented the best performance for NO_x conversion.
- 5 wt.% γ-MnO_2/TiO_2–Pal catalyst can offer 100% NO_x conversion at lower temperature.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 July 2015
Received in revised form 23 October 2015
Accepted 26 October 2015
Available online 30 October 2015

Keywords:
γ-MnO_2
TiO_2/Palygorskite
Low-temperature
Selective catalytic reduction (SCR)
NO_x conversion
Polymorphs

ABSTRACT

MnO_2 polymorphs such as α-, β-, γ-, and δ-MnO_2 were prepared and measured for the selective catalytic reduction of NO_x with NH_3 respectively. Subsequently, γ-MnO_2/TiO_2–Pal ternary composites were fabricated as an efficient catalyst for low-temperature NH_3-SCR and characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), temperature-programmed desorption of NH_3 (NH_3-TPD), temperature-programmed reduction of H_2 (H_2-TPR), isothermal N_2 adsorption/desorption (BET), and X-ray photoelectron spectroscopy (XPS). TEM images show that $m(\text{Pal}):m(TiO_2) = 2:1$ exhibits well dispersed particles and is the best ratio as a carrier of γ-MnO_2. Weak peaks of γ-MnO_2 in the XRD pattern suggest that γ-MnO_2 is considered to be in a poorly crystalline phase. It is evidenced that γ-MnO_2 catalysts present the best performance compared with others, and the optimum loading amount of γ-MnO_2 over the surface of TiO_2/Pal is about 5 wt.%. NH_3-TPD patterns show that 5 wt.% γ-MnO_2/TiO_2–Pal catalyst calcined in the range of (80–300 °C) displays the excellent NH_3 adsorption by the Brønsted acidic sites. H_2-TPR patterns show that the manganese oxide species occur change when calcination temperature is over 400 °C. The XPS spectrum of 5 wt.% γ-MnO_2/TiO_2–Pal reveals the high existing amount of Mn^{4+} ions over the surface of TiO_2/Pal, the results of which indicate that MnO_2 is the dominant phase with respect to Mn_2O_3 and MnO phases. The NH_3-SCR experiments demonstrate that 5 wt.% γ-MnO_2/TiO_2–Pal catalysts can attain almost 100% NO_x conversion at lower temperature scope (200–300 °C).

---

* Corresponding author. Tel.: +86 519 86330158; fax: +86 519 86330167.
E-mail address: Aijuan_xie@126.com (A. Xie).

http://dx.doi.org/10.1016/j.cej.2015.10.079
1385-8947/

1. Introduction

Nitrogen oxides (NO_x) are atmospheric pollutants that are harmful to the environment and human health. They contribute to acid rain, photochemical smog, ozone depletion and fine particle pollution. The emission control of NO_x from automotive exhausts and stationary sources such as power plant and incinerator has been a major environmental concern. Selective catalytic reduction (SCR) of NO_x with NH_3 has been extensively used to treat stationary exhausts. The commercialized industrial catalysts for NH_3-SCR of NO_x are WO_3–V_2O_5/TiO_2 and MoO_3–V_2O_5/TiO_2. Substantial work had been done to improve the performance of vanadium type catalysts via increase of Lewis acid, expansion of reaction temperature window, inhibition of initial sintering and improvement of SO_2 resistance [1–5]. However, commercial catalysts (V_2O_5–WO_3 (MoO_3)/TiO_2) are active within a narrow temperature scope of 300–400 °C, and they are normally installed prior to particulate removal facility to avoid reheating of the flue gas, which makes these catalysts susceptible to deactivation from sulfur and dust. Therefore, developing low-temperature SCR catalysts, which can be installed after the desulfurizer and particle removal device, is of very importance to avert poisoning.

Metal exchanged zeolites, such as Fe-ZSM-5, Cu-SSZ-13 and Cu-Chabazite, are probably the most promising zeolites for NH_3-SCR [6–13]. They have been found to show a high SCR activity and selectivity towards N_2, however zeolite based catalysts are active above 250 °C. It has been proven that manganese based catalysts have shown potential to achieve efficient NO_x conversions below 250 °C [14–19].

It has been shown that the dispersion of manganese oxides has a marked impact on the SCR reaction. Catalyst carriers are also believed to be important for SCR performance as they possess high surface areas, good thermal stability, and high active substance dispersion on surfaces. Palygorskite (Pal) is of interest as catalyst carrier because of its high thermal stability, strong mechanical strength and low cost [20–22]. As a carrier, TiO_2 possesses better resistance to SO_2 and could interact with MnO_2 to improve the dispersion of active component Mn species [23–25]. In recent years, MnO_2 has been reported for the low temperature NH_3-SCR [16,26–28], but few investigations have been done on low temperature NH_3-SCR over MnO_2 with different structures. Therefore, in the present study, different MnO_2 polymorphs, such as α-, β-, γ-, and δ-MnO_2, were prepared and γ-MnO_2 was supported with TiO_2–Palygorskite (Pal) as an efficient catalyst for low-temperature NH_3-SCR. Analysis on transmission electron microscope (TEM), X-ray diffraction (XRD), temperature-programmed desorption of NH_3 (NH_3-TPD), temperature-programmed reduction of H_2 (H_2-TPR), isothermal N_2 adsorption/desorption (BET) and X-ray photoelectron spectroscopy (XPS) were carried out to investigate the relationship between surface structure and catalytic activity. The results showed that among different MnO_2 polymorphs, γ-MnO_2/TiO_2–Pal exhibited excellent catalytic activity in the range of 200–300 °C.

2. Experimental

2.1. Materials preparation

2.1.1. Preparation of TiO_2-coated Pal

As the raw material, Pal was placed in the beaker and dispersed in deionized water to form a kind of suspended slurry, which was stirred at room temperature for 4 h and rested for 1 h to prepare a solid content of 4 g/100 mL of Pal slurry (denoted solution I). 25 mL of 2.5 M $TiCl_4$ was placed in the three-necked flask at room temperature and 125 mL of 1.5 mol L^{-1} NaOH was then dropwise added with vigorous stirring to form a milky white. Afterwards, 250 mL solution I was poured into the above mentioned solution and vigorously stirred at 80 °C for 2 h. Finally, 42 mL of 1.5 mol L^{-1} NaOH was added until the pH value of the supernatant became neutral (denoted solution II).

2.1.2. Preparation of γ-MnO_2/TiO_2–Pal catalysts

A series of γ-MnO_2/TiO_2–Pal catalysts were prepared. The typical synthetic process is described as follows: γ-MnO_2 was prepared from $MnSO_4$ using $(NH_4)_2S_2O_8$ as an oxidant. Stoichiometric amounts of $MnSO_4 \cdot H_2O$ and $(NH_4)_2S_2O_8$ were dissolved in deionized water and added into the solution II, then heated at 80 °C for 2 h with vigorous stirring. The resulting mixed liquor were filtered at once with hot and washed several times with deionized water to remove the impurity ions, then dried at 80 °C, ground and sieved (20–40 mesh) to obtain homogeneous powder.

2.1.3. Preparation of MnO_2 polymorphs

For comparison purposes, α-MnO_2 was synthesized by redox reaction between $MnSO_4$ and $KMnO_4$ in aqueous medium. 200 mL of 0.1 mol L^{-1} $KMnO_4$ solution was mixed with 200 mL of 0.15 mol L^{-1} $MnSO_4 \cdot H_2O$ solution and stirred continuously for 6 h to form a dark-brown precipitate, which was firstly washed with deionized water, and then centrifuged and dried at 70 °C in air for 12 h to obtain α-MnO_2. δ-MnO_2 was prepared by following the same route of synthesis of α-MnO_2, but with double stoichiometric amount of $KMnO_4$ [29]. β-MnO_2 was prepared just by Mn $(NO_3)_2$ decomposition. 50% $Mn(NO_3)_2$ solution was dried at 80 °C for 12 h in vacuum drying oven and at 110 °C for 2 h followed by calcination at 400 °C for 4 h in static air.

2.2. Catalyst characterization

The TEM images were recorded using a transmission electron microscope working at 200 kV.

The XRD analyses of the as-prepared samples were measured via an X-ray diffractometer with Cu Kα radiation, running at 60 kV and 30 mA with a scan range of 0–80° at 3°/min.

The Brunauer–Emmett–Teller (BET) surface areas of the as-synthesized samples were performed by the isothermal N_2 adsorption/desorption method at 77 K via Micromeritics Adsorption Instrument, which were then calculated from adsorbed nitrogen volume by an automatic volumetric apparatus following standard BET theory.

The total distribution about acidity and the acid of the catalysts were examined by the temperature-programmed-desorption (TPD) of NH_3 on a TP5080. About 0.1 g of sample (sieved to 0.2–0.3 mm) was inserted into a fixed-bed flow reactor using pure N_2 as the flow gas. The introduction of NH_3 was performed over 30 min followed by a purification with N_2 to remove the physically adsorbed NH_3 over the catalyst surface. Desorption under N_2 was then carried out at the range of 50–400 °C with a linear rate of 10 °C/min.

The H_2-TPR experiment was performed with a TP5080. In the H_2-TPR, 0.1 g of sample was used. TPR runs were performed with a H_2/N_2 (5%/95%) flow of 30 mL/min; the samples were heated from ambient temperature to 725 °C at a heating rate of 10 °C/min. The H_2 reduction curve was recorded using a thermal conductivity detector.

The X-ray photoelectron spectroscopy (XPS) data were examined with an Escalab250Xi electron spectrometer from Thermo Fisher Scientific by AlKα radiation. The data processing of XPS were referenced to the C1s line at 284.8 eV from adventitious carbon.