Chemical Engineering Journal 352 (2018) 39–44

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Facile synthesis of Mn-based nanobelts with high catalytic activity for selective catalytic reduction of nitrogen oxides

Qi Kai[a], Xie Junlin[a,c], Hu Hua[a], Han Da[a], Fang De[a,b], Gong Pijun[a], Li Fengxiang[a], He Feng[a,c], Liu Xiaoqing[b,*]

[a] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, PR China
[b] Center for Materials Research and Test, Wuhan University of Technology, Wuhan 430070, PR China
[c] School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, PR China

HIGHLIGHTS

- A redox-precipitation method without extra precipitator and calcination process.
- α-MnO_2 nanobelts with high surface area.
- Above 90% NO conversion within the testing range of 393–453 K.
- A Eley-Rideal mechanism is proposed with Brønsted acid sites mainly involved.

ARTICLE INFO

Keywords:
α-MnO_2 nanobelts
Redox-precipitation
NH_3-SCR
Characterization
Mechanism

ABSTRACT

The development of low-temperature SCR catalysts is of vital importance due to their potential application in downstream of the desulfurizer and electrostatic precipitator, where the flue gas temperature is usually bellow 473 K. In this study, various Mn-based nanobelts were synthesized by a facile redox-precipitation route and were further used as low-temperature SCR catalysts. In particular, the as-prepared α-MnO_2 nanobelts with exposed (1 1 0) surface were shown to be single crystallites with widths of 10–20 nm and lengths of 50–200 nm. The α-MnO_2 with porous and hierarchical nanostructure interweaved by α-MnO_2 nanobelts presented large specific surface area and exhibited high NO conversions and wide operating temperature window, reaching up to above 90% NO conversion within the testing range of 393–453 K. An Eley-Rideal (E-R) reaction mechanism is proposed with Brønsted acid sites involved in the SCR reaction for α-MnO_2. The possible growth mechanism of α-MnO_2 nanobelts was also tentatively discussed.

1. Introduction

Selective catalytic reduction (SCR) stands out and is recognized as the state-of-the-art technology for NO_x abatement internationally [1,2]. Development of low-temperature SCR catalysts is of vital importance owing to their potential applications in downstream of the desulfurizer and electrostatic precipitator, where the flue gas temperature is usually below 473 K [3]. MnO_2 has been paid particular attention in flue gas denitration due to its polyvalence, half-filled d orbital, low cost, novel physicochemical properties and environment-friendly natures [4–6].

The catalytic activities of catalysts mainly rely on the phase composition and structures, of which microstructures play a critical part [7]. The porous, hierarchically nanostructured materials are potentially high-performance catalysts due to their high surface area and open porous structure, which can facilitate gas diffusion, adsorption and activation [8]. The precipitation method is a good candidate to prepare catalyst powders in mass production [9–11]. Nevertheless, one of the primary hurdles in the nanostructures fabrication using precipitation is to obtain the well controlled morphologies and dimensions. Another disadvantage of the precipitation method is that recycling the precipitants is hard and is also challenging at the present stage (Fig. 1).

In this study, a simple but effective redox-precipitation method was devised combining $KMnO_4$ (serves as oxidizer and Mn source) with Mn$(Ac)_2$ (serves as reducer and Mn source) to synthesize high quality Mn-based nanobelts in mass production at room temperature and at atmosphere pressure. Three kinds of Mn-based nanobelts were obtained, showing high catalytic activities for selective catalytic reduction of nitrogen oxides. In particular, when the ratio of $KMnO_4$ to Mn$(Ac)_2$ is 2,

* Corresponding author.
E-mail address: lczr@whut.edu.cn (X. Liu).

https://doi.org/10.1016/j.cej.2018.07.002
Received 31 January 2018; Received in revised form 22 June 2018; Accepted 1 July 2018
Available online 02 July 2018
1385-8947/

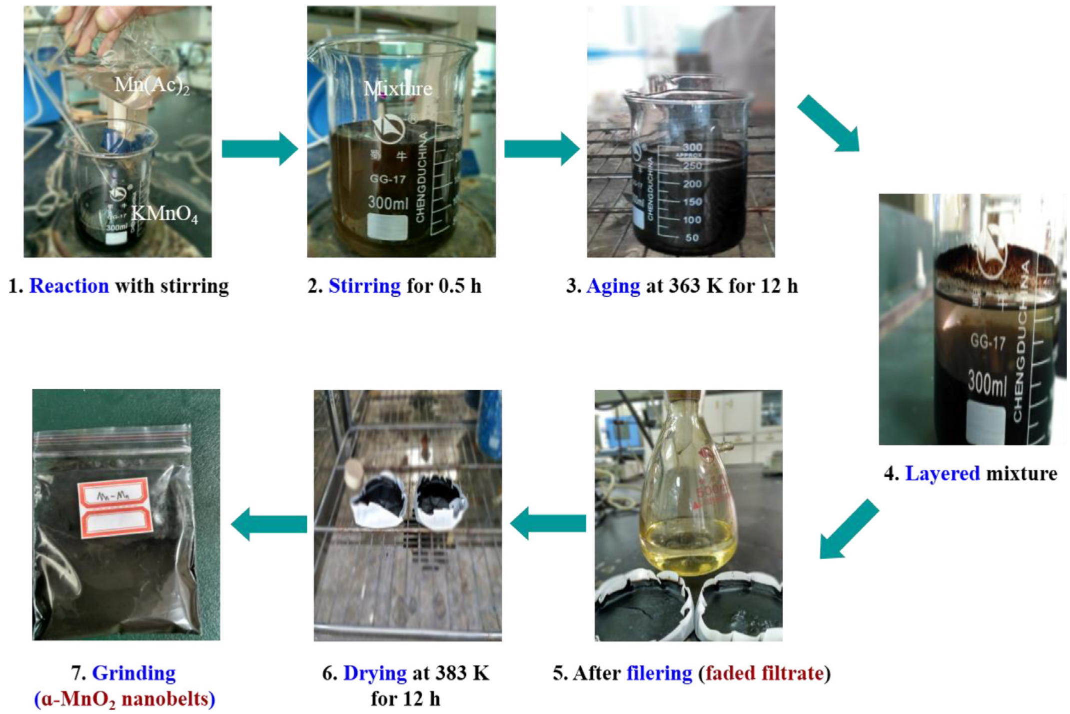

Fig. 1. The real flow charts of sample preparation.

the MnO_x prepared in this way exhibited the unique α- crystalline of MnO_2 and nest-like structure with large specific surface area interweaved by nanobelts in loose aggregate which usually require hydrothermal conditions. The specific surface area of α-MnO_2 nanobelts was as high as 123.1 $m^2 \cdot g^{-1}$. The performance of the selective catalytic reduction of nitrogen oxides using α-MnO_2 nanobelts as catalysts was evaluated. 90% NO conversion within the testing temperature range of 393–453 K is successfully achieved. The high catalytic activity is attributed to the large specific surface area, good dispersion and high Mn^{4+} concentration of α-MnO_2 [12,13].

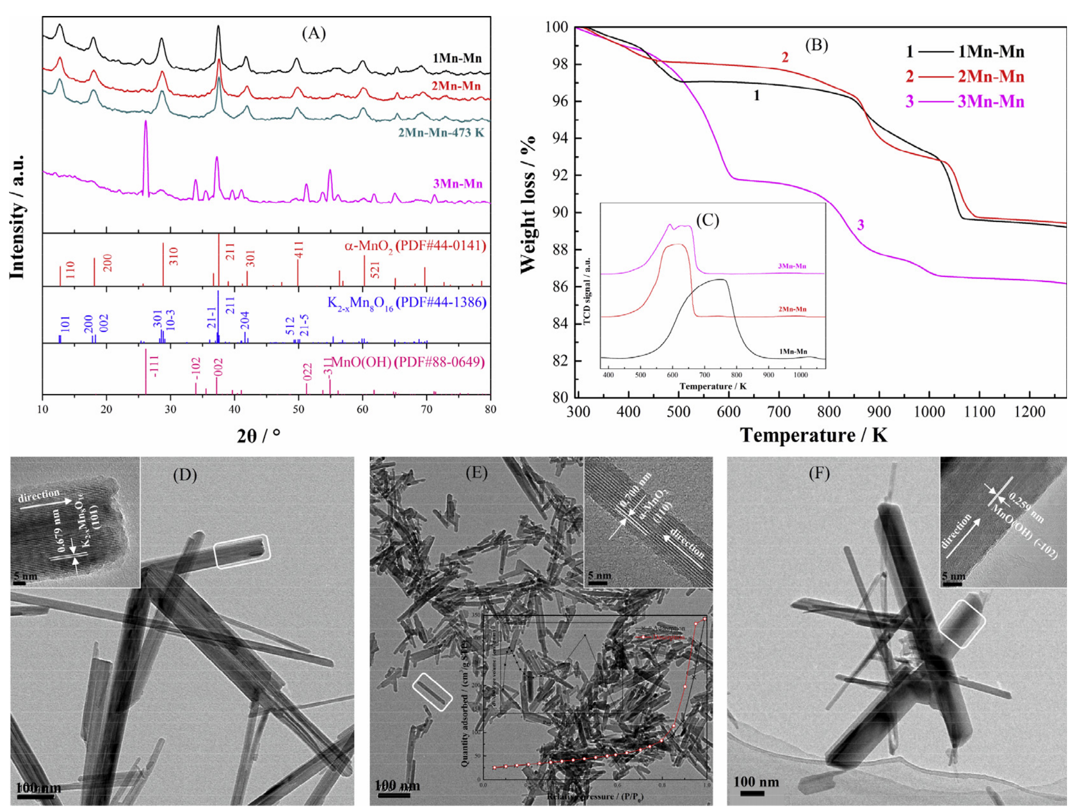

Fig. 2. (A) XRD patterns over Mn-Mn catalysts; (B) TG profiles of Mn-Mn catalysts; (C) H_2-TPR profiles of Mn-Mn catalysts; Microstructures of 1Mn-Mn (D); 2Mn-Mn (E); 3Mn-Mn (F).