Fuel Processing Technology 127 (2014) 1–6

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Microwave-assisted catalytic reduction of NO into N_2 by activated carbon supported Mn_2O_3 at low temperature under O_2 excess

Wentao Xu, Jicheng Zhou *, Hu Li, Pengfei Yang, Zhimin You, Yushang Luo

Key Laboratory of Green Catalysis and Chemical Reaction Engineering of Hunan Province, School of Chemical Engineering, Xiangtan University, Xiangtan 411105, PR China

ARTICLE INFO

Article history:
Received 18 January 2014
Received in revised form 3 June 2014
Accepted 3 June 2014
Available online 26 June 2014

Keywords:
Microwave catalysis
Microwave selective effect
NO reduction by AC
Mn_2O_3
Low temperature
O_2 excess

ABSTRACT

The catalytic reduction of NO by AC with high activity and selectivity to N_2 at low temperature under O_2 excess is a challenge. Herein, we report a novel method for selective catalytic reduction of NO into N_2 by activated carbon supported Mn_2O_3 in the microwave catalytic reaction mode. Furthermore, the effects of a series of reaction parameters, including microwave heating behavior, reaction temperature, outlet gas temperature, Mn_2O_3 loading, microwave input power and O_2 concentration have been investigated. Novel results were observed that microwave-assisted catalytic reduction of NO into N_2 over Mn_2O_3/AC is of high efficiency with 98.7% NO conversion and 99.8% NO selectivity to N_2 at temperature as low as 300 °C under O_2 excess. We also found that microwave irradiation exhibited microwave selective effect in the microwave catalytic reaction mode. The microwave catalytic reaction mode is a viable and promising method for flue gas control using selective catalytic reduction of NO by AC compared with the conventional reaction mode.

1. Introduction

Nitrogen oxides (NO_x), emitted from mobile and stationary sources, are considered to be one of the most dangerous air pollutants for their devastating effect on the atmosphere, ecosystem and human health [1]. The selective catalytic reduction with NH_3 (NH_3-SCR) is currently a popular method for the clean-up of flue-gas from fixed sources in spite of several drawbacks, such as storage and leakage inevitably and un-reacted reducing agents [2–5]. Hence, the reduction of NO_x by carbon provides an interesting alternative since the problems of NH_3 can be avoided [6,7]. Normally, NO_x reduction by AC occurs at temperatures as high as 500 °C in the conventional reaction mode (CRM) [8–11]. Thus, the use of AC has drawbacks that the AC burned off at temperatures higher than 300 °C [12], and under real $NO_x + O_2$ gas mixtures, carbon would be mainly consumed by O_2 [13], as a result it could not satisfy the requirements for practical application. Moreover, due to the high affinity of carbon for oxygen, the selectivity for NO_x reduction against combustion by oxygen is the main problem to be overcome for practical and competitive purposes [7]. It remains a challenge that the reduction of NO_x by AC by catalysis is of high activity and selectivity to N_2 at a low temperature under O_2 excess. Therefore, it is urgent to develop new methods for reduction of NO_x by AC so that the reaction can work effectively at the lowest possible temperature (below 300 °C).

Microwave (MW) technique has been applied in heterogeneous catalysis research in the past decade [14–18]. Using microwave technique in reduction of NO_x has provided some remarkable results [19–22]. Microwave catalytic NO_x removal has been investigated that using FeCu/zeolite as a catalyst and NH_4HCO_3 as a reducing agent could convert 95.8% NO_x to nitrates [23]. Microwave has been applied to a pyrolytic carbon matrix to enhance the reactions of NO_x with carbon to produce N_2 and CO_2 (without catalyst) [24]. Microwave discharge-assisted reduction of NO by CH_4 in the presence of excess O_2 over Co/HZSM-5 and Ni/HZSM-5 catalysts was studied [25]. However, a limited number of studies were devoted to the microwave-assisted catalytic reduction of NO into N_2 by AC by catalysis at low temperature under O_2 excess [26]. Moreover, it is not elucidated that what is the microwave "special effect" or "nonthermal" microwave effect [27–30], and the nature of microwave irradiation on chemical reaction [30] and on heterogeneous catalytic reaction. The reaction temperature can be decreased by microwave catalysis under microwave irradiation [31], hence a high-temperature reaction can work effectively at a low temperature. Furthermore, microwave has been demonstrated to enhance reaction selectivity [27,28,32,33], hence AC can react selectively with polar NO rather than non-polar O_2 in which it can reduce AC consumption to some degree, providing a viable and promising method for selective catalytic reduction of NO into N_2 by AC in the microwave catalytic reaction mode (MCRM).

To choose a proper catalyst for the microwave process is of great importance, such a catalyst has to be a good receptor of microwave energy, without changing its structure and properties under intense microwave radiation [22]. Mn_2O_3 is an excellent microwave absorbing material,

* Corresponding author. Tel.: +86 731 58298173.
E-mail address: zhoujicheng@sohu.com (J. Zhou).

http://dx.doi.org/10.1016/j.fuproc.2014.06.005
0378-3820/

which is capable of initiating and maintaining stable microwave discharge [34], but still now little attention is paid to its microwave catalytic properties.

Herein, we report microwave-assisted catalytic reduction of NO into N_2 by AC supported Mn_2O_3 at low temperature (below 300 °C) under O_2 excess. Furthermore, the effects of a series of reaction parameters, including microwave heating behavior, reaction temperature, outlet gas temperature, Mn_2O_3 loading, microwave input power and O_2 concentration have been investigated. Novel results were observed that microwave-assisted catalytic reduction of NO into N_2 by AC over Mn_2O_3/AC is of high efficiency with 98.7% NO conversion and 99.8% NO selectivity to N_2 at temperature as low as 300 °C under O_2 excess. However, to the best of our knowledge, it has not yet been investigated that selective catalytic reduction of NO into N_2 by AC supported Mn_2O_3 is of such high NO conversion and selectivity in the MCRM under mild conditions. Microwave-assisted catalytic reduction of NO into N_2 by AC supported Mn_2O_3 is more efficient and environmentally friendly compared with conventional SCR using NH_3 or CH_4 as the reducing agent. Our work attempts to evaluate the potential of applying this novel method as an effective NO_x emission control strategy.

2. Experimental

2.1. Preparation of Mn_2O_3/AC

The Mn_2O_3/AC catalysts were prepared with an impregnation method. Activated carbon (designated as AC, Φ3.0 mm, Sinopharm Chemical Reagent Co., Ltd.) was pretreated with the aqueous solutions of HNO_3 (20%), and then dried at 80 °C for 12 h. The desired amount of AC was impregnated with aqueous solution of $Mn(NO)_2$. The resulting slurry was dispersed in an ultrasonic bath for 1.5 h followed by progressive drying at 80 °C for 12 h and 110 °C for 6 h. Mn_2O_3/AC catalysts were obtained after calcining at 250 °C for 2 h. The Mn_2O_3 loading on the catalysts was in the range of 0–10 wt.%.

2.2. Catalyst characterization

X-ray diffraction (XRD) of samples was obtained on a Rigaku D/max-II/2500 X-ray powder diffractometer, Cu Ka radiation was employed and the working voltage and current were 40 kV and 30 mA, respectively. Surface images of the samples were investigated by a JEM2010 transmission electron microscopy (TEM).

2.3. Activity evaluation

2.3.1. Microwave reactor system

A new microwave catalytic reactor system was developed to study the role of the microwave irradiation in a continuous flow of gas–solid catalytic reaction systems. The experimental diagram is shown in Fig. 1. The reactor consisted of a microwave generator system and a reaction system. The microwave energy was supplied by a 2.45 GHz microwave generator where the power could be varied continuously in the range of 0–1000 W. The magnetron microwave source connected through a rectangular waveguide to a single-mode resonant cavity which was terminated with a tuning plunger. A quartz tube (i.d. 10 mm and 540 mm in length) at the center of the cavity was designed to carry out the experiments. The AC or Mn_2O_3/AC was filled in the middle of the reactor tube and both ends were sealed with asbestos. The temperature of the reaction bed was provided by microwave thermal effect and was precisely measured by the modified thermocouple probe inserted to the catalyst bed.

2.3.2. Activity tests

The reactant gas was composed of NO (molar fraction, 0.1%), O_2 (molar fraction, 0–13.5%) and the balance N_2. Ten milliliter catalyst was used for each run and the space velocity (GHSV) was 1020 h^{-1}. For comparison, the CRM and MCRM were carried out in the same size reactor with the same amount of reaction bed under identical conditions. In the CRM, the reaction test was carried out by using a microreactor device (MRT-6123; Beijing Xin Hang Shield Petrochemical Technology Co., Ltd.). The NO concentration of the outlet gas was analyzed by an online NO_x analyzer (42C, Thermo Environmental Instruments Co., Ltd., U.S.). In addition, the analysis system has GC (Agilent 7890A) with two thermal conductivity detectors, a column of Poropak Q for N_2O analysis and a column of 5A zeolite for CO analysis, and the analysis system has 900D Portable 4 component Infrared analysis instrument (Beijing Huayun Analytic Instrument Institute) for CO analysis. In this reaction, N_2 was the aim product, NO_2 was the by-product, and N_2O and CO (both very undesirable products) were not detected (only when the reaction temperature reaches 300 °C, trace amount of CO was detected and its molar fraction was 0.03%). Therefore, the NO conversion and NO selectivity to N_2 could be calculated by the formulas as follow:

$$X_{NO} = \frac{C_0(NO) - C_1(NO)}{C_0(NO)} \times 100\% \quad , \quad S_{NO} = \frac{C_0(NO) - C_1(NO) - C_1(NO_2)}{C_0(NO) - C_1(NO)} \times 100\%$$

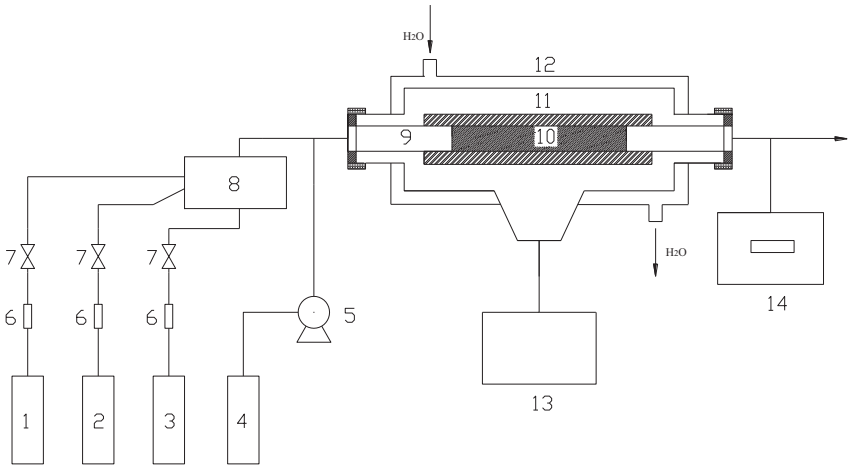

Fig. 1. Schematic diagram of microwave catalytic reactor system. 1. NO; 2. O_2; 3. N_2; 4. Storage tank; 5. Metering pump; 6. Mass flow meter; 7. Valve; 8. Premixer; 9. Quartz reactor; 10. Fixed bed; 11. Thermal insulation; 12. Resonant cavity; 13. Microwave generator; 14. On-line NO_x analyzer.