Fuel Processing Technology 152 (2016) 102–107

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

The effects of oxygen and metal oxide catalysts on the reduction reaction of NO with lignite char during combustion flue gas cleaning

Ning Yang [a,c], Jiang-long Yu [a,b,*], Jin-xiao Dou [a], Arash Tahmasebi [a], Hui Song [b], Behdad Moghtaderi [b], John Lucas [b], Terry Wall [b]

[a] Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China
[b] Chemical Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia
[c] Hebei College of Industry and Technology, Shijiazhuang, China

ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form 11 June 2016
Accepted 12 June 2016
Available online 17 June 2016

Keywords:
Catalytic NO reduction
Flue gas cleaning
NO_x emission
Activated-char

ABSTRACT

The development of lignite-char-supported metal oxide catalyst for reduction of nitric oxide (NO) is investigated in this paper. The characteristics of NO reduction by copper and iron oxide catalysts supported on activated lignite chars (ALC) was studied using a fixed-bed reactor at 300 °C. The results showed that the impregnation of Cu on ALC resulted in higher catalytic reactivity during NO reduction compared with that of Fe. Chemisorption of O_2 and NO on Cu/ALC catalyst was found to play an important role in denitrification. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analyses showed that chemically adsorbed oxygen facilitates the formation of C(O) complex and oxidation of Cu^0 to Cu^+ for Cu/ALC catalyst. The C(O) intermediates and C* production formed due to the fact that C/O_2 reaction promoted the reduction of NO. It is suggested that the catalytic reaction of NO in this case comprised of C/O_2 reaction, C(O)/NO reaction and formation of N_2 and CO_2. Cu seemed to have significantly promoted the C(O) formation and CO oxidation compared with Fe. The catalytic reactivity of Cu species for C(O) formation and CO oxidation followed the order of $Cu^0 > Cu^+ > Cu^{2+}$. Fe_3O_4 was believed to be the active phase in Fe catalyst. The oxygen and char-supported metal catalysts significantly promoted C/NO reaction, and therefore may lead to a lower operation temperature of NO_x removal.

1. Introduction

NOx is one of the major air pollutants in combustion flue gases from coal fired power plants and industrial furnaces as well as in exhaust gases of vehicles [1]. NOx is known as the major reactants during the formation of photochemical smog which has caused severe impact on air quality and human health [1]. Nitric oxide (NO) is one of the major NOx pollutants, accounting for 90% of the total NOx in the combustion flue gas. NO can be oxidized to NO_2 in air leading to the formation of acid rain and photochemical smog formation when interacted with the PAH (poly-aromatic hydrocarbon) in the atmosphere [2]. Therefore, the removal of NO from the combustion flue gases has become increasingly important [3].

Commercially available post-combustion technologies of NOx emission control include calcium-based flue gas denitrification, selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR). The catalysts for NH_3-SCR process are normally metal or metal oxides supported on SiO_2, TiO_2, carbon-based materials, and zeolites. Especially, V, Cu, and Fe are well known as the low temperature SCR catalysts [1]. When the residual oxygen and SO_2 are present in the exhaust gases, it reduces the reactivity of this type of catalysts for NO reduction reactions [4]. Numerous efforts have been reported for testing of different reducing agents and development of new catalysts to increase the NO removal efficiency, i.e. >80%, in the presence of oxygen [5–7]. Previous studies indicated that carbon is a promising reducing agent for the removal of diluted NO [2,8,9]. Metals loaded on lignite char (LC) may significantly promote NO reduction in the presence of oxygen at temperatures as low as 300 ° C [10,11]. Metal-loaded lignite char may potentially pave the way to efficient cleaning of NO [12,13]. However, the kinetics and mechanism of the direct reduction of NO with carbon catalyzed by transition metals in the presence of oxygen have not been fully understood. In this study, the catalytic NO reduction by Cu and Fe oxides supported on activated lignite chars in the presence of O_2 was studied systematically. The mechanisms for NO reduction and CO_2 formation were also elucidated.

2. Experimental

2.1. Catalyst preparation

Hailar lignite from Inner Mongolia region of China was used in this study. The proximate analysis of the lignite sample is given as follows:

---

* Corresponding author.
E-mail address: jianglong.yu@newcastle.edu.au (J. Yu).

http://dx.doi.org/10.1016/j.fuproc.2016.06.010
0378-3820/

Table 1
The results of BET analysis of different samples.

Samples	S_{BET} (m^2/g)	S_{Mi} (m^2/g)	V_t (cm^3/g)
LC	62.59	58.38	0.18
LC-Fe	268.88	206.39	0.15
LC-Cu	275.12	210.23	0.16

S_{BET}: total surface area; S_{Mi}: microporous surface area; V_t: total pore volume.

moisture content, 30.87% (as received basis); volatile matter, 38.28% (dry basis); fixed carbon, 46.82% (dry basis); and ash content, 14.90% (dry basis). The raw lignite samples were crushed and sieved to a particle size of 75–125 μm, and then dried at 105 °C under nitrogen. The dried coal sample was acid-washed using 0.4 N HCl aqueous solution for 12 h. The resulted slurry was filtered and washed by using de-ionized water until a constant pH (5.0–5.5) was achieved. Co-precipitation method was used for Fe and Cu loading onto the acid-washed coal samples. The ratio of Fe or Cu to acid-washed coal was 1:10 by weight. Prior to co-precipitation, the acid-washed coal samples were mixed with ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) aqueous solutions at 50 °C under ultrasound for 5 h. Ammonia aqueous solution was then gradually added to the mixture until the solution pH reached 10. The obtained slurry was then filtered and washed by using de-ionized water. The samples were then dried at 105 °C overnight in a vacuum oven. The above prepared lignite sample was then gasified and activated in a fixed-bed quartz reactor heated by an electric furnace at 800 °C in 15% (vol.) steam balanced with nitrogen for 30 min. The proximate analysis of the char from the acid-washed coal was as follows: moisture content, 1.26%, volatile matter, 3.05% (d.b.); fixed carbon, 91.97% (d.b.); and ash content, 3.72% (d.b.). The structural properties of char are shown in Table 1. The prepared chars impregnated with Fe and Cu were assigned as LC-Fe and LC-Cu, respectively.

2.2. Denitrification experiments on fixed-bed reactor

The denitrification experiments were carried out at 300 °C in a fixed-bed quartz reactor with an inner diameter of 10 mm, heated in an electric furnace at ambient pressure and at a space velocity of 6000 h^{-1}. The experimental setup is shown in Fig. 1. About 1.3 g char was charged into the reactor during each experiment. The simulated flue gas containing 1500 ppmv NO, 5% O_2, and balanced by N_2 was then introduced into the reactor through the top inlet and the outlet gas composition (NO, CO_2 and CO) was measured by a MGA 5 Flue Gas Analyzer. NO conversion was calculated according to the following equations:

$$X = \frac{C_{in} - C_{out}}{C_{in}} \tag{1}$$

$$N_c = \frac{v_{sp} V_{bj} M_{NO}}{V_m m_c} \times \left[\int_0^t (C_{in} - C_{out}) dt \right] \times 10^3 \tag{2}$$

where, X is the conversion of NO (%), C_{in} and C_{out} are the inlet and outlet concentration of NO (ppmv), respectively, N_c is the total NO reduction capacity mg/g·cat.), ν_{sp} is the space velocity (h^{-1}), V_{bj} is the volume of the catalyst samples in the reactor (l), M_{NO} is molar mass of nitric oxide (g/mol), V_m is the molar volume of NO at 1 atm and 25 °C (l/mol), and t is the reaction time of samples (h). m_c denotes the mass of catalysts (g).

2.3. TG-MS experiments

Non-isothermal decomposition experiments were carried out by thermogravimetry-mass spectroscopy (TG-MS) (NETZSCH STA 449 F3 coupled with NETZSCH QMS 403 C). The catalyst sample of about 2 mg was loaded into a Pt crucible. The mass loss and gaseous products were continuously recorded by TG and MS, respectively. The samples were heated in the temperature range of 30–600 °C with a heating rate of 5 °C min^{-1} in different gas environments, e.g. 1500 ppmv NO balanced with Ar, 1500 ppmv NO and 5% O_2 balanced by Ar, and 5% O_2 balance by Ar, respectively. The gas flow rate was 100 mL min^{-1}. Both pure lignite char (LC) and Cu-loaded lignite char (LC-Cu) were analyzed.

2.4. Catalyst sample characterization

Crystal phases in samples were identified by Shimadzu 7000 powder XRD. The Cu Kα radiation was operated at 30 mA and 40 kV (scanning rate at 3° min^{-1} over a 2θ range of 10–90°). Catalyst samples before and after denitrification were analyzed by using a Thermo Fisher Nicolet IS5 FTIR spectrometer. For IR spectra acquisition, the pellet samples were prepared by grinding 1.0 mg of char with 100 mg KBr followed by the pelletization.

3. Results and discussion

3.1. Conversion of NO under different conditions

It can be seen in Fig. 2 that nearly complete conversion of NO was achieved with both LC and LC-Cu in the first stage of denitrification reaction. The NO conversion sharply decreased to about 30% for the LC sample after 10 min. However, in the case of LC-Cu catalyst, a significantly improved NO reduction after 10 min was achieved. The NO conversion for LC-Cu catalyst was approximately 20% higher than that of LC for the time span of 20–70 min. LC-Cu catalyst gave much longer breakthrough time compared with the LC sample. When 5% O_2 was added in the feed gas, the NO conversion was enhanced at higher temperatures. In the first 30 min of the reaction, NO conversion was nearly 100% at 100, 200, and 300 °C. After 30 min, NO conversion decreased at 100 and 200 °C. At 100 °C, the NO conversion dropped rapidly to 50% and 30% after 120 min and 150 min, respectively. At 200 °C, the times at which NO conversion decreases to 50% and 30% were 150 min and 250 min, respectively. The highest NO conversion and longest

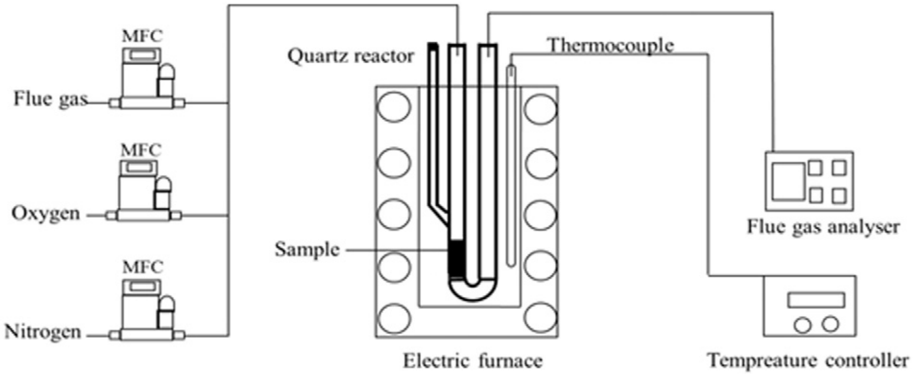

Fig. 1. Schematic diagram of the fixed-bed experimental setup.