Fuel 206 (2017) 318–324

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Low temperature catalytic performance of coal-fired flue gas oxidation over Mn-Co-Ce-O_x

Yonghua Guo, Huiying Wei, Genyuan Zhao, Xueqin Ma, Wenshuang Zhu, Yanzhao Yang *

Key Laboratory for Special Functional Aggregate Materials of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

HIGHLIGHTS

- A Mn-Co-Ce-O_x catalyst was synthesized and efficient on NO and CO oxidation under low temperature.
- The catalysts were characterized by XRD, BET, H_2-TPR and XPS methods.
- The mechanism of dual redox cycles in the Mn-Co-Ce-O_x catalyst was proposed.
- The catalyst showed outstanding sulfur tolerance and thermal stability.

ARTICLE INFO

Article history:
Received 16 February 2017
Received in revised form 5 May 2017
Accepted 7 June 2017

Keywords:
Catalytic oxidation
NO/O_2
Flue gas
Low temperature oxidation

ABSTRACT

A series of Mn-Co-Ce-O_x were prepared using co-precipitation method and tested for low temperature catalytic oxidation of NO and CO with O_2. The best catalytic result was obtained by $Mn_{0.2}Co_{0.3}Ce_{0.5}$ catalyst, which yielded 100% NO and CO conversion at 185 °C and 105 °C under space velocity at 60,000 h^{-1} respectively. XRD, BET, TEM, H_2-TPR, XPS and Raman were used for the structure and redox properties investigation of mixed oxide. The catalyst characterization suggested that the high catalytic oxidation performance was attributed to dual redox cycles ($Mn^{3+} + Co^{3+} \leftrightarrow Mn^{4+} + Co^{2+}$, $Mn^{3+} + Ce^{4+} \leftrightarrow Mn^{4+} + Ce^{3+}$). In the SO_2 and H_2O poisoning test, 67% of NO converted to NO_2 over the $Mn_{0.3}Co_{0.2}Ce_{0.5}$ catalysts and recovered to 82% quickly, which displayed high resistance against H_2O and SO_2. The catalyst shows good stability between 24 h test.

1. Introduction

Nitrogen oxides (NO_x), especially NO, have became the major pollutants because of the worldwide use of coal in energy production which are hazardous to both environment and human, causing ozone hole, photochemical smog and the acid deposition. Therefore, Researchers have made many efforts for NO_x emission reduction to protect environment, such as selective non-catalytic reduction (SNCR) [1], selective catalytic reduction (SCR) [2], selective catalytic oxidation (SCO) method [3]. Although SCR is a traditional choice for NO_x reduction for decades because of the high efficiency and well establishment, there still remain several problems [4]. Most SCR processes run at high temperature (300 °C–500 °C), which need extra heat. Moreover, a large reactor volume is needed when the reducing agent ammonia used in this technology, which may cause additional pollution. SCO is a promising method in NO_x decrease which could oxide NO into NO_2 and removed easily by adsorption at low temperature without additional oxidant. Many reagents can be used to absorb the mixed gas (NO + NO_2) such as lime or ammonia water, and the suitable ratio of NO/NO_x (about 50–60%) which could achieve the maximum absorption efficiency [5,6]. Therefore, the SCO method provide a promising method to actualize SCR cost effective because of the possibility to avoid the ammonia-corrosion of ammonia in SCR [7].

Until now, many researchers have focused on exploiting efficient and stable catalysts for NO oxidation [8]. Except for noble metals like Pt [9,10], Ag [11] and Au [12], many metal oxide catalysts such as transition metal oxide [13,14] and perovskite-type oxides [7] have been investigated for NO oxidation. Metal oxides are now drawing attention since they are at low price and easily prepared. But there are still some problems, such as NO conversion at low temperature difficult to be improved and poor sulfur resistance, which are the key to put catalysts into use under the industrial environment. Mn [15], Co [6,16] and Ce [17,18] based catalysts showed their good performance for NO oxidation. Mn has excellent NO oxidation ability and great interaction with Ce,

---

* Corresponding author.
E-mail address: yzhyang@sdu.edu.cn (Y. Yang).

http://dx.doi.org/10.1016/j.fuel.2017.06.034
0016-2361/

which has draw many attention for the remarkable oxygen storage and redox properties [19,20]. In recent years, some studies have paid attention to Mn-Ce or Co-Ce mixed oxides [21,22]. Qi et al. prepared Mn-Ce mixed oxides and doped Zr to increase the sulfur tolerance [23]. Qiu investigated that Co was the most active metal for NO oxidation among the metals (Co, Mn, Fe, Cr and Ni) doped in CeO_2 [18]. Chong prepared a series of Co-Ce-Ti oxides and found that the excellent redox ability was result from the strong interaction between Ce and Co [13]. Yi researched the low temperature activity of Mn-CoO_x modified by nonthermal plasma and found that the efficient synergetic effect between Co and Mn is the most important reason for high catalytic performance [24].

In this paper, we studied the NO oxidation effect of Mn-Co-Ce-O_x catalysts with different mole ratios and different calcination temperatures. XRD, BET, TEM, H_2-TPR, XPS and Raman were used to investigate catalytic activities, and the maximum efficiency in low temperature was achieved by $Mn_{0.2}Co_{0.3}Ce_{0.5}$ catalyst. Besides, the catalytic performance of $Mn_{0.2}Co_{0.3}Ce_{0.5}$ catalyst in the presence of SO_2 and steam had also been investigated, and 67% NO conversion was obtained. After the poisoning test, the catalyst recovered to 82% quickly, and showed excellent sulfur tolerance. Considering CO may exist in flue gas when coal fired without enough oxygen or the coal quality is poor, we also tested CO conversion at the same time.

2. Experimental section

2.1. Catalyst preparation

Mn-Co-Ce-O_x catalysts were prepared through co-precipitation method. Briefly, Nitrate salts of Ce and Co were dissolved in deionized water at room temperature and $Mn(NO_3)_2$ solution (50 wt%) was added in. The mole ratio of (Mn + Co)/Ce used were 1:1 and the mole ratios of Co/(Mn + Co + Ce) were 0, 0.1, 0.2, 0.3, 0.4, and 0.5. Then, the aqueous solution of Na_2CO_3 was mixed with stirring until pH = 10. After being stirred for 1 h, the mixtures were filtered and washed with deionized water and alcohol 3 times. The obtained solid was dried at 60 °C overnight and the catalysts were calcined at 200 °C–500 °C for 4 h. The preparation of CeO_2 was with the same method. In this work, the samples were denoted as Mn_x-$Co_yCe_{0.5}$, where x, y represent the molar ratio of Mn and Co to the content of total metal. The Nitrite salts (>99.9%) were all received from Tianjin Kermel Co. Ltd. Sodium carbonate (Na_2CO_3, 99.8%) was obtained from Tianjin BoDi Chemical Reagent Factory. The above reactants were used without any further purification.

2.2. Characterization

The X-ray diffraction (XRD) experiments were performed on a Rigaku D/Max 2200PC diffractometer with Cu Kα radiation (λ = 0.15418 nm). Transmission electron microscopy (TEM, JEM 1011-CXII, 100 kV) and high resolution transmission electron microscopy (HRTEM, JEM-2100) with an accelerating voltage of 200 kV were used to investigate the micromorphology of catalysts. Temperature-programmed reduction with H_2 (H_2-TPR) was measured by a PCA-1200 instrument. 50 mg catalyst was pretreated under pure O_2 at 300 °C for 30 min. After cooled down to room temperature, the samples were heated to 800 °C with a rate of 10 °C·min^{-1} in a mixed stream with 5% H_2 and 95% Ar (30 mL·min^{-1}). Raman spectra were measured by a LabRAM HR4800 spectrometer with the spectral window from 200 cm^{-1} to 1200 cm^{-1} at an excitation laser wavelength of 514 nm. The XPS spectra and images were acquired on an ESCALAB 250 photoelectron spectrometer using Al Kα radiation.

2.3. Catalytic activity measurement

Catalytic activity evaluation of feed gas was performed in a fixed-bed flow microreactor of a quartz tube mounted in an electrical furnace under atmospheric pressure. The gaseous mixtures of 300 ppm of CO, 500 ppm of NO, 4.0% of O_2, and Ar in balance were fed to the catalyst bed (50 mg catalyst mixed with 300 mg quartz sand) at a space velocity (SV) of 60,000 mL·h^{-1}·g_{cat}^{-1}. The gas mixtures followed the industry actual condition, and 200 ppm of SO_2 and 4.0% H_2O were introduced when used. The catalysts were heated with a rate of 3 °C·min^{-1} and the gas products were measured by an online gas analyzer (Gasboard-3000).

3. Results and discussion

3.1. Activity test

Results of NO and CO oxidation activities of Mn-Co-Ce-O_x catalysts calcined at 300 °C with different contents of Co are given in Fig. 1. As the content of doped Co increasing, it is found that the efficiency of catalysts improved with the mole ratios of Co/(Mn + Co + Ce) reached 0.2. Then, NO conversion decreases with the mole ratio increasing. The order of catalytic activity of catalysts was: $Mn_{0.3}Co_{0.2}Ce_{0.5} > Mn_{0.2}Co_{0.3}Ce_{0.5} > Mn_{0.4}Co_{0.1}Ce_{0.5} > Mn_{0.5}Ce_{0.5} > Mn_{0.1}Co_{0.4}Ce_{0.5} > Co_{0.5}Ce_{0.5}$. From the test result, T_{100} (the completely transformation temperature) of $Mn_{0.2}Co_{0.3}Ce_{0.5}$ catalyst is about 185 °C for NO and 105 °C for CO conversion, which signifies

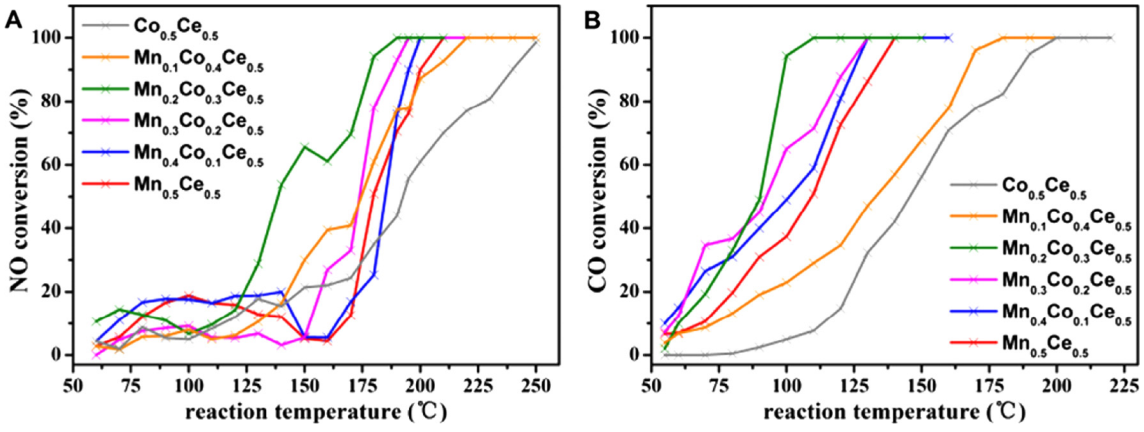

Fig. 1. Oxidation activity of soot. (A) NO conversion (B) CO conversion on Mn-Co-Ce-O_x catalysts.