Chemical Engineering Journal 327 (2017) 1066–1076

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Effects of contact model and NO_x on soot oxidation activity over Pt/MnO_x-CeO_2 and the reaction mechanisms

Hailong Zhang [a], Shandong Yuan [b], JianLi Wang [c,*], MaoChu Gong [c], Yaoqiang Chen [c,*]

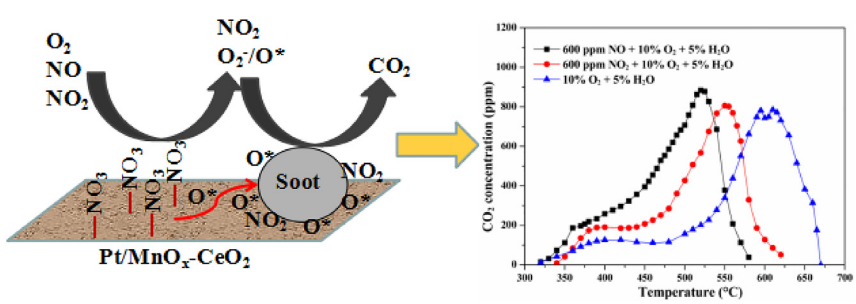
[a] College of Chemical Engineering, Sichuan University, Chengdu 610064, PR China
[b] Institute of New Energy and Low-Carbon Technology, Sichuan University, Chengdu 610064, PR China
[c] College of Chemistry, Sichuan University, Chengdu 610064, PR China

HIGHLIGHTS

- NO and NO_2 has no promotion for the soot oxidation in the tight contact.
- The promotion of NO_x in loose contact is mainly related to active oxygen species.
- NO shows better promotion than NO_2 due to formation of more surface nitrates.
- Active oxygen species would play a key role in NO_x-assisted soot oxidation.

GRAPHICAL ABSTRACT

The improved activity of Pt/MnO_x-CeO_2 in NO_x + O_2 would be mainly attributed to the formation of active oxygen species (O*) during surface nitrate decomposition. Furthermore, the NO in reaction gas shows greater promoting roles than NO_2 due to the formation and decomposition of more surface nitrates.



ARTICLE INFO

Article history:
Received 26 February 2017
Received in revised form 15 May 2017
Accepted 5 June 2017
Available online 7 June 2017

Keywords:
Pt/MnO_x-CeO_2
Soot oxidation
Catalyst-soot contact sites
Nitrate decomposition
Reaction mechanism

ABSTRACT

This study aims to compare the promoting roles of NO and NO_2 additions on soot oxidation over Pt/MnO_x-CeO_2 under tight and loose contacts and further reveal the mechanisms for the promoted reactions by DRIFTS (diffuse reflectance infrared fourier transform spectroscopy) and GCMS (gas chromatograph mass spectrometer). The soot oxidation tests show that the promotion of NO_x cannot be exhibited under tight contact and NO addition displays a greater promoting role than NO_2 addition under loose contact. The mechanism investigations indicate that more surface nitrates form on the catalyst in NO and their decomposition effectively enhances the formation and desorption of more active oxygen species, which would be a key role in the accelerated soot oxidation reactions. However, the promoting role of NO can not be found in tight contact, it may be due to the inhibition of nitrate formation by soot coverage on the surface of the catalyst. This work also confirms that active oxygen would be main contributor for soot oxidation despite the presence of NO_2.

1. Introduction

The soot emission from diesel engines has become a very serious environmental problem and is affecting human health in China. With the growing concern on the effects of diesel soot on environment and human health, the particulate matter (PM) emis-

* Corresponding authors.
E-mail addresses: wangjianli@scu.edu.cn (J. Wang), nic7501@scu.edu.cn (Y. Chen).

http://dx.doi.org/10.1016/j.cej.2017.06.013
1385-8947/

sions can be effectively reduced by placing a diesel particulate filter (DPF) in the exhaust pipe [1–3]. However, it is difficult that the soot collected in the filter is burned at the low exhaust temperature (200–400 °C), and the soot combustion at high temperature (≥550 °C) can arouse a larger energy consumption [4–6]. Thus the advanced catalysts (e.g., [7–11]) coated on DPF have been widely investigated to decrease the temperature of soot combustion.

It has been confirmed that, among many catalysts for soot oxidation, MnO_x-CeO_2 mixed oxides can exhibit an excellent catalytic activity during soot oxidation in both O_2- and NO_x-assisted conditions, which is attributed to the synergistic effect between MnO_x and CeO_2 and the strong redox ability [9,11–15]. In the publication [16], it was found that the cooperative effect of MnO_x and CeO_2 as well as higher dispersion of CeO_2 and Mn_2O_3 as active species over the support ZSM-5 could greatly enhance the catalytic activity. It has been also reported that the incorporation of Mn^{x+} into CeO_2 would greatly promote the oxygen mobility and storage capacity, which effectively improves the availability of surface active oxygen, thereby the better redox ability and catalytic activity would be obtained [10,14,17].

In general, NO_2 contained in the exhaust gases could easily reach soot surface to oxidize soot at low temperatures in the range of 250–400 °C due to its stronger oxidizing ability than O_2 [9,18–20]. It has been evidenced that MnO_x-CeO_2 mixed oxides have high oxidation activity of NO into NO_2 and better NO_x storage ability at low temperatures, the produced NO_2 over the catalyst would directly involve in the soot oxidation reactions [10,17,21]. In addition, It has been reported that Pt catalysts have high catalytic activity in oxidizing NO to NO_2 and thereby exhibit better soot oxidation activity [22,23]. The Pt-containing catalysts might be more suitable candidates for the NO_x-assisted soot oxidation under realistic exhaust conditions. In Liu's work [17], the noble metal Pt with a lower loading amount (0.5 wt.%) was introduced into MnO_x-CeO_2 supported on Al_2O_3 and the catalyst exhibited a better NO oxidation activity than a high-loading Pt/Al_2O_3 catalyst (1 wt.%). Furthermore, the presence of Pt could greatly improve the reducibility of MnO_x-CeO_2 mixed oxides in view of a spillover mechanism over the platinum atoms and a synergistic effect between Pt species and the supports, thus enhancing the catalytic activity [11,17].

In order to further study the oxidation mechanism of soot in the presence of NO_x and O_2, various investigators have done many studies and revealed two fundamental reactions during soot oxidation processes in the absence of catalysts: the direct and cooperative reactions [18,24,25]. The direct oxidation reactions (Eqs. (1) and (2)) are triggered when O_2 or NO_2 reaches the carbon surface along with the C-NO_2-O_2 cooperative reactions (Eqs. (3) and (4)). Jeguirim et al. [18] have further reported that the soot oxidation rate of the cooperation reaction could be effectively enhanced in the presence of Pt/Al_2O_3 catalyst due to the continuous production of NO_2. The sum of the mechanisms of soot oxidation reactions in C-NO_2-O_2 system may be showed as follows:

$$C + NO_2 \rightarrow CO_x + NO \tag{1}$$

$$C + O_2 \rightarrow CO_x \tag{2}$$

$$C + NO_2 + O_2 \rightarrow CO_2 + NO \tag{3}$$

$$C + NO_2 + O_2 \rightarrow CO + NO_2 \tag{4}$$

It was also reported that, during the cooperative reactions (Eqs. (3) and (4)), the presence of NO_2 would promote the decomposition of –C(O) complexes, which generate from O_2 chemisorption, on the carbon surface due to the formation of intermediate nitro-oxygenated species (–C(ONO_2)) [13,24]. Early in 1999, Oi-Uchisawa et al. [26] thought that some oxidized surface species, phenols and carboxylates etc., might form on soot surface by NO_2 attack and then their further oxidation and decomposition would occurred. In Setiabudi's study [27], it was found that the surface nitrates such as monodentate and bidentate nitrates formed by DRIFTS analysis after the adsorption of NO_x on ceria and the decomposition of these nitrates into NO_2 effectively enhanced the soot oxidation rates. Wu et al. [13] studied the effects of NO on soot oxidation activity over MnO_x-CeO_2 mixed oxides, the same results were also confirmed by *in situ* DRIFTS. Furthermore, it has been reported that the super-oxygen species (O_2^-) resulting from the decomposition of surface nitrates might play an important role during soot oxidation reactions [27,28].

Besides, the contact between soot and catalysts is poor under practical conditions, which would not be benefitable to the soot-oxygen reactions in spite of high oxygen concentration (5–15%) in diesel exhaust pipe [29]. In general, the catalytic soot oxidation reactions occur at the soot-catalyst interface and the soot oxidation rate strongly depends on the intensity of contact between soot and catalyst [30]. According to the literature [29–32], main types of physical contact used are "loose contact" and "tight contact", and the soot-catalyst mixture obtained by tight contact shows lower activation energy and oxidation temperature than that by loose contact due to more soot-catalyst contact sites. In Aneggi's work [33], it was found that a Ce^{3+}/Ce^{4+} redox mechanism process in ceria-catalyzed soot oxidation reactions depended on the soot-catalyst contact sites. In order to enhance the catalytic combustion of soot, some researchers have paid more attention to the improvement of soot-catalyst contact by the optimization of catalyst morphology [31] and structure [34,35].

However, a systematic study on the effects of NO_x (NO and NO_2) on the C-NO_x-O_2 reactions over Pt/MnO_x-CeO_2 catalyst under tight and loose contact conditions and the reaction mechanisms are rarely done in the previous works. In the present study, MnO_x-CeO_2 mixed oxides were prepared by co-precipitation route and the Pt/MnO_x-CeO_2 catalyst with 0.5 wt.% Pt was obtained by impregnation method. The oxidation of soot over Pt/MnO_x-CeO_2 was evaluated under O_2 and NO_x/O_2 reaction gases with 5% H_2O by soot-TPO (soot temperature programmed oxidation) experiments in a fixed bed reactor. The tight and loose contacts between soot and catalysts were used as the mixed modes in soot-TPO tests. Furthermore, the possible reaction mechanisms for soot oxidation over Pt/MnO_x-CeO_2 are also studied and discussed by DRIFTS (diffuse reflectance infrared Fourier transform spectra) and GCMS (gas chromatograph mass spectrometer) in this work.

2. Experimental

2.1. Catalyst preparation

MnO_x-CeO_2 mixed oxides with a Mn/Ce molar ratio of 1:4 were prepared by a co-precipitation method, $Ce(NO_3)_3 \cdot 6H_2O$ (95% pure) and $Mn(NO_3)_2$ (50 wt.%) were used as the precursors. These precursors were dissolved in deionized water and mixed with a buffer solution (pH > 9.0) consisting of NH_3 H_2O and $(NH_4)_2CO_3$ (chemical reagents, Beijing). The precipitates were filtered and dried by a spraying apparatus, then calcined in air at 500 °C for 3 h in a muffle furnace. The final sample was impregnated with an aqueous solution of $Pt(NO_3)_4$ (30.50 wt.%, Heraeus), the loading amount of Pt was 0.5 wt.% on the support. The resulting powders were dried at 120 °C for 2 h and calcined at 450 °C for 2 h. The morphology and actual element contents of the catalyst are shown in Fig. 1 and Table 1, respectively.