Fuel 227 (2018) 79–88

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Promotional effect of CuO loading on the catalytic activity and SO_2 resistance of MnO_x/TiO_2 catalyst for simultaneous NO reduction and Hg^0 oxidation

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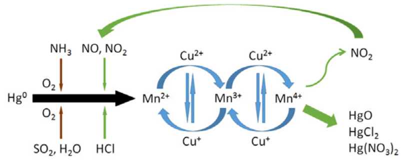
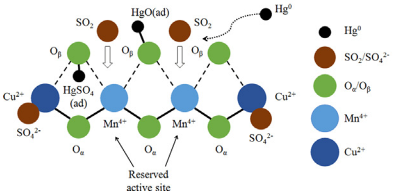
GRAPHICAL ABSTRACT





ARTICLE INFO

Keywords:
Mercury
CuMnTi ternary mixed oxide
Catalysis
Coal combustion
Flue gas

ABSTRACT

CuO loaded MnO_x/TiO_2 mixed oxide (CuMnTi) synthesized by an ultrasonic-assisted impregnation method was for the first time employed for simultaneous nitrogen monoxide (NO) reduction and elemental mercury (Hg^0) oxidation under selective catalytic reduction (SCR) atmosphere with the presence of NH_3. The CuMnTi catalyst exhibited a wide temperature window from 150 to 250 °C for both NO reduction and Hg^0 oxidation. At the optimal temperature of 175 °C, CuMnTi reduced 96.4% of the inlet NO and oxidized 100% of the inlet Hg^0 at a very high gas hourly space velocity (GHSV) of 40,000 h^{-1}. O_2, HCl and NO significantly promoted Hg^0 oxidation and offset the adverse effect of detrimental flue gas components such as water vapor, SO_2 and NH_3. The protection effect of CuO over MnO_x reserved enough active sites of CuMnTi for Hg^0 oxidation in the presence of NH_3 or SO_2. Compared with MnO_x/TiO_2 (MnTi), the superior redox property, enlarged Hg^0 adsorption capacity and decent SO_2 resistance of CuMnTi ternary system were evidenced to account for its improved catalytic activity. This study indicated future potential for applying CuMnTi catalyst in simultaneous NO reduction and Hg^0

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https://doi.org/10.1016/j.fuel.2018.04.074
Received 13 March 2018; Received in revised form 10 April 2018; Accepted 15 April 2018

oxidation in low-temperature (150–250 °C) and low-rank (sub-bituminous and lignite) coal combustion flue gases.

1. Introduction

In August 2017, following 128 countries signing Minamata Convention to face the increasingly serious mercury pollution problem, the convention came into force and aimed to limit the mercury emission globally [1]. Among various emission sources of mercury, the coal-fired facilities is always a main source of atmospheric mercury pollution [2,3]. Elemental mercury (Hg^0) is regarded as the most difficultly removed form of discharged mercury from coal combustion due to its high volubility and insolubility in water [4–6]. By far, the most mature technique for degrading Hg^0 in coal-fired flue gas is activated carbon injection (ACI) [7,8]. However, the most common adsorbent, activated carbon (AC), suffers many drawbacks like high operating cost, low stability, adverse impacts on downstream flue gas desulfurization (FGD) system and compromising effect on the utility of fly ash, hence impedes the application of ACI in industrial [9–11]. On the contrary, relatively low cost, decent durability and better efficiency make catalytic oxidation the most promising alternative for Hg^0 emission control, because the oxidized mercury is easily captured in widely installed FGD systems [12,13].

Nitrogen oxides (NO_x) are another air contaminants discharged from coal combustion power plant that lead to environmental pollution like acid rain, photochemical smog and ozone depletion [14,15]. Selective catalytic reduction (SCR) of NO with ammonia (NH_3) over metal oxides catalysts was commercialized to remove NO_x from coal-fired power plants for more than decades [16]. Metal oxide based SCR catalysts, originally employed to remove NO_x from flue gas, happen to be able to promote the oxidation of Hg^0 to Hg^{2+} [17,18]. It is possible to achieve a simultaneous NO_x reduction and Hg^0 oxidation over SCR catalysts. However, a downstream configuration of simultaneous NO_x reduction and Hg^0 oxidation system, i.e., after particulate matter control devices, is essential for preventing catalysts from the poisoning effect of continuous exposure to high-concentration particles [19]. In this section, the temperature of flue gas is generally between 150 °C and 200 °C. It makes the traditionally commercial vanadia based SCR catalyst deficient because of its compromised catalytic activity when temperature is below 300 °C [20,21]. Moreover, catalytic activity of vanadia based SCR catalysts for Hg^0 oxidation was highly dependent on the HCl concentration and unsuitable for low-rank coal flue gas treatment [22]. Thus, it is highly urgent to develop a new SCR catalyst accommodating for simultaneous NO_x reduction and Hg^0 oxidation at low temperature (100–200 °C) under low-rank coal combustion flue gas conditions [23].

One of the most active and well-investigated catalysts for NO_x reduction and Hg^0 oxidation in low-temperature range are manganese oxides (MnO_x) contained materials [24–28]. Valence changed during low-temperature oxidizing process of manganese from Mn^{4+} to Mn^{3+} and then to Mn^{2+}, as wildly accepted mechanism for MnO_x based catalysts in both NO_x reduction and Hg^0 oxidation. The large-span valence change made them ideal for satisfying the temperature request [25,28]. However, the formation of manganese sulfate ($MnSO_4$) occupying adsorption sites over MnO_x surface accounts for largely suppressed catalytic activity of it in the presence of sulfur dioxide (SO_2) [29]. Supported by titanium dioxide (TiO_2) is a strategy to enhance the SO_2 resistance of MnO_x based catalysts, but the catalytic activity of TiO_2 supported MnO_x (MnO_x/TiO_2) is still unsatisfactory in real-world applications [23].

Besides TiO_2, a second active component was also introduced into binary metal oxides system to enhance their catalytic performances and/or SO_2 resistance [23,28,29]. For example, addition of copper oxide (CuO) to metal oxide catalysts greatly enhanced their resistance to SO_2 [30–32]. With the addition of CuO to cerium-titanium mixed oxide, CuO-CeO_2/TiO_2 (CuCeTi) was free of the influence of SO_2 due to a protection effect of CuO over CeO_2, i.e., SO_2 would combine with CuO firstly and hence the CeO_2 sites would be protected from poisoned by SO_2 [33]. Much more, CuO containing catalysts even could utilize SO_2 to promote NO reduction beyond 300 °C. This was attributed to the adsorption of SO_2 on CuO surface forming more acid sites for gas ammonia (NH_3) adsorption [34]. Nevertheless, the activation temperature for CuO catalyst is generally beyond 200 °C, higher than the temperature in downstream configuration (150–200 °C) [31]. A combination of CuO with metal oxides with low-temperature activity such as MnO_x will make up their operating temperature defects [35,36]. Therefore, CuO-MnO_x/TiO_2 (CuMnTi) exhibited excellent catalytic activity and SO_2 resistance in SCR of NO at low flue gas temperatures [31,37,38]. However, concerning to simultaneous NO reduction and Hg^0 oxidation over the CuMnTi catalyst, no study has been reported.

In this work, CuMnTi catalyst synthesized by an ultrasonic-assisted impregnation method was applied in simultaneous NO reduction and Hg^0 oxidation. The influence of individual flue gas components and NH_3 on Hg^0 oxidation and the involved mechanisms were explored by Hg-TPD and other characterizations. The protection effect of CuO over MnO_x was found. The enhanced catalytic activity and SO_2 resistance due to CuO addition to MnO_x/TiO_2 binary metal oxide was also discussed.

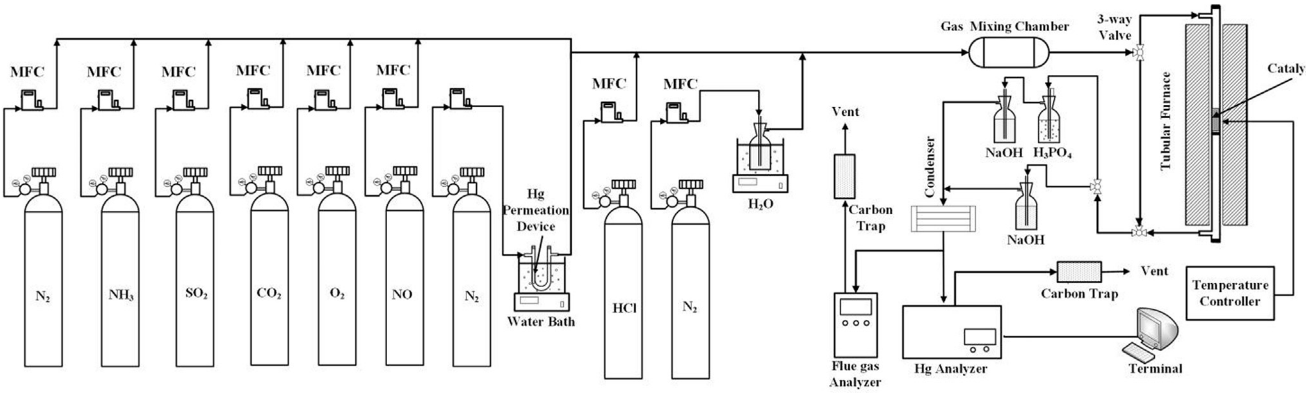

Fig. 1. Schematic diagram of the NO reduction and Hg^0 oxidation activity test system.