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Experimental study on reduction of NO by CH_4 over $La_{0.8}Sr_{0.2}MnO_3/\alpha$-$Al_2O_3$ in excess of O_2

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ABSTRACT

Selective catalytic reduction of NO is necessary for the environment but the present adopted NH_3-SCR has its weaknesses. This paper proposes CH_4-SCR of NO with perovskite catalyst ($La_{0.8}Sr_{0.2}MnO_3/\alpha$-$Al_2O_3$) and experiments were done to study the effect of key factors (resident time, temperature and the initial O_2 concentration). XRD patterns and SEM image show that $La_{0.8}Sr_{0.2}MnO_3$ is a catalyst with perovskite structure and this kind of structure has been proved to be efficient in SCR. Experiments show that CH_4 can convert NO efficiently in association with catalyst $La_{0.8}Sr_{0.2}MnO_3/\alpha$-$Al_2O_3$ and the max NO conversion ratio is over 90%. The longer the resident time is, the higher the conversion of NO is. The conversion of NO increased with the increase of temperature when the initial concentration of O_2 ranged from 0% to 3% and moderate O_2 at high temperatures can promote the reduction of NO by filling oxygen vacancies in lattice and taking part in the reactions. The new catalyst $La_{0.8}Sr_{0.2}MnO_3/\alpha$-$Al_2O_3$ could work efficiently in the widest range of oxygen concentration at 800 °C and it reached 90% with the oxygen concentration ranging from 4% to 6%. This research will provide further data to improve the process of SCR in the power plant.

1. Introduction

The acid rain and urban smog caused by nitrogen oxides (NO_x) are the most serious environment problems [1]. The catalytic removal of NO_x is one of the most important ways to decrease the impact of NO_x on the environment [2]. For many years, a considerable amount of literature has been published on selective catalytic reduction (SCR). As is known, the typical reducing agent of SCR of NO_x in power plant is NH_3 (NH_3-SCR). The present adopted NH_3-SCR has its weaknesses such as expensive catalysts (V_2O_5/TiO_2) and releasing unreacted ammonia which may bring second pollution, flog and haze [3–5]. And the ammonia is a high corrosive and toxic gas and its oxidation may generate N_2O, NO and NO_2. Therefore, it is urgent to promote a new reducing agent with proper catalysts.

In recent years, the experimental studies and previous theoretical efforts have paid much attention to new reducing agents of SCR. SCR using hydrocarbons as reducing agents (SCR-HCs) is a technology that is still found in its development stage [6–11]. Researchers have shown an increased interest in CH_4-SCR [12–20]. Several studies have revealed that the key step of SCR is the oxidizing reaction of the reducing agent. The energy of H–C bond in CH_4 is 438.5 kJ/mol while the energy of H–N bond in NH_3 is 449.4 kJ/mol. It suggests that CH_4 is more active compared with NH_3. Since twenty centuries, a considerable amount of literature has been published on using transitional metal oxides (Co, Pd, In, Ag, Cu, etc.) supported on zeolite as the catalyst of CH_4-SCR [5,21–27]. In 1993, Li proposed using Co-ZSM-5 and Ga-ZSM-5 as the catalyst of CH_4-SCR[28]., then he investigated the effect of O_2 on reduction of NO by methane with Co-ZSM-5 [29]. Pt, Pd, Ni and In were found and identified gradually to be efficient in catalyzing CH_4-SCR [30–33]. In 1998, Burch studied the efficient of CH_4-SCR with Pt, Pd and In supported on Al_2O_3 and SiO_2 [34]. In 2011, Chen studied CH_4-SCR with Co-Beta and the stability of the catalyst [35]. In 2004, Sowade presented that the addition of CeO_2 on In-ZSM-5 can improve the oxidation of NO and promote CH_4-SCR [36]. Unfortunately, some of these catalysts have problems when applied in engineering, such as weak in hydrothermal stability, high cost and inhibited seriously by O_2 [2,17,37–39].

Metal oxide ABO_3 has a perovskite structure, in which A-site atom is metal ion with larger radius (La,K) and B-site atom is transition metal ion (Mn, Fe) [40]. Fig. 1 shows the structure diagram of ABO_3 [41]. A-site atom plays a role in stabilizing the lattice structure. B-site atom and oxygen in lattice take part in the reactions and catalysis [42]. Metal oxide catalysts ABO_3 are widely used

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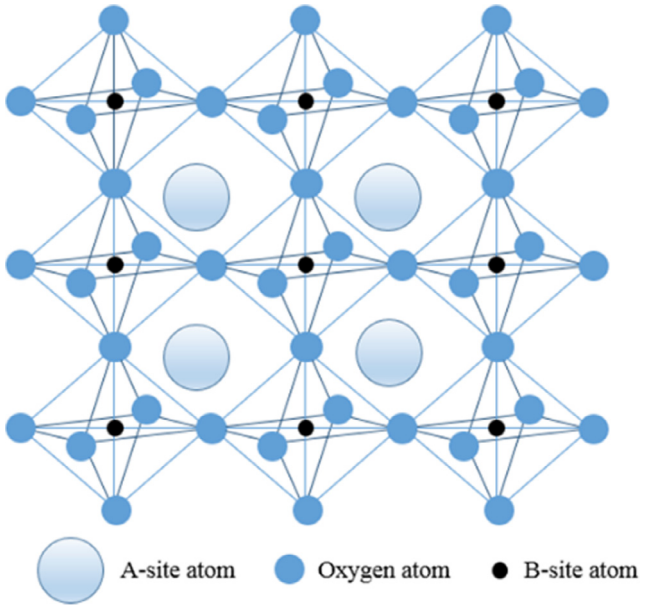

Fig. 1. The structure diagram of metal oxide ABO_3.

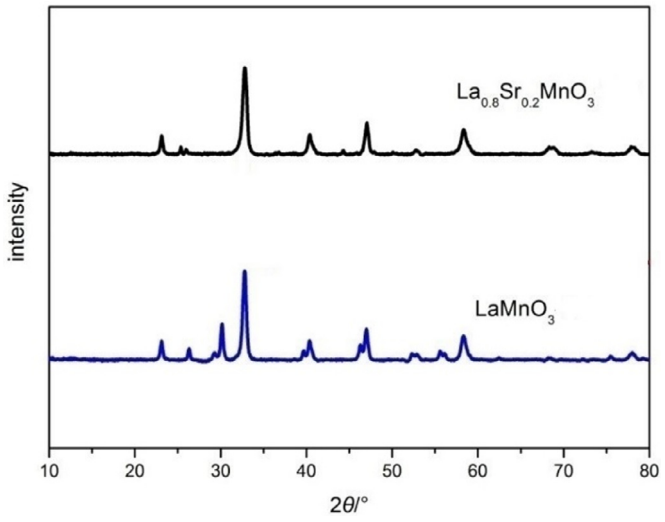

Fig. 2. XRD patterns of $La_{0.8}Sr_{0.2}MnO_3$ and $LaMnO_3$.

in purification of automobile exhaust, industrial flue gas treatment and photo catalysis [43–45].

Catalysts with perovskite structure are efficient on catalyzing CH_4 oxidation and NO decomposition which were identified by many researchers [2,37,46–50]. ABO_3 can catalyze the combustion of CH_4, in which lattice oxygen reacts with CH_4 and CO absorbed on the catalyst, while O_2 in air replenishes the vacant lattice. ABO_3 can also catalyze the decomposition of NO, in which lattice oxygen plays a role in oxygen desorption and N_2 production after the combination of NO molecule [37]. Teraoka investigated the process that $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.6}Sr_{0.4}Mn_{0.8}Ni_{0.2}O_3$ catalyze NO decomposition [51]. Tofan studied the way $La_{1-x}Sr_xM_{1-y}O_{3-\delta}$ (M = Co, Ni, Cu) catalyzes the decomposition of NO. Giannakas studied NO–CO reactions with catalyst $LaFeO_3$ series where $La_{0.8}Ce_{0.2}FeO_3$ has the best work in catalyzing NO–CO reactions [52]. Moreover, ABO_3 metal oxide has good oxidation activity and thermos ability. It can be stable in high temperature over 1000 °C [52].

Perovskites are considered as the potential catalyst candidates for CH_4-SCR with regard to their cost-effective catalytic materials and excellent hydrothermal stability. $LaMnO_3$ is a typical perovskite metal oxide. Sr^{2+} can be added in the crystal and instead of part of La^{3+}, which can improve the stabilization of the lattice. The structural stability of ABO3 metal oxides can be calculated according to Gold-Schmidt formula. t is employed here to measure the structural stability:

$$t = (r_A + r_O)/\left[\sqrt{2}(r_B + r_O)\right] \quad (1)$$

in which r_A, r_B and r_O are separately the ionic radius of A, B and O. when $0.75 < t < 1.0$, the metal oxides have stable ABO3 structure. The t of $La_{0.8}Sr_{0.2}MnO_3$ is 0.899. Therefore, it has good stability in structure.

$La_{0.8}Sr_{0.2}MnO_3$ may have outstanding performance in the SCR of NO_x by CH_4. Therefore, we tried to use $La_{0.8}Sr_{0.2}MnO_3$ supported on α-Al_2O_3 to catalyze the CH_4-SCR and the catalyst efficiency was investigated in this study. In this study, $La_{0.8}Sr_{0.2}MnO_3/\alpha$-$Al_2O_3$ catalyst was prepared using co-impregnation method. Catalysts were characterized by XRD and SEM. The key factors of the CH_4-SCR studied in this work were resident time, temperature and the concentration of O_2 in the flue gas. Their effect on the conversion of NO was the focus of this work.

2. Preparation of catalyst

The catalyst (La: Sr: Mn = 0.8:0.2:1) supported on alumina (α-Al_2O_3) globules were prepared by co-impregnation method. Alumina globules were employed here instead of any expensive powder supports with higher surface area due to its engineering practicability and convenience of replacement in a real industry boiler. The precursor solution was prepared with $La(NO_3)_3 \bullet nH_2O$, $Sr(NO_3)_2$, $Mn(NO_3)_2$ and citric acid by sol–gel method. Citric acid played a role of metal ion complexing agent here, helping the reaction of metal ions and forming large molecular weight compounds instead of separately metal salt or oxide [53]. Typically, the calculated quantities of metal nitrates and citric acid (the same molar as $La(NO_3)_3$) were mixed together and dissolved in a sufficient quantity of deionized water. A few drops of diluted nitric acid were added to the dissolution to avoid the hydrolysis reaction and formation of metal hydroxide. The dissolution was stirred for 40 minutes at 40 °C to help metal nitrates and citric acid to be dissolved completely. The α-Al_2O_3 globules (BET: 300 m^2/g; bulk density: 0.62 g/mL; diameter: 3–5 mm) were activated in muffle roaster for 180 min at 500 °C. Next, the activated alumina globules were soaked in the precursor solution for 30 minutes at 90 °C. Then the solid was washed with deionized water and dried overnight (16 h) at 120 °C. At last, the leftover was calcined for 4 h at 700 °C in muffle roaster to obtain the catalyst with perovskite structure. And the catalyst was kept in a desiccator for further use.

3. Catalyst characterization

Powder X-ray diffraction (XRD) studies were conducted using the PANalytical X' Pert Pro instrument. Scanning electron microscope (SEM) studies were carried out using the JEOL JSM-6390A scanning electron microscope. The samples were observed by magnifying 20,000 times. The flue gas through the reactor with catalyst was measured by Fourier transform infrared spectroscopy (FTIR). The FTIR investigations were performed using a Gasmet Dx4000 spectrometer equipped with a Peltier cooled MCT detector, which has a spectral resolution of 8 cm^{-1} and sampling frequency up to 10 scan/s.

Fig. 2 shows the XRD (X-ray diffraction) patterns of $La_{0.8}Sr_{0.2}MnO_3$ and $LaMnO_3$. As

Fig. 2 shows, the two catalysts have similar X-ray diffraction spectrograms (same diffraction peaks $2\theta = 30.2°$, 32.5°, 40.3°, 47°, 58.2°). The characteristic diffraction peak of ABO_3 perovskite

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