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Short communication

Nanoflower-like Mg-doped MnOx for facile removal of low-concentration NOx at room temperature

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ABSTRACT

Nanoflower-like Mg doped MnOx (Mg/MnOx) is synthesized *via* a facile and scalable redox reaction strategy for facile removal of low-concentration NOx at room temperature. The optimized sample Mg/MnOx exhibits good activity, giving 100% NO removal efficiency at room temperature for 10 h under extremely high space velocity of 120,000 $mL^{-1} g^{-1} h^{-1}$ and low NO inlet concentration of 10 ppm. The Mg/MnOx is found to gradually get inactive resulted from the generated NO_2 and large amount of adsorbed NO covering active sites based on the results of characterizations and performance. Furthermore, the superior monolithic catalyst indicates great potential in actual application.

1. Introduction

With development and construction of big cities, the increasing number of underground car parks and road tunnels, which can ease burden of overpopulation on traffics, has caused several environmental problems. Large amount of vehicle fumes are concentrated in these semi-closed spaces resulting from low-ventilated efficiency, threatening to human health. Among them, NOx is approximately several to ten of ppm, containing nearly 90% NO [1]. At present, the most common and well-developed technology for NO removal is selective catalytic reduction (SCR) and NOx storage/reduction (NSR) [2–5]. However, such technologies are only effective for high concentration NO removal and usually need high temperature, not suitable for application in semi-closed spaces [6]. Therefore, the low-concentration NO removal at room temperature still exists as a big challenge and few reports on this issue are published.

Differing from NO, it's easier for NO_2 to be absorbed by alkaline solution due to its' high solubility in aqueous solution [7]. Therefore, we can first oxidize NO to NO_2 and then use alkaline solution to absorb NO_2 in the outlet gas. However, the oxidation reaction rate gets extremely slow at room temperature when NO concentration drops down to 10 ppm in those semi-closed spaces [8]. Therefore, it is urgent but challenging to develop an efficient catalyst, which can first efficiently oxidize low concentration NO to NO_2 at room temperature, then remove NO_2 together with residuary NO in the outlet gas by using absorption of alkaline solution (*i.e.*, $2NO_2 + 2NaOH = NaNO_2 + NaNO_3 + H_2O$; or $NO_2 + NO + 2NaOH = 2NaNO_2 + H_2O$) to achieve the efficient removal of NOx.

In our previous work, the crystalline mesoporous X-Mn(X = Fe, Zn, Co, Ni) bimetal oxides have been synthesized for low-concentration NO removal at room temperature, but these catalysts exhibit some drawbacks, such as short duration time and poor water-resistance, only 4 h for 100% removal ratio [9–10]. Afterwards, a Mg-doped manganese oxide OMS-2 (Octahedral Molecular Sieve with 2 × 2 tunnel structure) using ultrasonic-assisted method has been synthesized with good water-promoted performance [11]. However, it's hard to control the ultrasonic temperature and it needs additional energy-consuming cooling system, not applicable for practical mass production. Hence, it deserves much investigation in developing a highly efficient catalyst with good catalytic activity and water-resistance for actual application.

Amorphous manganese oxides have been widely reported and exhibit extremely high performance in many catalytic reactions, including the removal of high-concentration NO at high temperature [12–14]. Their excellent catalytic activity can be attributed to the rich oxygen vacancies and/or surface active oxygen species, which accelerates the mobility of lattice oxygen [15,16]. Besides, heteroatom doping in the manganese oxides can also improve catalytic activities to some extent, which is ascribed to the generated defects or synergistic

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effects [12,17,18]. Very recently, we have synthesized a novel nanoflower-like weak crystallization manganese oxide for the efficient NO removal. It's found that the Mn-vacancies and hydrated surfaces in this amorphous structure can significantly reduce barriers of NO_2 desorption on catalyst which is determined as the rate-determining step in the reaction of $2NO + O_2 \rightarrow 2NO_2$ [19].

On basis of our previous researches, herein, we further dope a certain amount of alkaline earth Mg ions into weak crystalline manganese oxides *via* a scalable and facile redox-precipitation reaction using $KMnO_4$, $Mn(CH_3COO)_2{\cdot}4H_2O$ and $Mg(CH_3COO)_2{\cdot}4H_2O$ as manganese and magnesium sources. The synthesized Mg doped MnOx (Mg/MnOx) shows loose nanoflower morphology, which is resulted from the large amount of released CO_2 gas during reaction. The effects of preparation parameters are detailedly investigated. Moreover, a possible deactivation mechanism of NOx adsorption (mainly induced by NO_2) on catalyst surfaces is proposed based on results of catalytic activity and characterizations.

2. Experimental

The detailed catalyst preparation, NO removal activity and characterizations are shown in the Supplementary data. The as-synthesized samples are denoted as Mg(c)-MnOx-T-t, in which c represents different mole ratios of precursors $Mg(CH_3COO)_2{\cdot}4H_2O$ to $Mn(CH_3COO)_2{\cdot}4H_2O$, T represents synthesis temperature (°C) and t represents drying time (h). As a reference, pure manganese oxide was prepared using the same process without adding $Mg(CH_3COO)_2{\cdot}4H_2O$ and is denoted as MnOx-60-12.

3. Results and discussions

3.1. The effects of preparation conditions

The effects of synthesis parameters, including synthesis temperature, Mg doping content and drying time, etc., on the performance of catalytic activity were firstly investigated to obtain the optimized reaction condition (Fig. S1). Combined with results in Table S1, it confirms that BET surface areas and inter-particle pile pore sizes are two main factors influencing the catalyst's NO removal ratio *via* most exposure of active sites and efficient contact or adsorption within suitable-sized pile pores. Detailed discussions are shown in Supplementary data.

3.2. Characterization and catalytic performance

Fig. S4 shows scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images of the optimized sample Mg(0.5)-MnOx-60-12 and reference MnOx-60-12 without Mg doping, revealing the morphology of loosely aggregated flower-liked nanospheres constituting of nanoplates. The loose structure with interconnected pile pore channels is also responsible for high BET surface areas (listed in Table S1) and beneficial for diffusion of reactants and products. Besides, the corresponding selected area of electronic diffraction (SAED, inset of Fig. S4c) indicates that Mg (0.5)-MnOx-60-12 presents very weak crystallinity. As a reference, in Fig. S4d, MnOx-60-12 shows similar nanoflower-like morphology, suggesting that Mg doping has no distinct effects on morphology.

Detailed comparisons of NO removal ratio and real time outlet gas concentration for the optimized Mg(0.5)-MnOx-60-12 and reference MnOx-60-12 are illustrated in Figs. 1 and S5. Apparently, appropriate Mg doping will enhance facile removal of NO, as discussed in Fig. S1. The real time outlet concentration curves in Figs. 1b and S5 both show clearly three steps exist in the whole catalytic process. In the stage I, no NO concentrations are detected, while the NO_2 concentration gradually increases, suggesting that the catalyst can completely adsorb NO and catalytically oxidize NO into NO_2 simultaneously. In stage II, the catalyst starts to get slowly inactive, weakening its' ability to catalytically oxidize NO into NO_2 since more and more active sites are covered, so the NO outlet concentration gradually increases. Nevertheless, it can still partly catalyze NO into NO_2, just as shown that the NO_2 outlet concentration still increases with time, but with slower increase rate. In stage III, the NO_2 concentration gradually decreases accompanying with increase of NO concentration, implying that the catalyst completely lost its further catalytic oxidation capability of NO. Therefore, the completely deactivated catalyst would finally remain only a small amount of NO_2 on its surface while with large amount of NO remaining, which would be also confirmed in the following MS (Mass Spectra) curves (Fig. 3a). Interestingly, it is noted that the NO_2 concentration of MnOx-60-12 is constantly lower than that of Mg(0.5)-MnOx-60-12, as shown in the Figs. 1b and S5, further confirming that Mg doping can accelerate the catalytic oxidation capability and thus improve NO removal performance. Furthermore, we have also conducted the NO removal tests either in dry simulated reactant gas or practical moisture air for comparison, confirming good water-resistance (Fig. S6). The results and discussions are shown in Supplementary data.

3.3. The mechanism of deactivation

All catalysts surely get deactivated after a period of time, and researches on their deactivation mechanism can guide our future work. In order to investigate the deactivation mechanism of the catalyst Mg (0.5)-MnOx-60-12, more detailed measurements have been carried out. As shown in Fig. 2a, the FTIR (Fourier Transform Infrared spectroscopy) analysis is carried out to detect whether nitrate species could be formed. Interestingly, there are no distinct differences between the fresh and deactivated samples, demonstrating that the catalyst gets deactivated not owing to the cover of active sites by nitrate species, which is different from the previously reported results [9–10].

Additionally, the in-situ DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) tests are further performed. Fig. 2b shows the time-dependent spectra of Mg(0.5)-MnOx-60-12 after introducing the mixed gas including 10 ppm NO, 79% N_2 and 21% O_2 at room temperature. After introducing the mixed gases, the band at $1625\ cm^{-1}$ of weak-adsorbed NO_2, closing to the asymmetric vibration band of gaseous NO_2, appears immediately [20], which confirms that the catalyst has obvious catalytic oxidation ability to transform NO into NO_2. And the band at $1865\ cm^{-1}$, which is ascribed to weak-adsorbed NO [21,22], gradually appears as the result of more and more NO being adsorbed onto the catalyst during the catalytic process. The bands $1337\ cm^{-1}$ and $1554\ cm^{-1}$ are attributed to the existence of NOx species adsorbed on sites of Mg species [23]. Moreover, no obvious nitrate species NO_3^- bands are observed during the whole test, which is consistent with the FTIR results in Fig. 2a. Therefore, it is considered that it's the gradually accumulated NO and NO_2 (mainly induced by NO_2) and their slow desorption that lead catalyst's active sites to be covered and cause deactivation eventually.

In order to further demonstrate our deactivation mechanism of NOx adsorption, we perform the temperature-dependent Mass Spectra (MS) curves of the deactivated sample (Fig. 3a). It is clear that there is no characterized peak of NOx at over 100 °C, where nitrate species should be decomposed and NOx should be released, further confirming the absence of nitrate species. It is noted that a distinctive NO desorption peak occurs below 100 °C, implying that a large amount of NO has been physically adsorbed onto the deactivated catalyst surface after the whole catalytic test. Besides, a small peak of NO_2 desorption at 70–80 °C can also be observed. Since the MS measurement is performed on the completely deactivated sample, only a small amount of NO_2 remains on catalyst compared with large amount of NO. More detail, since the difficulty of NO_2 desorption [19], NO_2 gradually cover the active sites, causing decreased catalytic oxidation capability for $2NO + O_2 \rightarrow 2NO_2$. Afterwards, more and more NO was directly adsorbed on catalyst without conversion into NO_2, followed by the final result