

Electrolytic manganese anode mud as the low temperature NH₃-SCR catalyst: the effect of K and Pb

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ABSTRACT

Electrolytic manganese anode mud is a promising low temperature SCR catalyst. In this study, the effect of Pb and K ion in EMAM on the low temperature SCR was investigated via experimental and DFT method. Pb modification can improve the surface unsaturation so that the oxidation ability of MnO₂ is improved. Therefore, ammonia is easily oxidated on the surface of Pb-MnO₂. K ion can moderate the surface of MnO₂ and lower the energy barrier of dehydrogenation for low temperature SCR process. However, Pb can inhibit N₂O formation thereby improving the N₂ selectivity.

Keywords: Low temperature SCR, Electrolytic manganese anode mud, Lead, Potassium

NONMENCLATURE

Abbreviations

EMAM	Electrolytic manganese anode mud
LT SCR	Low temperature Selective Catalytic Reduction

1. INTRODUCTION

China is the world's leading manufacturer and exporter of electrolytic manganese metal (EMM) [1]. The electrolytic method used to produce manganese metal is typically linked with the creation of a substantial amount of waste residue in the anode

region of the electrolytic cells [2–4], which is referred to as electrolytic manganese anode mud (EMAM). By and large, the EMAM comprises around 75% manganese, 5% lead (derived from the lead alloy anode), and a variety of other heavy metal components, including Co, Ni, Sn, and Cr, as well as soluble salts and waste acid[4–6]. As a result, it is classed as a hazardous waste.

Nitrogen oxides (NO_x) emitted from the fuel burning process are one of the most significant contributors to the formation of multiple environmental problems (i.e., acid rain, smog and haze). In previous work, the NaCl treated EMAM (Electrolytic manganese anode mud) was proven to have a high-efficient low temperature selective catalytic reduction of NO_x. α -MnO₂ existing in EMAM is the key active component for LT SCR [5,6]. However, Lead is still one of the common impurities with a content of appr. 2 wt. % after NaCl treatment process. In addition, the potassium ion in the EMAM remained a certain content after many times water wash process. It also should be taken into account because alkali metals generally have a certain effect on the SCR process [7]. In order to take full advantage of EMAM to produce low temperature SCR catalyst, it is much meaningful to figure out the effect of Pb and K ion on the low temperature SCR in the EMAM.

Herein, in this work, Pb and K ion was added during synthesizing α -MnO₂ samples via hydrothermal method aiming at studying the effect of Pb and K ion on the low temperature SCR process. Through experimental and theoretical calculation methods, the comprehensive reciprocal relationship and effect of Pb and K on the low temperature SCR were investigated.

2. CATALYST PREPARATION

Synthesis of α -MnO₂. A hydrothermal technique was used to prepare the α -MnO₂. In the typical procedures, 3.16 g of KMnO₄ and 1.42 g of (NH₄)₂C₂O₄•H₂O were dissolved into deionized water under vigorous magnetic stirring, and the volume was increased to 70mL. Finally, the solution was transferred to a 100 mL autoclave (which was made of stainless steel and walled with Teflon). The autoclave was kept in an electric oven at 180°C for 24h. The autoclave was left for natural cool down to room temperature. The precipitates were separated by suction filtration and the sediment was washed three times with deionized water and then dried at 110 °C for 24h.

Synthesis of α -MnO₂-K. α -MnO₂-K was prepared by the same synthesis route as for α -MnO₂ but 2 mmol KNO₃ were dissolved simultaneously with the other two chemicals.

Synthesis of α -MnO₂-Pb. α -MnO₂-K was prepared by the same synthesis route as for α -MnO₂ but 2 mmol Pb(NO₃)₂ were dissolved simultaneously with other two chemicals.

3. RESULTS AND DISCUSSION

3.1 The content of treated EMAM

By reason of the foregoing, NaCl treated EMAM has a super good LT SCR performance from 50°C to 300°C. Even it is better than that of some modified α -MnO₂ catalysts. In Table 1, EMAM was placed in a flask containing sodium chloride solution and 2 vol % concentrated HCl. The solid-to-liquid ratio was 1:5. The content of Mn (in MnO₂), Pb (in PbO) and K (in K₂O) is around 95 wt %, 3 wt % and 1 wt %, respectively. They remain roughly the same no matter how long the leaching duration is.

Table 1 Leaching experiment conditions and results

Trial	1	2	3	4
NaCl concn(g/L)		300		
Reaction duration(min)	240	480	720	960
Adding HCl(vol.%)		2		
Reaction temperature (°C)		90		
MnO ₂	95.1	94.9	94.6	94.8
PbO	2.8	3.06	3.21	3.1
K ₂ O	1.1	1.1	1.2	1.2

In the previous study, the Pb content of original EMAM sample were even high no matter in the nano-rod or bulk structures. After NaCl leaching treatment, the Pb content significantly reduced in the nano-rod structure of the original EMAM, but still remained a high level in the bulk structure of the original EMAM. It indicated that the lead that grows in the bulk structure is much difficult to be extracted, while that grows on the nano-rod structure is easy to be removed. Multiple studies[8–10] have shown that Pb has a poisoning effect on the NH₃-SCR catalyst. While the NaCl treatment brought super excellent LT NH₃-SCR activity, which indicated that nano-rod structure is of more importance than bulk structure in the EMAM sample.

The results of K content in the two structures were just the opposite. There was a reduction in K content in both two structures after NaCl treatment, but it kept with a certain amount and evenly dispersed in the structures. In Table 1, after a long period leaching test, the content of K⁺ remained a constant, which indicated that the K⁺ incorporated in the tunnels of α -MnO₂. The result is highly consistent with the conclusions of Ref[7]. K⁺ ions in the tunnel would promote the adsorption and activation of NH₃ has been proved. This step is crucial for the subsequent reaction steps of NH₃-SCR. Therefore, promotion effect of K⁺ is one of the significant factors to the excellent LT NH₃-SCR activity of the treated EMAM sample.

3.2 NH₃-SCR catalytic activity

The NH₃ oxidation and the catalytic reduction of NO_x, over the MnO₂ with different facets exposed, were shown in the range of 100°C -400°C in Fig. 1, 50°C for each step. In Fig. 1 (a), NO_x begins to emerge at 200 °C. With the temperature increasing, Pb modified MnO₂ has the higher NO_x selectivity, however, K doped can decrease the trend of that. In Fig. 1(b), the efficiencies of NO_x conversion also are distinct-different. Pb would inhibit the SCR activity dramatically, while K doped MnO₂ has higher low temperature SCR activity.

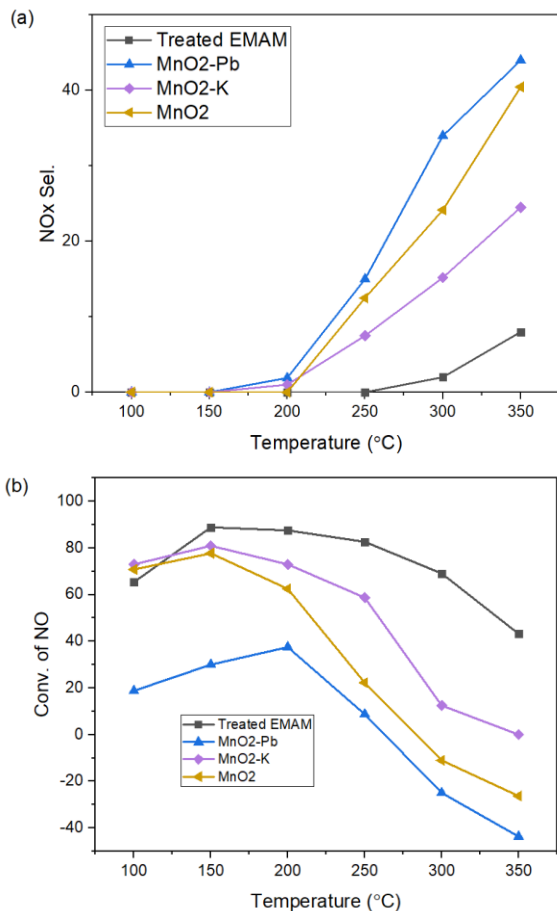


Fig. 1 Ammonia oxidation and reduction over different samples (a) NH₃ oxidation under O₂ atmosphere; (b) NH₃ reduction under O₂ and NO atmosphere. Reaction condition, [NH₃] = [NO]=500 ppm, O₂=5 vol.%, N₂ balance, GHSV=270 000·h⁻¹.

3.3 XRD study

To confirm as-synthesized samples, XRD analysis was performed. As shown in Fig. 2, all the synthesized samples showed identical diffraction peaks to the pure α -MnO₂ (JCPDS, PDF #44-0141). But the intensities of some specific peaks were different, which indicates that Pb and K modification would affect the growth of crystal facets. In terms of Pb-MnO₂, the relative intensity of (310) facet is strengthened, while the diffraction peak for (200) facet is relatively higher for K-MnO₂. In the previous study, ammonia prefers to take participate in oxidation reaction on the (310) facet, and NO_x is more easily reduced by ammonia on the surface of (100).

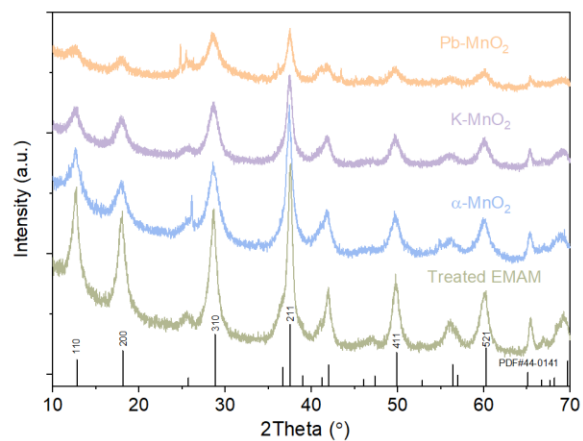


Fig. 2 XRD patterns of different samples

3.4 XPS study

In Fig. 3, different Mn species were fitted from Mn2p_{3/2} peaks. Mn2p_{3/2} peaks consist of three Mn valence species, Mn⁴⁺ species (around 643 eV)[23,24], Mn³⁺ species (around 642 eV)[25] and Mn²⁺ species (around 640.7 eV)[26]. Pb modified MnO₂ has higher Mn³⁺ species peak, indicating that Pb ion can enhance the unsaturated structure on the surface of MnO₂. On the contrary, K doped MnO₂ has higher proportion of Mn⁴⁺ species.

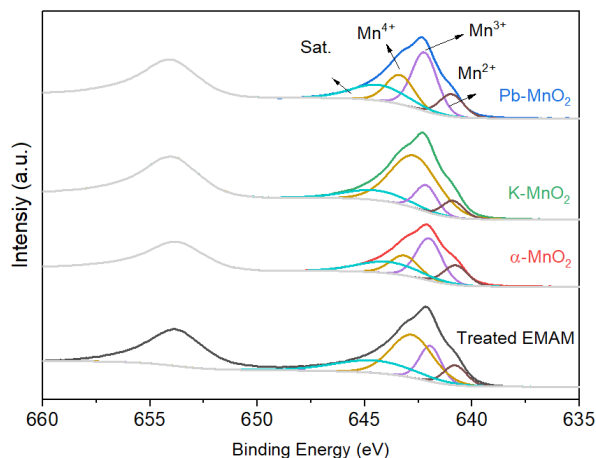


Fig. 3 XPS patterns of different samples

3.5 in situ DRIFTS study

In situ DRIFTS were conducted to investigate the surface intermediates in reduction of NO_x over modified α -MnO₂ at low temperature (150 °C). The samples were first purged with NH₃ or NO+O₂ for 1 h followed by N₂ purging. NO+O₂ and NH₃ were then introduced into the IR cell at 150 °C, and spectra were recorded as a function of time.

In Fig. 4 (a) and (b), the biggest difference is that there is no any N₂O emerging on the surface of Pb-MnO₂, while obvious N₂O peaks emerging at 2200 and

2240 cm^{-1} on the surface of K-MnO₂. It indicates that Pb modification would inhibit N₂O formation and increase the N₂ selectivity.

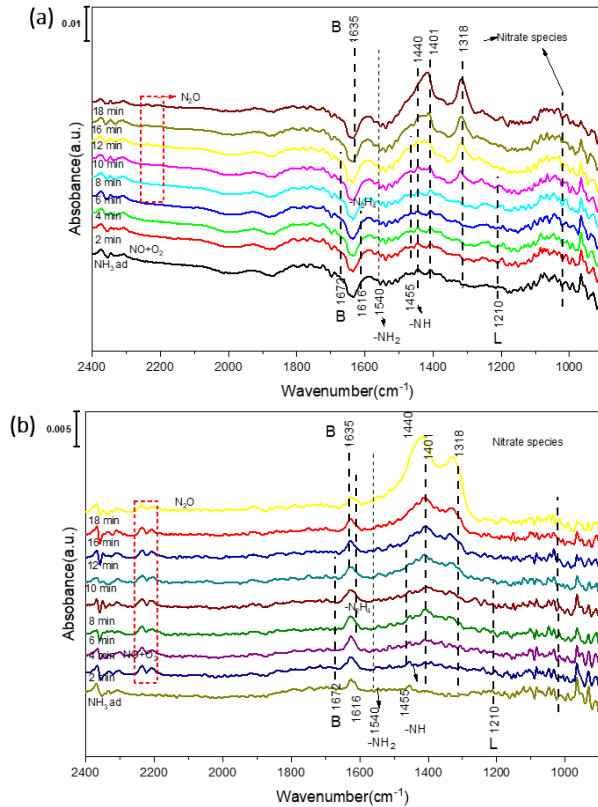


Fig. 4 DRIFT spectra taken at 150 °C upon passing NO+O₂ over the NH₃ pre-adsorbed on samples of at Pb-MnO₂(a) and K-MnO₂ (b)

3.6 Theory/calculation

The first-principal calculation, based on density-functional theory and utilizing the VASP program, can assist better to understand the difference in exposed facets of α -MnO₂ and their effect on NH₃-SCR. As the previous studied, the facets (1 0 0) and (1 1 0) have low surface energy of 0.245 and 0.224 J/m², respectively, and are thus thermodynamically stable facets. While the high-index (3 1 0) facet has the highest surface energy of 0.32 J/m², it is relatively unstable. As a result of reducing the overall surface energy of crystals, these facets with high surface energy will disappear in the bulk of the crystals based on the Wulff building theory[11]. The facets with (1 0 0) and (1 1 0) facets had similar low surface energies in these calculations, which explained why the facets with (1 0 0) and (1 1 0) facets were clearly noticed in the majority of studies on α -MnO₂. However, because of their higher stability, lower surface energy, and fewer active sites, facets with (1 0 0) and (1 1 0) facets are often less reactive, resulting in much inferior overall performance. It is commonly

accepted that surfaces with a larger percentage of under-coordinated atoms are more reactive in heterogeneous processes than those with a lower percentage. These reactive facets also have a relatively high surface energy, which is why they are so reactive. In contrast, surfaces with a high density under-coordinated atoms result in a high surface energy for the crystal facet. Therefore, in the vast majority of cases, high-energy facets are the guarantee of high performance in practical applications. Therefore, NaCl treatment led to more nano structures exposed so that more (3 1 0) facets participated in the reaction of LT-SCR. Therefore, in the calculation process, α -MnO₂ with (3 1 0) facet exposed was chosen as the basic calculation model.

To reveal further the role of impurities, such as Pb and K species, in EMAM catalyzed NH₃-SCR, on account of NH₃ adsorption and dehydrogenation is the initial and critical step of the NH₃-SCR process [26], models consisted of a 3×1 super cell of α -MnO₂ exposing the (3 1 0) surface were built for considerations of two aspects: 1) some Mn atoms were substituted with Pb atom, which stands for Pb doping on the surface α -MnO₂; 2) Pb and K atoms were stored in the tunnels of α -MnO₂, which indicates Pb or K atoms incorporated into the lattice of α -MnO₂. (Fig. 5)

In terms of NH₃-SCR, no matter Eley–Rideal (E–R) or Langmuir–Hinshelwood (L–H) mechanisms have both been postulated and largely accepted. They all started from NH₃ adsorption and activation, and then activated ammonia would react with adsorbed or gaseous NO to form an activated transient state and then decomposes to N₂ and H₂O. Therefore, NH₃ adsorption and activation are the vital step for NH₃-SCR. In contrast, K⁺ insertion increased the adsorption energy of NH₃ on original α -MnO₂ (3 1 0) surface significantly (-1.99eV vs -1.78eV) (Fig. 6). While the energy barrier of the first N-H dissociation reduced from 0.56eV to 0.52eV after K⁺ insertion on the Mn site. However, no matter Pb²⁺ was incorporated into the tunnel or doped on the surface of α -MnO₂, the NH₃ adsorption energies were greatly reduced (-1.78eV→-1.27eV and -0.66eV respectively). Meanwhile, Pb²⁺ in the tunnel raised the energy barrier for the dehydrogenation of the first H atom, Pb doped on the surface has similar effect on that. Therefore, Pb atom suppresses NH₃ activation reaction and is unfavorable for low-temperature NH₃-SCR. In the model of 310- α -MnO₂ with Pb on the surface and K⁺ in the tunnel, the adsorption energy and energy barrier both went down by comparison with the models of Pb²⁺

incorporated solely into the tunnel and doped solely on the surface of α -MnO₂, which means K⁺ in the tunnel could moderate the inhibition effect of Pb on the NH₃-SCR reaction. These calculation results fully explained why NaCl leaching can greatly improve the low temperature NH₃-SCR activity of EMAM.

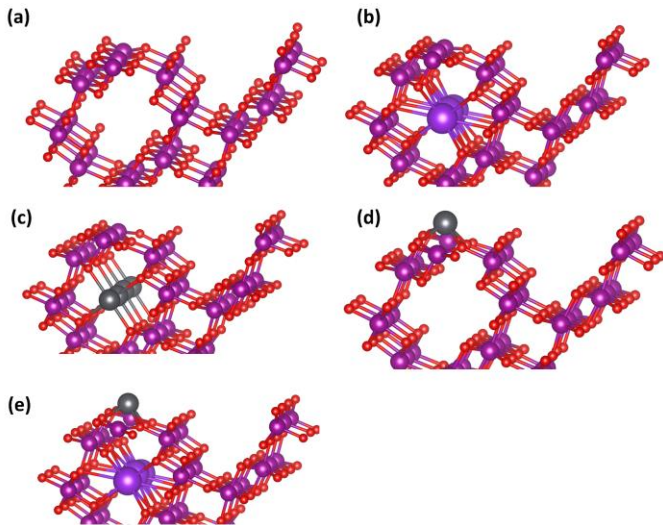


Fig. 5 The side view of the structure model of (a)original α -MnO₂ with (3 1 0) facets exposed; (b) K ion incorporated in the tunnel of α -MnO₂; (c) Pb ion incorporated in the tunnel of α -MnO₂; (d) Pb ion doped on the surface of α -MnO₂; (e) K ion incorporated in the tunnel and Pb ion doped on the surface simultaneously of α -MnO₂. Red spheres are oxygen atom, purple is manganese atom, big purple spheres are K atom and gray spheres are Pb atom.

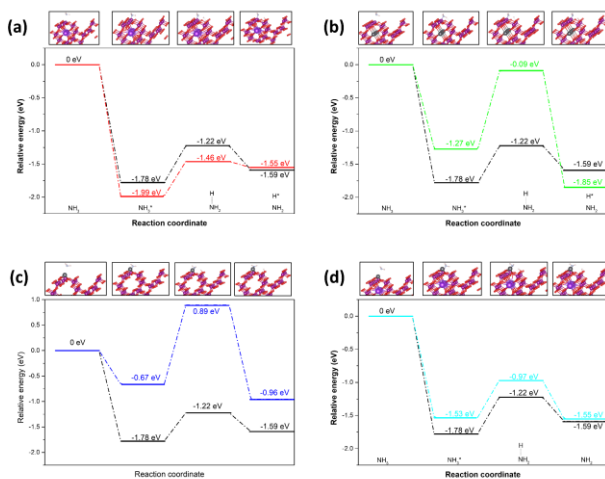


Fig. 6 Energy profiles of NH₃ dissociation on the Mn site of (a) K ion in the tunnel; (b) Pb ion in the tunnel; (c) Pb ion doped on the surface; (d) K ion in the tunnel and Pb

ion doped on the surface of α -MnO₂ for the processes

$$\text{NH}_3^* + \text{O}_{\text{bri}} \rightarrow \text{NH}_2 + \text{O}_{\text{bri}}\text{H}.$$

4. CONCLUSIONS

In this study, the effect of Pb and K ion in EMAM on the low temperature was investigated via experimental and DFT calculation method. Pb modification can improve the surface unsaturation so that the oxidation ability of MnO₂ is improved. Therefore, ammonia is easily oxidated on the surface of Pb-MnO₂. K ion can moderate the surface of MnO₂ and lower the energy barrier of dehydrogenation for low temperature SCR process. However, Pb can inhibit N₂O formation thereby improve the N₂ selectivity.

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