



## Effect of H<sub>2</sub>O on catalytic performance of manganese oxides in NO reduction by NH<sub>3</sub>

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### ABSTRACT

The effects of H<sub>2</sub>O on catalytic performance of hollandite manganese oxide (HMO) and  $\beta$ -MnO<sub>2</sub> are comparatively studied in selective catalytic reduction of NO by NH<sub>3</sub> (NH<sub>3</sub>-SCR). The results showed that the HMO possessed higher catalytic activity than  $\beta$ -MnO<sub>2</sub> in the presence of H<sub>2</sub>O, and the NH<sub>3</sub>-SCR reaction occurring on the HMO predominantly followed an Eley-Rideal mechanism via reacting adsorbed NH<sub>4</sub><sup>+</sup> with gaseous NO. According to the NH<sub>3</sub>-TPD analyses, XPS results and the HRTEM observations coupled with the theoretical calculations, the results elucidated that (i) the initial formation of the NH<sub>4</sub><sup>+</sup>(H<sub>2</sub>O)<sub>3</sub>OH<sup>-</sup> double ionic clusters were energetically favorable in the presence of H<sub>2</sub>O, (ii) the OH<sup>-</sup> ions from the double ionic clusters reacted with Lewis acid sites of the manganese oxides to transform into Brønsted acid ones, concomitant with release of the NH<sub>4</sub><sup>+</sup> ions, and (iii) the NH<sub>4</sub><sup>+</sup> ions both from the double ionic clusters and from reaction of NH<sub>3</sub> with Brønsted acid sites can be efficiently adsorbed on the {1 1 0} facets of the HMO to complete the NH<sub>3</sub>-SCR reaction cycles, whereas the NH<sub>4</sub><sup>+</sup> ions are not stable on the {1 1 0} facets of  $\beta$ -MnO<sub>2</sub>. Therefore, the excellent catalytic performance of the HMO predominantly originates from the special structural {1 1 0} facet due to it being suitable for adsorption of NH<sub>4</sub><sup>+</sup> active species.

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### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>,  $x = 1$  or  $2$ ) as the major air pollutants can cause adverse effects such as urban smog, acid rain and ozone depletion, which badly threaten the environment and human health [1–3]. The selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR) has been proven to be a promising technology to treat stack gases from stationary sources. The commercial V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts promoted with WO<sub>3</sub> or MoO<sub>3</sub> have been effective for NO removal within a narrow temperature window of 300–400 °C [4]. However, they still have some disadvantages such as the strong inhibiting effect of H<sub>2</sub>O [4,5], the poor low-temperature activity and the intrinsic toxicity of V<sub>2</sub>O<sub>5</sub>. To avoid the toxicity of V<sub>2</sub>O<sub>5</sub>, one of the methods is to use environment-benign manganese-based catalysts, which show much higher catalytic activity than other transition metal oxides at low- and medium-temperatures [5–8]. However, H<sub>2</sub>O still exhibits inhibiting and/or deactivating effects on the NH<sub>3</sub>-SCR activity of the manganese-based catalysts especially at low temperatures. Therefore, development of a new catalyst possessing excellent hydrophobic ability at low temperatures remains a great challenge.

H<sub>2</sub>O not only presents in the stack gases, but also is one of the products in the NH<sub>3</sub>-SCR reactions. The effect of H<sub>2</sub>O on the activity of the catalyst frequently results from its competitive adsorption with reactants (NH<sub>3</sub> and/or NO) on the active sites [9–11], which can be divided into two aspects: reversible inhibition and irreversible deactivation. Kijlstra and coworkers [9] studied the influence of H<sub>2</sub>O on the catalytic activity of the supported manganese oxides by using temperature-programmed desorption (TPD) techniques at temperatures below 200 °C. The results showed that H<sub>2</sub>O exhibited both reversible inhibiting effect and irreversible deactivating one. The former was due to competitive adsorption between H<sub>2</sub>O and NH<sub>3</sub>/NO on the active sites, and the latter was caused by surface hydroxyls formed by dissociative adsorption of H<sub>2</sub>O. The surface hydroxyls accommodated the active sites and did not leave at temperatures lower than 250 °C. Amiridis and coworkers [11] found that addition of H<sub>2</sub>O to the NH<sub>3</sub>-SCR system over the V<sub>2</sub>O<sub>5</sub>-based catalysts resulted in 40–50% decrease in the turnover frequency of NO due to competitive adsorption of H<sub>2</sub>O with NH<sub>3</sub> on the active vanadium sites, confirmed by *in situ* Raman spectra.

Among transitional metal oxide catalysts, hollandite manganese oxides (HMO) show excellent hydrophobic property [12], which as environmental catalysts have successfully applied for adsorption of NH<sub>3</sub> and the NH<sub>3</sub>-SCR reactions [13,14]. The basic building unit of the HMO is a MnO<sub>6</sub> octahedron, which constructs one-dimensional 0.47 nm × 0.47 nm tunnel by both edge-linking and corner-linking

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