# Jahn-Teller's effect on the redox property of Fe-doped α-$MnO_2$ catalyst to oxidize NO

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**Abstract:** Doping is one of the most widely used methods to tune the performance of the catalysts. In this work, the doping of Fe in α-$MnO_2$ is selected as a model catalyst. Rietvelt fitting of the synchrotron radiation source X-ray diffraction (SR-XRD) combined with density functional theory calculation (DFT) were applied to investigate the lattice changes induced by Fe-doping. It is discovered that the embedding of Fe yields a higher concentration of oxygen vacancies, which decreases the valence of Mn. This leads to Jahn-Teller's distortion that increases a portion of Mn-O bond length significantly, promoting its oxidation activity.

**Keywords:** Jahn-Teller's effect, redox property, doping.

## 1. Introduction

NO and $NO_2$ are among the major pollutants emitted in the atmosphere and will further participate in the ozone and secondary organic aerosol formation. Therefore, the removal of NO is pivotal for pollution control. NO oxidation is involved in both lean $NO_x$ trap (LNT) and selective catalytic reduction (SCR) techniques[1, 2], and thus is focused in our research.

Doping is a fundamental method to tune the catalyst performance and the understanding of doping will benefit in further designing new catalysts[3, 4]. Previous research mainly focused on the electronic effects of the dopants on nearest atoms[3]. Recently, Shao-Horn et al. proposed that the dopant will also affect the location of O 2p band to further influence the tendency to form oxygen vacancy[5]. In our research we further develop the concept and suggest that the formed oxygen vacancy will decrease the valence of the metal cations, which will induce Jahn-Teller's distortion in $MnO_2$. Herein, the distorted Mn-O is feasible to break to participate in the NO oxidation.

## 2. Experimental

All the samples were synthesized by hydrothermal method. A certain amount of $MnSO_4 \cdot H_2O$, $KMnO_4$, $Fe_2(SO_4)_3$ and $K_2SO_4$ were dissolved and kept at 140 °C for 12 h. After washing, the sediments were dried and calcined at 300 °C for 2 h in air. The samples are denoted as $MnFe_x$ where $x$ is the molar ratio of Fe:Mn determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

NO oxidation reaction was tested in a fixed bed reactor with an inner diameter of 6 mm. And 50 mg catalysts samples (40 - 60 meshed) were filled at the center of the reactor. A mixture of 500 ppm NO, 10 % $O_2$ balanced with $N_2$ with total flow rate of 200 $mL \cdot min^{-1}$ was used to test the catalytic performance of the samples, to reach a space velocity of 240,000 $mL \cdot g^{-1} \cdot h^{-1}$. The catalysts were stabilized in the mixture at 80 °C for 0.5 h, then the temperature was elevated at a rate of 2 $°C \cdot min^{-1}$ until 300 °C. The concentration of NO and $NO_2$ were monitored by an online Fourier transform infrared spectrometer (MultiGas 2030HS, MKS), which recorded each spectrum for every 6 s, equivalent to 0.2 °C as interval in the experiment.

Structure of the catalysts was analyzed by X-ray diffraction spectrometry with a synchrotron radiation source (SR-XRD) at Beijing Synchrotron Radiation Facility (BSRF). The X-ray wavelength was fixed at 1.3807 Å, and a $2\Omega$ - $\Omega$ step-scanning method was applied to obtain the spectra from 10° to 100. The stepping length was 0.02°. Rietveld fitting was conducted to resolve the structure of the catalysts by using GSAS-II package[6].

## 3. Results and discussion

As can be seen in Fig. 1, as the molar ratio of Fe:Mn rises, the conversion ratio of NO increases to a maximum for $MnFe_{0.7}$ and then decreases for excess Fe:Mn ratio. The tendency is also confirmed by the activation energy as in Fig. 1(b). The activation energy is less than 40 $kJ \cdot mol^{-1}$ for $MnFe_{0.4}$ and $MnFe_{0.7}$, much less than that for $MnFe_{0.0}$ and $MnFe_{4.9}$, which excess 60 $kJ \cdot mol^{-1}$. Therefore, there are inherent reasons that determine the activity after doping. The excess doping of Fe results in the formation of an inactive phase $KFe_3(SO_4)_2(OH)_6$ (not shown here), and the accumulation of this phase can explain the drop of catalysis rate in Fig. 1. In the case where only a small amount of Fe is doped, the doping promotes the activity, which is of interests in this research.

The lattice oxygen is confirmed to be pivotal for NO oxidation for $MnFe_x$, so the relationship between lattice oxygen and dopants is investigated. Rietveld fitting results of SR-XRD are shown in Fig. 2. As can be seen in Fig. 2(a), with the increase of the dopants, a portion of Mn-O bonds are significantly lengthened. The longer Mn-O bonds with a similar local environment tend to be broken to participate in the oxidation reaction. The cause of the change of bond length is the Jahn-Teller's distortion, which is shown in Fig. 2(b). The fitting results clearly show that the lattice is distorted after Fe-doping. Therefore, the benefits of doping can be concluded in the induce of Jahn-Teller's distortion, which promotes the oxidation ability of the catalysts.

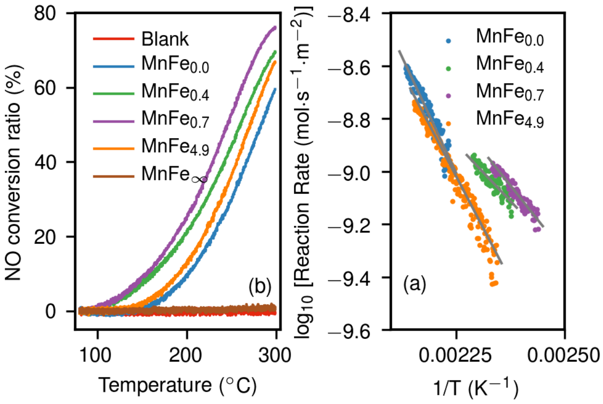

**Figure 1.** (a) NO conversion ratio for the catalysts. (b) Arrhenius' plot for the NO oxidation reaction.

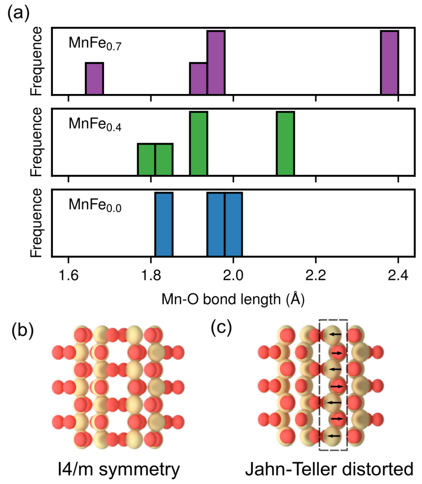

**Figure 2.** (a) Mn-O bond length obtained from Rietveld fitting. (b-c) Projection of Rietveld fitting results to *xOz* plane for $MnFe_{0.0}$ and $MnFe_{4.9}$, respectively.

## 4. Conclusions

The promotion of oxidation property of Fe-embedded α-$MnO_2$ can be ascribed to Jahn-Teller's effect. It is observed that on the condition that the α-$MnO_2$ phase is stabilized, the embedding of Fe in skeleton will enhance oxidation activity, related to the tendency of Mn-O bond to break. Jahn-Teller's distortion will selectively elongate some of the Mn-O bonds, making them more feasible to be attacked to participate in the reaction. The cause of Jahn-Teller's distortion is due to the decrease of Mn valence to $Mn^{3+}$. The role of Fe embedding is to induce oxygen vacancies; to balance the charge equilibrium, the valence of Mn is decreased. Owing to the generality of Jahn-Teller's effect among oxides, this discovery could be applied as a new viewpoint to account and design other catalysis systems.

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