



Origin of the superior activity of surface doped SmMn_2O_5 mullites for NO oxidation: A first-principles based microkinetic study



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ABSTRACT

Using first-principles based microkinetic analysis, we conduct a comprehensive investigation on the NO oxidation process on SmMn_2O_5 mullite's active surface under experimentally relevant conditions. The influencing factor for NO oxidation activity is identified and Mars-van Krevelen (MvK) and Eley-Rideal (ER) mechanisms are found to contribute to the high activity of pristine SmMn_2O_5 mullites in high and low temperature regions, respectively. We further study the activity of surface (Ba/Sr/La) doped SmMn_2O_5 . It is found that surface doping of Ba primarily destabilizes the nitrite (NO^*) species to promote NO oxidation performance via MvK mechanism. Due to the stronger ability of O_2 (O_2^*) dissociation along the ER route, Sr and La doped mullites are predicted to have greatly enhanced reaction activity in a wide temperature region. Our study gives insight into the NO oxidation ability of pristine and surface doped SmMn_2O_5 that are beneficial for further optimization of mullite based catalyst performance.

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1. Introduction

NO_x are hazardous by-products of lean combustion in diesel engines, which leads to environmental problems such as photochemical smog, acid rain and ozone depletion. Efficient NO oxidation is regarded as a critical reaction step in improving the DeNO_x efficiency through subsequent selective catalytic reduction (SCR) or NO_x storage reduction (NSR) technologies [1,2]. While platinum group metals (PGM) have the good NO oxidation capability, their scarcity (hence cost) severely limits the large scale in practical development and applications. In past few years, transition metal oxides (TMOs) such as MO_x ($M = \text{Co}, \text{Cr}, \text{Mn}, \text{Ce}$) have attracted much attention due to their ability of NO oxidation with the advantage of facile synthesis and lower cost [1]. It was found that Co_3O_4 and MnO_x catalyst can achieve a maximal NO-to- NO_2 conversion ratio of 66% and 59%, respectively [1,3]. Addition of CeO_2 to MnO_x can further promote the conversion ratio of NO-to- NO_2 [4]. Wang et al. reported that Fe-doped CeO_2 and single-phase Cr-Zr mixed

oxides are also efficient NO oxidation catalysts due to the facile formation of oxygen vacancies [5,6]. However, it is general consensus that oxidation states change in simple oxides over extended redox cycles will lead to reduced activity or deactivation in the duration of catalytic reactions [7,8].

To mitigate the loss of active phase under reacting environments due to stoichiometry change, stable ternary TMOs with skeleton backbone structures, such as perovskites (ABO_3) and mullites (AB_2O_5), have been explored as promising candidates for the NO oxidation reaction. It has demonstrated that strontium-doped LaCoO_3 achieved higher NO-to- NO_2 conversions than the commercial platinum-based diesel oxidation catalyst under realistic conditions [9,10]. Choi et al. attributed the outstanding performance of NO oxidation of Sr-doped LaCoO_3 to the destabilization of extra-lattice oxygen and enhanced total oxygen exchange capacity [11]. SmMn_2O_5 mullite has also been proposed as a new type of oxide catalyst for NO oxidation with the active site of exposed Mn-Mn dimers via combining experimental and theoretical study [12]. A series of Mn based mullites with different A site elements were investigated utilizing soft X-ray absorption by Li et al. and were found that p - d orbital hybridization between the O_{bulk} and the Mn_{oct} could increase the NO-to- NO_2 conversion activity [13]. Cho et al. studied the thermal stability of mullite RMn_2O_5 ($R = \text{Bi}$,

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Y, Pr, Sm, Gd) and found mullites to have a thermal stability region wider than binary oxides and perovskite phase RMnO_3 compounds [14]. Our group has also conducted studies on NO oxidation of SmMn_2O_5 using theoretical and experimental methods. Detailed first-principles analysis on the surface reaction routes had identified the $(0\ 1\ 0)^{4+}$ surface with exposed Mn-Mn dimer as the active surface towards NO oxidation [8]. Experiments further indicated that introduction of dopants can effectively alter the stabilities of reaction intermediates and kinetics of NO oxidation activity on SmMn_2O_5 [15]. However, previous studies of NO oxidation on mullites mostly concentrated on energetics of elementary reaction steps, which could not fully quantify the catalytic activity of mullites under realistic experimental pressure and temperature conditions. We aim to bridge the gap by establishing a concrete link between NO reaction rates on mullites' active surface and factors like the temperature, pressure, and surface coverage in the general framework of first-principles based microkinetic simulations [16–19].

In this work, we report a comprehensive first-principles based microkinetic study on the NO oxidation mechanisms (MvK and ER mechanisms) on the active surface of pristine and surface (Ba/Sr/La) doped SmMn_2O_5 under experimentally relevant temperatures and pressure conditions. Microkinetic results are used to gain insight into the main factors influencing its catalytic performance. The stability of NO^* species and the splitting capacity of adsorbed O_2^* species are good indicators for NO oxidation ability along MvK and ER pathways, respectively, and MvK and ER mechanisms contribute to the high activity of pristine SmMn_2O_5 at different temperature ranges, respectively. Surface doping of Ba primarily destabilizes the nitrite (NO^*) species to facilitate NO oxidation performance along MvK pathway. On the other hand, due to its stronger ability of splitting adsorbed O_2 (O_2^*) in the ER mechanism, Sr and La doped mullites are identified to have an enhanced reactivity in a wide temperature region. Our results indicate surface doping as an effective strategy for further promoting mullites' NO oxidation activities.

2. Computational methods

2.1. DFT simulation setup

Density functional theory (DFT) calculation [20,21] is implemented in the Vienna ab-initio Simulation Package (VASP) [22–24]. The exchange and correlation energy is in the form of generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) [25]. Our benchmarking shows that the PBE exchange correlation function can reasonably describe properties of SmMn_2O_5 mullites (As seen in Supplementary Information). Projector augmented wave (PAW) [26] method is used to depict the electron-ion interactions. The cutoff energy for the plane wave basis is set to 400 eV and Monkhorst–Pack k-meshes of $7 \times 5 \times 1$ are used for the active surface. We adopt a vacuum thickness of at least 15 Å so that the interactions between the neighboring layers can be neglected. The Gaussian broadening with a width of 0.05 eV is used for the integration of the first Brillouin zone. The structure is fully optimized until the Hellmann–Feynman force is smaller than 0.05 eV/Å. As Mn possess magnetic moments, the spin polarization is included in the total energy calculations [8]. Climbing-image nudged elastic band (CI-NEB) method is performed to find the reaction barrier. Since the $(0\ 1\ 0)^{4+}$ of SmMn_2O_5 is the most active surface towards NO oxidation [8], we primarily focus reactions on this surface in this work (unless otherwise stated). The oxygen vacancy formation energy (E_{O_v}) and the adsorption energy ($E_{ad(X)}$) are respectively defined as

$$E_{O_v} = E_{slab-0} + E_{O_2/2} - E_{slab}, \quad (1)$$

$$E_{ad(X)} = E_{slab+X} - E_{slab} - E_X \quad (2)$$

where E_{slab-0} , E_{slab} and E_{O_2} are energies of the surface with an oxygen vacancy, the ideal surface and O_2 molecule, respectively. E_{slab+X} and E_X correspond to energies of the surface with the adsorbate and the adsorbate itself, respectively.

2.2. Microkinetic modeling

To further quantify the reaction mechanisms and reaction rate contributions of different routes, a steady state microkinetic model is used to solve for the surface coverage of all reaction intermediates. De Donder relations provide a straight forward way of determining the number of kinetic parameters required to calculate the overall reaction rate [27] and related details are shown in the Section 2 of Supplementary Information.

The rate constant (k_i) of the adsorption can be obtained by applying the collision theory:

$$k_i = \frac{S\sigma}{\sqrt{2\pi m_A k_B T}} \quad (3)$$

Where S is the sticking coefficient with an assumed value of unity for all adsorbed species. σ is the average area of an active site and is set as $8.7 \times 10^{-19} \text{ m}^2$, which is the size of unit cell on the $(0\ 1\ 0)^{4+}$ surface containing Mn-Mn dimers. The other parameters are the molecular mass m_A , Boltzmann constant k_B and reaction temperature T .

The rate constant (k_i) of desorption or dissociation could be obtained from the transition state theory method [28]:

$$k_i = \frac{k_B T}{h} \exp\left(\frac{\Delta S_i}{k_B}\right) \exp\left(\frac{-\Delta H_i}{k_B T}\right) = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_i}{k_B T}\right). \quad (4)$$

Where ΔS_i , ΔH_i and ΔG_i are the activation entropy change, reaction enthalpy changes and Gibbs free energy change, respectively. The activation entropy change ΔS_i of transition state is small and approximates to zero according to previous literature [29]. ΔH_i is corrected with zero-point energy obtained from frequency calculations (Details of enthalpy, entropy and Gibbs free energy calculations can be found in the Section 3 of Supplementary Information). The reaction equilibrium constant $K_i = k_{i,f}/k_{i,r}$ represents the ratio of the forward ($k_{i,f}$) and reversed reaction rate constants ($k_{i,r}$).

Once the steady state microkinetic model is obtained, the rate determining step (RDS) of the reaction can be identified by the degree of rate control (denoted as X_i) [30–32]:

$$X_i = \frac{k_i}{\text{TOF}} \left(\frac{\partial \text{TOF}}{\partial k_i} \right)_{k_j, k_{j \neq i}} \quad (5)$$

Where TOF is turnover frequency which represents reaction rate of an active site. A positive value of X_i indicates a promotional contribution to the reaction, while a negative X_i corresponds to the hindering effect of the reaction.

During the simulation, the total pressure is set as standard atmosphere pressure and reactant gases consist of 400 ppm NO and 10% O_2 . The ranges of reaction temperature and NO conversion ratio are from 275 to 570 K and 1% to 85%, representative of experimentally relevant NO oxidation reaction conditions [15].

3. Results and discussion

3.1. DFT study on NO oxidation route on SmMn_2O_5

3.1.1. The geometrical structure of SmMn_2O_5 $(0\ 1\ 0)^{4+}$ slab

In this study, we have chosen a more idealized system based on the previous study which indicates that Mn-Mn dimer is responsible

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