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COMMUNICATION

Microwave selective effect: a new approach towards oxygen inhibition removal for highly-effective NO decomposition by microwave catalysis over BaMn_xMg_{1-x}O₃ mixed oxides at low temperature under excess oxygen

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A significant microwave selective effect to oxygen inhibition removal was found for NO decomposition through microwave catalysis over BaMn_xMg_{1-x}O₃ catalysts. Especially, the NO conversion and N₂ selectivity were respectively up to 99.8% and 99.9% for BaMn_{0.9}Mg_{0.1}O₃ catalyst even at coexistence of 10% oxygen and low temperature of 250 °C.

Nitrogen oxides (NO_x), emitted from various of stationary and mobile sources, are recognized to be one of the most dangerous atmospheric pollutants.¹ It has been developed several practical NO_x emission control technologies, including three-way catalysts, NO_x storage-reduction catalysts, and selective catalytic reduction (SCR) processes.² Among the various deNO_x strategies, the direct decomposition of NO into N₂ and O₂ (2NO→N₂+O₂) is the most desirable one with respect to both environmental and economic considerations, because it does not involve the addition of toxic reducing agent and the products are nontoxic.^{3,4} Several catalysts, such as the noble metals,⁵⁻⁷ oxides,⁸⁻¹² and metal ion-exchanged zeolites,¹³⁻¹⁵ have been extensively investigated for the direct decomposition of NO in the conventional reaction mode (CRM). Among these catalysts, perovskites are considered to be the most promising catalysts for the direct decomposition of NO in view that they are low-cost materials and sustainable for the long-term operation.^{2,3,9,16} However, the NO decomposition over perovskites is strongly inhibited by the coexistence of oxygen in the gaseous mixtures and also the produced O₂, leading to the NO conversion drastically decrease.^{2,3,9,16-19} Iwakuni *et al.*¹⁸ studied the catalytic performance of BaMnO₃-based perovskites for the decomposition of NO, and N₂ yield over Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O₃ decreased from 75% to 40% by the coexistence of 5% oxygen at 850 °C.

To avoid oxygen inhibition effect by the adsorbed oxygen over perovskites, two methods have been reported until to date. The one is that noble metal-doped perovskites (Ag/La_{0.6}Ce_{0.4}CoO₃) showed some degree of activity in the narrow temperature range and the presence of oxygen.²⁰ The other one is that the group of Caro^{3,21} reported the decomposition of NO and N₂O over a novel perovskite (BaCo_xFe_yZr_{1-x-y}O_{3.8}) hollow fiber membrane reactor, and the complete NO conversion with around 95% N₂ yield was achieved at 875 °C, which was considered to be a breakthrough in this field. However, an additional reducing agent (such as CH₄) must be adopted to remove the surface oxygen in this membrane reactor. Therefore, it is still great challenge to develop novel and efficient strategies for the highly-effective direct decomposition

of NO in the presence of excess oxygen.

Of late, the microwave-accelerated heterogeneous catalytic reactions have attracted tremendous attentions by providing dramatic enhancement of reaction rate under mild conditions.^{22,23} Furthermore, microwave irradiation has been well demonstrated to enhance reaction selectivity that differing from conventional methods²²⁻²⁶. Although using microwave irradiation to accelerate chemical reactions is rapidly growing, it is still not elucidated for the nature of microwave irradiation on chemical reactions. Moreover, there is no literature report on the direct decomposition of NO by microwave catalysis over mixed oxides, in particular the perovskites. Therefore, we attempt to investigate the catalytic performance of perovskites for the microwave direct catalytic decomposition of NO in this work.

Our previous work studied the microwave selective catalytic reduction of NO over Mn₂O₃/AC with 98.7% NO conversion and 99.8% N₂ selectivity at the environment of excess oxygen and temperature as low as 300 °C.²⁷ Herein, we report the highly-effective direct NO decomposition by microwave catalysis over BaMn_xMg_{1-x}O₃ mixed oxides at low temperature under excess oxygen. We found a significant microwave selective effect for the oxygen inhibition removal during the direct decomposition of NO. A complete NO decomposition with the NO conversion and N₂ selectivity respectively up to 99.8% and 99.9% was achieved over the BaMn_{0.9}Mg_{0.1}O₃ catalyst at temperature as low as 250 °C under excess oxygen in the microwave catalytic reaction mode (MCRM). To the best of our knowledge, this is the first report on the direct decomposition of NO with such high efficiency through microwave catalysis at low temperature under excess oxygen. Our work attempts to build a new approach to oxygen inhibition removal for the direct decomposition of NO.

Fig. 1 displays the NO conversion as a function of temperature over these BaMn_{1-x}Mg_xO₃ catalysts in the MCRM. Surprisingly, even at 100 °C (an extremely low temperature for the direct decomposition of NO), the NO conversion can reach 49.7% for BaMnO₃, 52.1% for BaMn_{0.9}Mg_{0.1}O₃, 52.7% for BaMn_{0.8}Mg_{0.2}O₃, 56.8% for BaMn_{0.7}Mg_{0.3}O₃, and 49.8% for BaMn_{0.6}Mg_{0.4}O₃ in the MCRM. NO conversion over these five catalysts firstly increases and then decreases with an increase of temperature (100-400 °C). Importantly, the best conversion in each reaction is up to 99.5% for BaMnO₃ at 250 °C, 99.8% for BaMn_{0.9}Mg_{0.1}O₃ at 250 °C, 98.2% for BaMn_{0.8}Mg_{0.2}O₃ at 300 °C, 99.1% for BaMn_{0.7}Mg_{0.3}O₃ at 250 °C, and 98.7% for BaMn_{0.6}Mg_{0.4}O₃ at 300 °C, which are

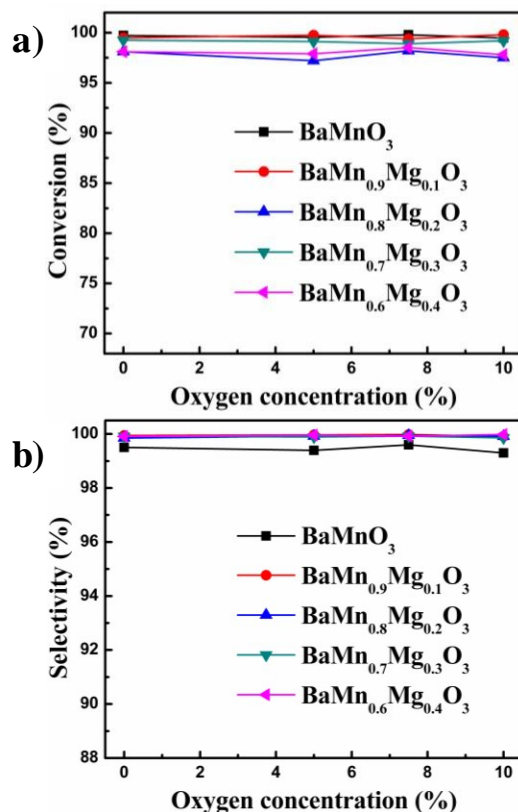
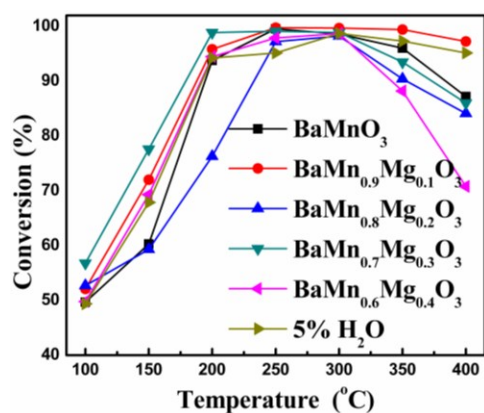


Fig. 1 The influence of reaction temperatures on the NO conversion over BaMn_{1-x}Mg_xO₃ catalysts and 5% water vapor over BaMn_{0.9}Mg_{0.1}O₃ in the MCRM (Reaction conditions: molar fraction of O₂, 5%; molar fraction of NO, 0.1%; W/F = 1 g s cm⁻³; and N₂ as the balance)

close to complete NO conversion. Tang *et al.*²⁸ used Fe/ZSM-5 as a catalyst for NO decomposition in the microwave heating mode, whereas the highest NO conversion was only 70% in their report.

In fact, industrial off-gases often contain oxygen. To further demonstrate the impressively high activity of BaMn_{1-x}Mg_xO₃ catalysts in the MCRM, the direct decomposition of NO over BaMn_{1-x}Mg_xO₃ were performed under excess oxygen, and the results are presented in Fig. 2. It is surprised that oxygen concentrations (0-10%) do not inhibit the catalytic NO decomposition reaction in the MCRM. Moreover, N₂ selectivities are more than 99.9% in the MCRM (Fig. 2b). The dramatically high selectivity indicated that the undesired consecutive reactions for converting NO to N₂O or NO₂ almost did not take place in the MCRM, and all the NO molecules almost directly converted into N₂ and O₂. Apparently, BaMn_{1-x}Mg_xO₃ catalysts exhibit excellent endurance to excess oxygen in the MCRM. Comparatively, Tang *et al.*²⁸ studied the direct decomposition of NO over Fe/ZSM-5 catalyst in the microwave heating mode, and they also demonstrated good endurance performance to excess oxygen concentration ranging from 2% to 10%. However, the NO conversion will sharply decrease from 55% to 40% as the oxygen concentration gradually increased from 0% to only 2%.²⁸ On the other hand, Jiang *et al.*³ reported the decomposition of NO over a BaCo_xFe_yZr_{1-x-y}O_{3-δ} perovskite membrane, and a complete NO conversion was achieved at 875 °C as the oxygen concentrations less than 3%. Unfortunately, NO conversion will decrease to 87% as the oxygen concentration above 5%.³

The above results indicated oxygen inhibition removal for the direct decomposition of NO over BaMn_{1-x}Mg_xO₃ catalysts in the MCRM. The results can probably be attributed to the microwave selective effect under microwave irradiation. It is well-known that the microwave electromagnetic field is beneficial to activate polar molecules.^{23,29} Therefore, it is speculated that the NO adsorbed on the surface of catalysts rather than the oxygen in the gas phase, can be activated effectively by the microwave electromagnetic field. The similar explanation was also reported by previous researches from our group^{27,30} and others.^{31,32} The NO molecules and O₂ molecules can all be physically adsorbed on the active sites. However, only the physical adsorption of NO molecules can

Fig. 2 The influence of oxygen concentrations on the NO conversion (a) and N₂ selectivity (b) over BaMn_{1-x}Mg_xO₃ catalysts in the MCRM (Reaction conditions: reaction temperature, 250 °C; molar fraction of NO, 0.1%; W/F = 1 g s cm⁻³; and N₂ as the balance)

become chemical adsorption on the active sites and further convert to N₂ in the MCRM. Meanwhile, the physical adsorption of O₂ molecules is not enough to activate at low temperature under microwave selective effect and then they lose reactivity with NO to generate NO₂. Therefore, BaMn_{1-x}Mg_xO₃ catalyst can still exhibit excellent endurance to excess oxygen in the MCRM. This significant microwave selective effect can provide a new route to address the problem of strong oxygen inhibition in NO decomposition.

The effect of water vapor on NO conversion in the MCRM over BaMn_{0.9}Mg_{0.1}O₃ was studied (Fig. 1). Although the NO conversion decreases slightly in the presence of water vapor, the BaMn_{0.9}Mg_{0.1}O₃ catalyst still displays a high catalytic activity after the introduction of water vapor.

A durability test over BaMn_{0.9}Mg_{0.1}O₃ was performed in the MCRM. As shown in Fig. 3, BaMn_{0.9}Mg_{0.1}O₃ can still display a high stability in the MCRM. Surprisingly, NO conversion and N₂ selectivity are respectively higher than 97.7% and 99.9% in dry conditions and 94.6% and 99.8% under water vapor conditions within 20 h at 300 °C. Furthermore, XRD patterns (Fig. S3c, ESI†) for BaMn_{0.9}Mg_{0.1}O₃ suggest that the mixed oxide structure of BaMn_{0.9}Mg_{0.1}O₃ does not differ significantly before and after microwave irradiation. Apparently, BaMn_{0.9}Mg_{0.1}O₃ catalyst exhibits excellent endurance to water vapor in the MCRM.

We investigated the catalytic activity and microwave heating profile of the BaMn_{0.9}Mg_{0.1}O₃-1000 sample (calcined at 1000 °C

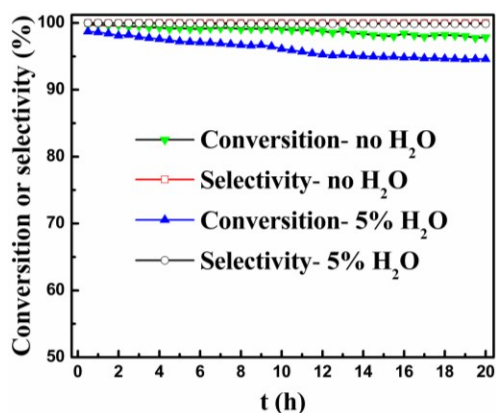


Fig. 3 Time profile of NO conversion and N₂ selectivity over BaMn_{0.9}Mg_{0.1}O₃ catalyst in the MCRM (Reaction conditions: molar fraction of O₂, 5%; molar fraction of NO, 0.1%; W/F = 1 g s cm⁻³; N₂ as the balance; and reaction temperature, 300 °C)

and possesses perovskite structure, Fig. S3b, ESI†). Surprisingly, the BaMn_{0.9}Mg_{0.1}O₃-1000 exhibits very poor microwave-absorbing ability compared with the BaMn_{0.9}Mg_{0.1}O₃ (calcined at 700 °C) at the microwave power of 150W (Fig. S2, ESI†), and the catalytic performance of BaMn_{0.9}Mg_{0.1}O₃-1000 is much worse than the BaMn_{0.9}Mg_{0.1}O₃ in the MCRM (Fig. S4, ESI†).

We also studied the catalytic activity of BaMn_{0.9}Mg_{0.1}O₃ under identical conditions in the CRM, and the results are shown in Fig. S5 (ESI†). Among the reaction temperature ranges of 450-650 °C, N₂ formation starts at 450 °C and the highest NO conversion and N₂ yield are respectively only 38.5% and 24.1% at 650 °C. However, BaMn_{1-x}Mg_xO₃ catalysts still display good catalytic activity at low temperature in the MCRM (Fig. 1). It is obvious that microwave catalysis remarkably enhances the activity of BaMn_{1-x}Mg_xO₃ for the decomposition of NO.

In addition, we calculated the apparent activation energies (E_a') of BaMn_{1-x}Mg_xO₃ catalysts for the direct decomposition of NO (Table S1, ESI†). Surprisingly, E_a' of BaMn_{1-x}Mg_xO₃ in the MCRM are as low as 11.6-27.8 kJ/mol. Therefore, E_a' in the MCRM are much lower than the corresponding E_a' values of similar BaMn_{1-x}Mg_xO₃ in the CRM, and the direct decomposition of NO in the MCRM can operate at a lower temperature with a dramatically higher conversion than that in the CRM.

In conclusion, we believe the most significant aspect of this study is that it reports the microwave selective effect: a new approach to oxygen inhibition removal for a difficult (strong oxygen inhibition) and important catalytic decomposition reaction for the direct decomposition of NO under excess oxygen. Importantly, the oxygen concentration has surprisingly no effect on the catalytic performance of decomposition of NO over BaMn_xMg_{1-x}O₃ catalysts in the MCRM. A complete NO decomposition with NO conversion and N₂ selectivity respectively up to 99.8% and 99.9% was achieved over the BaMn_{0.9}Mg_{0.1}O₃ catalyst at the environment of excess oxygen and temperature as low as 250 °C in the MCRM.

Although only the catalysts of BaMn_{1-x}Mg_xO₃ and the reaction of direct NO decomposition were used as a case study, we believe that this novel process can be extended to other catalysts and strong oxygen inhibition reactions, such as direct decomposition

of NO over noble metals, oxides, and metal ion-exchanged zeolites catalysts, and also the situation for the direct catalytic decomposition of N₂O.

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