Electronic Supplementary Information

Microwave selective effect: a new approach towards oxygen inhibition removal for highly-effective NO decomposition by microwave catalysis over $BaMn_xMg_{1-x}O_3$ mixed oxides at low temperature under excess oxygen

Wentao Xu, Jicheng Zhou*, Yingpiao Ou, Yushang Luo, Zhimin You

Key Laboratory of Green Catalysis and Chemical Reaction Engineering of Hunan Province, School of Chemical Engineering, Xiangtan University, Xiangtan 411105, P.R.China

S1. Experimental section

S1.1Preparation of catalysts

$Ba(Ac)_2$ (AR grade), $Mn(NO_3)_2$ (AR grade) and $Mg(NO_3)_2$ (AR grade) were primarily dissolved in deionized water according to the molar ratio of $BaMn_{1-x}Mg_xO_3$ (x=0,0.1,0.2,0.3,0.4). Citric acid and glycol were added into the aqueous solution, where the mole number of the complexing species were 1.25 times of metal ions including Ba^{2+}, Mn^{2+} and Mg^{2+}. The aqueous solutions were stirred at 80 °C for 2.5 h to obtain spongy amorphous gels. The acquired gels were dried at 120 °C overnight and submitted to decomposition in air at 400 °C for 2 h and then calcined at 700 °C for 4 h.

For comparison, the $BaMn_{0.9}Mg_{0.1}O_3$-1000 sample was calcined at 400 °C for 2 h and then at 1000 °C for 6 h.

S1.2 Catalysts Characterization

The catalysts were analyzed by X-ray diffraction (XRD, Rigaku D/max-II/2500). The

working voltage and current were respectively 40 kV and 40mA, and Cu Ka radiation was employed.

S1.3 Activity evaluation

S1.3.1 Microwave reactor system

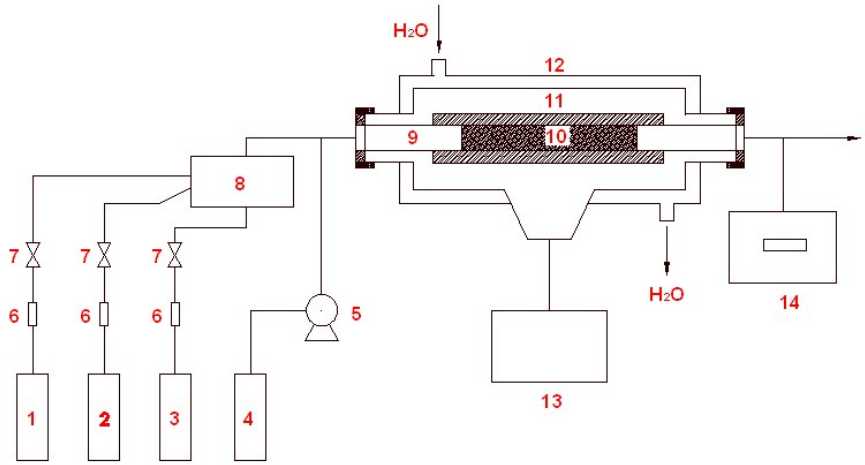

Fig. S1 Schematic diagram of microwave catalytic reactor system

1. NO; 2.O_2; 3.N_2; 4. Storage tank; 5. Metering pump; 6. Mass flow meter; 7. Valve; 8.Premixer; 9. Quartz reactor; 10. Fixed bed; 11. Thermal insulation; 12. Resonant cavity; 13. Microwave generator; 14. On-line NO_x analyzer

A new microwave catalytic reactor system was developed to research the role of the microwave irradiation in a continuous flow of gas-solid catalytic reaction system. The experimental diagram is shown in Fig. S1. The reactor consisted of a microwave generator system and a reaction system. The microwave energy was supplied by a 2.45 GHz microwave generator where the power could be adjusted continuously in the range of 0-1000 W. The magnetron microwave source was connected through a rectangular waveguide to a resonant cavity (Φ28mm*32mm, the space of microwave irradiation is not only the catalyst but the whole cavity). A quartz tube (i.d.10 mm and 540 mm in length) at the center

of the cavity was designed to perform the experiments. The catalyst was put in the middle of the reactor tube, and both ends were sealed with asbestos. The temperature of the reaction bed was provided by microwave thermal effect and was precisely measured by the modified thermocouple probe inserted to the catalyst bed.

Most commercially available microwave experimental apparatus are not well suited to investigate the microwave effects,[S1,S2] which may be attributed to the reasons as following:

(1) Applied microwave power may not be measured precisely.

(2) During the experiment, the reaction medium may not be irradiated by continuous and invariable microwave (pulsed or intermittent microwave input power do not satisfy invariable microwave power condition).

(3) Constant-temperature conditions may not be achieved, especially in the isothermal kinetic experiments.

(4) The reaction temperature may not be measured precisely because of the low quality temperature transducers or the temperature gradients formed in the reaction medium.

By contrast, the advantages of this reactor system are as follows:

(1) Continuously adjustable microwave power is range 0-1000W, and the frequency is 2450 MHz.

(2) The temperature of the catalyst bed can be precisely controlled by microcomputer.

(3) The precise monitoring of the reaction temperature is important to investigate the microwave effects.[S2] Therefore, an improved thermocouple probe was inserted to the catalyst bed, which is used to precisely measure the temperature of the catalyst bed.

(4) Microwave source emits microwave and irradiates on the reaction tube, and the

circulating water system is set around the periphery of the furnace chamber to absorb the microwave that avoid damage to the magnetron caused by the reflected microwave, which could protect the magnetron and make microwave catalytic reaction able to run for a long time.

S1.3.2 Activity tests

The reactant gas mixtures were composed of NO (the molar fraction of 0.1%), O_2 (the molar fraction of 0-10.0%) and the balanced N_2. The catalysts (2.0 g, 20-60 mesh) were used for each run and the reactant feed rates were fixed at W/F = 1 g s cm^{-3}, where W and F were respectively the catalyst weight and the total flow rate of reactant gas (F=120 ml min^{-1}). The concentrations of the NO and NO_2 in the outlet gas were analyzed through an online NO_x analyzer (42C, Thermo Environmental Instruments Co., Ltd., U.S.). In addition, the analysis system has GC (Agilent 7890A) with a Poropak Q column and a thermal conductivity detector for the N_2O analysis. In the microwave catalytic reaction mode (MCRM), N_2 was the principal product, NO_2 was the by-product, and N_2O could not be detected. Therefore, the NO conversion and N_2 selectivity could be calculated by the formulas as follows:

$$X_{NO} = \frac{C_0(NO) - C_1(NO)}{C_0(NO)} \times 100\% \quad , \; S_{NO} = \frac{C_0(NO) - C_1(NO) - C_1(NO_2)}{C_0(NO) - C_1(NO)} \times 100\%$$

(X_{NO} represents the NO conversion, S_{NO} represents the N_2 selectivity, $C_0(NO)$ represents the NO concentration before the reaction, $C_1(NO)$ represents the NO concentration after the reaction, $C_1(NO_2)$ represents the NO_2 concentration after the reaction)

S2. Results and discussion

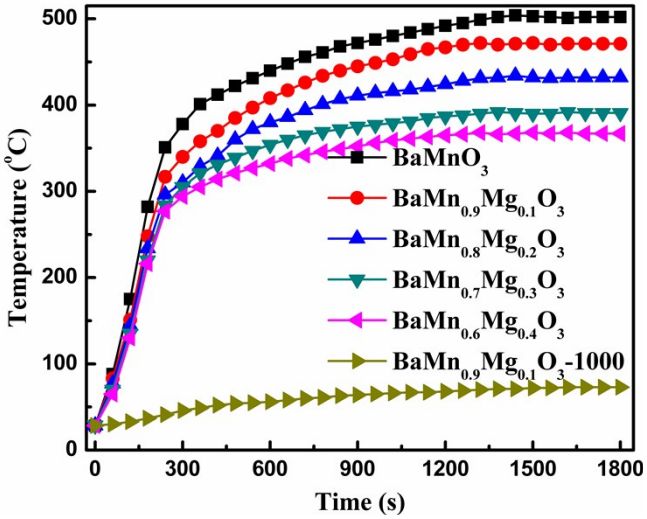

Fig. S2 Microwave heating profiles of $BaMn_{1-x}Mg_xO_3$ and $BaMn_{0.9}Mg_{0.1}O_3$-1000 at the microwave power of 150 W in the MCRM

The new microwave catalytic reactor is essentially different from the previous microwave reactor, and the required reaction temperature of the catalysts relates to the microwave absorbing properties of the catalyst itself. In another word, the catalyst must be matched with microwave. Therefore, we investigated the microwave heating profiles of $BaMn_{1-x}Mg_xO_3$ catalysts at the microwave power of 150W in the MCRM, and the results are shown in Fig S2. The catalysts bed temperature increases with the microwave irradiation time and then reaches to a stable temperature, and the microwave absorbing ability increases with the increasing of the Mn content in $BaMn_xMg_{1-x}O_3$ (except for $BaMn_{0.9}Mg_{0.1}O_3$-1000). The stable bed temperature maintained at 502 °C of $BaMnO_3$, 471 °C of $BaMn_{0.9}Mg_{0.1}O_3$, 432 °C of $BaMn_{0.8}Mg_{0.2}O_3$, 391 °C of $BaMn_{0.7}Mg_{0.3}O_3$, 367 °C of $BaMn_{0.6}Mg_{0.4}O_3$ and 73 °C of $BaMn_{0.9}Mg_{0.1}O_3$-1000 respectively at the microwave power of 150 W under microwave irradiation for about 30min. In the following experiments, the catalyst bed temperature in the MCRM was controlled by adjusting the microwave power.

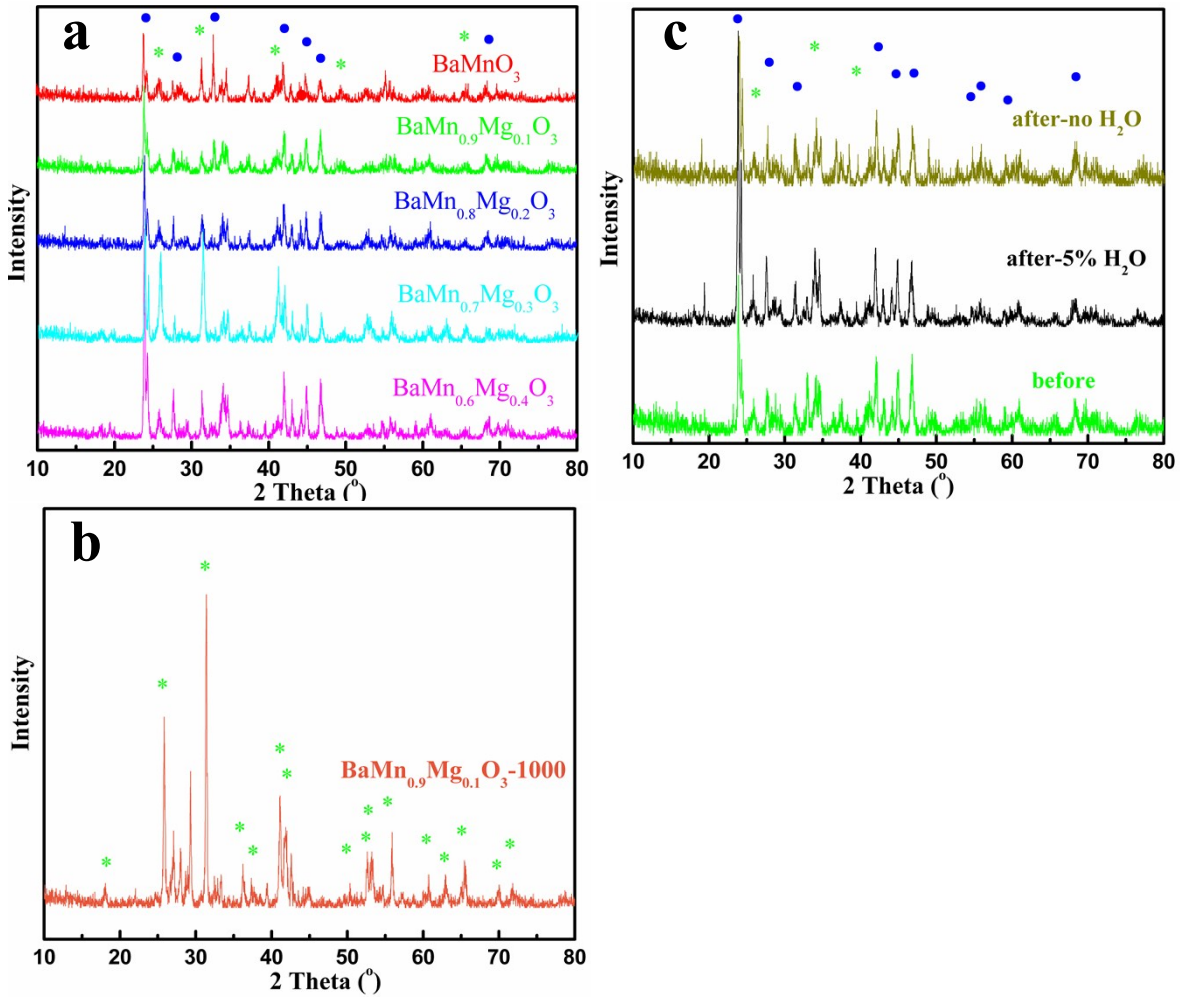

Fig. S3 XRD patterns of $BaMn_{1-x}Mg_xO_3$ (a), $BaMn_{0.9}Mg_{0.1}O_3$-1000 (b), and $BaMn_{0.9}Mg_{0.1}O_3$ before and after microwave reaction (c) (● $BaCO_3$ and ∗ $BaMnO_3$)

Fig. S3 shows the XRD patterns of the $BaMn_{1-x}Mg_xO_3$ samples. Although all the $BaMn_{1-x}Mg_xO_3$ samples (x=0, 0.1, 0.2, 0.3, 0.4, calcined at 700 °C) contain the diffraction peaks of $BaMnO_3$ phase, the main diffraction peaks of all these $BaMn_{1-x}Mg_xO_3$ samples can be assigned to $BaCO_3$ phase, indicating that the $BaMn_{1-x}Mg_xO_3$ samples are a kind of mixed oxides (Fig. S3a). However, the main diffraction peaks of the $BaMn_{0.9}Mg_{0.1}O_3$-1000 sample (calcined at 1000 °C) can belong to the $BaMnO_3$ phase (Fig. S3b), demonstrating that $BaMn_{0.9}Mg_{0.1}O_3$-1000 possesses perovskite structure.

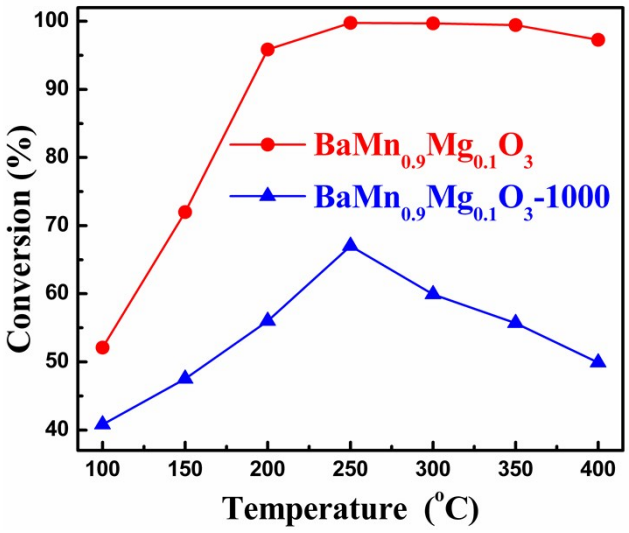

Fig. S4 The influence of reaction temperatures on the NO conversion over $BaMn_{0.9}Mg_{0.1}O_3$-1000 in the MCRM (Reaction conditions: molar fraction of O_2, 5%; molar fraction of NO, 0.1%; W/F = 1 g s cm^{-3}; and N_2 as the balance)

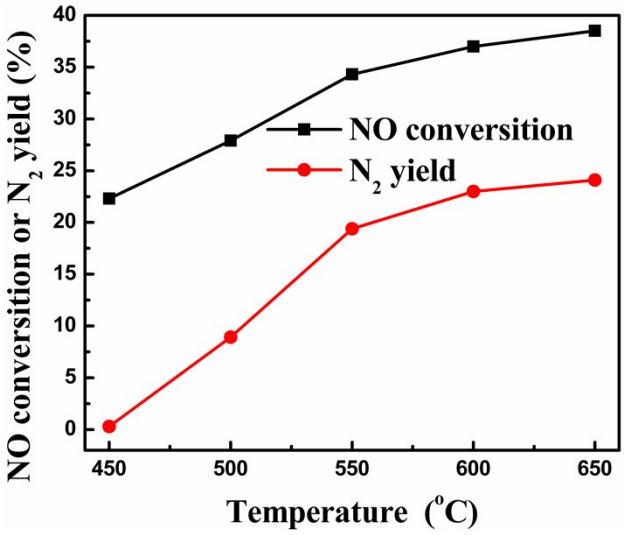

Fig. S5 The influence of reaction temperatures on the NO conversion and N_2 yield over $BaMn_{0.9}Mg_{0.1}O_3$ in the CRM (Reaction conditions: molar fraction of O_2, 5%; molar fraction of NO, 0.1%; W/F = 1 g s cm^{-3}; and N_2 as the balance)

Table S1 The apparent activation energies (Ea') of direct catalytic decomposition of NO

Mode/Temperature conditions	Catalysts	Ea' (KJ/mol)[a]	Reference
Direct decomposition of NO	No catalyst	364	S3
CRM, 579-733K	Cu-ZSM-5	123	S4
MCRM, 200-250 °C	$BaMnO_3$	15.5	This work
MCRM, 200-250 °C	$BaMn_{0.9}Mg_{0.1}O_3$	27.8	This work
MCRM, 200-250 °C	$BaMn_{0.8}Mg_{0.2}O_3$	23.9	This work
MCRM, 200-250 °C	$BaMn_{0.7}Mg_{0.3}O_3$	24.2	This work
MCRM, 200-250 °C	$BaMn_{0.6}Mg_{0.4}O_3$	11.6	This work
CRM, 873-923K	$La_{0.87}Sr_{0.13}Mn_{0.2}Ni_{0.8}O_{3-\delta}$	102	S5

[a] The apparent activation energies (Ea') were calculated by Arrhenius equation; The first-order with respect to NO was used to calculate kinetic data.[S6]

S3. References:

(S1) C. O. Kappe, B. Pieber and D. Dallinger, *Angew. Chem. Int. Ed.*, 2013, **52,** 1088.

(S2) B. Ergan and M. Bayramoglu, *Ind. Eng. Chem. Res.*, 2011, **50,** 6629.

(S3) H. Bosch and F. Janssen, *Catal. Today*, 1988, **2,** 369.

(S4) V. Tomasic, Z. Gomzi and S. Zrncevic, *Appl. Catal., B*, 1998, **18,** 233.

(S5) C. Tofan, D. Klvana and J. Kirchnerova, *Appl. Catal. A,* 2002, **226,** 225.

(S6) T. Yasutake, H. Tomohiro and K. Shuichi, *J. Chem. Soc., Faraday Trans.*, 1998, **94,** 1887.