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1 Electronic Supplementary Information

2 Microwave catalytic effect: a new exact reason for microwave-driven

- 3 heterogeneous gas-phase catalytic reaction
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8 S1. Experimental section

9 S1.1Preparation of catalysts

10 S1.1.1 Preparation of $BaMn_{0.8}B_{0.2}O_3$ (B=Cu,Co,Ni) and $BaCoO_3$ catalysts

11 The used BaMn_{0.8}B_{0.2}O₃ (B=Cu,Co,Ni) and BaCoO₃ mixed oxides were prepared by sol-gel

12 method. Ba(NO₃)₂ (AR grade) and Mn(NO₃)₂ (AR grade) or Cu(NO₃)₂ (AR grade) or 13 Ni(NO₃)₂ (AR grade) or Co(NO₃)₂ (AR grade) were firstly dissolved in deionized water 14 according to the stoichiometric amounts of BaMn_{0.8}B_{0.2}O₃ (B=Cu,Co,Ni) and BaCoO₃ 15 mixed oxides. Afterward, glycol and citric acid (the mole amounts of complexing species 16 were 1.25 times of total metal cations) were added into the solutions. Subsequently, the 17 solutions were stirred at 80 °C until forming amorphous gels. The obtained gels were firstly 18 dried at 120 °C overnight, and then calcined in air at 400 °C for 2 h and finally calcined at 19 700 °C for 4h. The SEM characterization of BaMnO₃ and BaCoO₃ was carried out using a 20 JEOL JSM-6700F instrument.

21 S1.1.2 Preparation of MeO_x-Cu-ZSM-5 (Me=Mn,Ni) catalyst ^{S3}

22 Cu-ZSM-5 was prepared by the ion exchange method. H-ZSM-5 (Si/Al=50 supplied by

1 Nankai University, China) was exchanged with an aqueous solution of 0.01 mo1/L Cu(AC)₂
2 (AR grade, Shenyang Agent Company, China) according to the ratio of H-ZSM-5 and
3 aqueous solution which was 15g/L. Then the solution was adjusted the pH to 7 through
4 ammonia and stirred for 12 h at 50 °C. After filtration, the sample was washed with
5 deionized water and then dried at 100 °C for 10 h and calcined at 500 °C for 6h. Ion
6 exchange had been carried out for 2 times to obtain a final Cu-ZSM-5 zeolite catalyst
7 containing 5 wt.% of Cu.

MeO_x-Cu-ZSM-5 (Me=Mn,Ni) catalysts were prepared by mechanical mixing method.
Ni₂O₃ (AR grade, Shanghai Qiangshun Chemical Reagent Co., Ltd. of China) or MnO₂ (AR
grade, Taijin Fengchuan Chemical Reagent Co., Ltd. of China) was added into Cu-ZSM-5,
and then grinded sufficiently and mixed uniformly in the Mortar.

12 S1.2 Activity evaluation

13 S1.2.1 Microwave reactor system



14

15 Fig. S1 Schematic diagram of microwave catalytic reactor system

16 1. NO; 2.O₂; 3.N₂; 4. Storage tank; 5. Metering pump; 6. Mass flow meter; 7. Valve; 8.Premixer; 9.

17 Quartz reactor; 10. Fixed bed; 11. Thermal insulation; 12. Resonant cavity; 13. Microwave generator; 14.

18 On-line NO_x analyzer

A microwave catalytic reactor system was applied to research the role of the 1 microwave irradiation in a continuous flow of gas-solid catalytic reaction system. The 2 3 experimental diagram is shown in Fig. S1. The reactor consisted of a microwave generator 4 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 0-5 1000 W. The magnetron microwave source was connected through a rectangular waveguide 6 to a resonant cavity ($\Phi 28 \text{ mm}^* 320 \text{ mm}$, the space of microwave irradiation is not only the 7 catalyst but the whole cavity). A quartz tube (i.d.10 mm and 540 mm in length) at the center 8 of the cavity was designed to perform the experiments. The catalyst was put in the middle of 9 the reactor tube, and both ends were sealed with asbestos. The temperature of the reaction 10 bed was provided by microwave thermal effect and was precisely measured by the modified 11 thermocouple probe inserted to the catalyst bed. 12

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:

15 (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 isothermalkinetic experiments.

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

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

2 (1) Continuously adjustable microwave power is range 0-1000W, and the frequency is
3 2450 MHz.

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

5 (3) The precise monitoring of the reaction temperature is important to investigate the 6 microwave effects.^{S2} Therefore, an improved thermocouple probe was inserted to the 7 catalyst bed, which is used to precisely measure the temperature of the catalyst bed.

8 (4) Microwave source emits microwave and irradiates on the reaction tube, and the 9 circulating water system is set around the periphery of the furnace chamber to absorb the 10 microwave that avoid damage to the magnetron caused by the reflected microwave, which 11 could protect the magnetron and make microwave catalytic reaction able to run for a long 12 time.

13 S1.2.2 Activity tests

14 The reactant gas mixtures were composed of NO (the molar fraction of 0.1%), O₂ (the molar fraction of 0-10.0%) and the balanced N₂. For the NO decomposition over BaBO₃ 15 (B=Mn,Co) catalysts, the catalysts (2.0 g, 20-60 mesh) were used for each run and the 16 reactant feed rates were fixed at W/F = 1 g s cm⁻³, where W and F were respectively the 17 catalyst weight and the total flow rate of reactant gas (F=120 ml min⁻¹). For the NO 18 decomposition over MeO_x-Cu-ZSM-5 (Me=Mn,Ni) catalysts, five milliliter catalysts was 19 20 used for each run and the space velocity (GHSV) was 1440 h⁻¹. For comparison, the CRM and MCRM were carried out in the same size reactor with the same amount of reaction bed 21 22 under identical conditions. The concentrations of the NO and NO_2 in the outlet gas were

1 analyzed through an online NO_x analyzer (42C, Thermo Environmental Instruments Co., 2 Ltd., U.S.). In addition, the analysis system has GC (Agilent 7890A) with a Poropak Q 3 column and a thermal conductivity detector for the N₂O analysis. In the microwave catalytic 4 reaction mode (MCRM), N₂ was the principal product, NO₂ was the by-product, and N₂O 5 could not be detected. Therefore, the NO conversion (X(NO)) and N₂ yield ($Y(N_2)$) could be 6 calculated by the formulas as follows:

7
$$X(NO) = \frac{C_0(NO) - C_1(NO)}{C_0(NO)} \times 100\% , \ Y(N_2) = \frac{C_0(NO) - C_1(NO) - C_1(NO_2)}{C_0(NO)} \times 100\%$$

8 ($C_0(NO)$ represents the NO concentration before the reaction, $C_1(NO)$ represents the NO concentration 9 after the reaction, $C_1(NO_2)$ represents the NO₂ concentration after the reaction)

1 S2. Results and discussion



2

3 Fig. S2. Effects of reaction temperature on NO conversion (X) and N₂ yield (Y) over BaMnO₃ and

4 BaCoO₃ catalysts in the CRM (Reaction conditions: molar fraction of O₂, 5%; molar fraction of NO,

5 0.1%; W/F = 1 g s cm⁻³; and N₂ as the balance)





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8 Fig. S3 The NO conversion for the direct decomposition of NO in the MCRM and CRM over MeO_x-Cu-

9 ZSM-5 (Me=Mn,Ni) catalysts^{S3} (Reaction conditions: molar fraction of O₂, 5%; molar fraction of NO,

^{10 0.1%;} GHSV = 1440 h⁻¹; and N₂ as the balance)



2 Fig. S4 Microwave heating profiles of BaMn_{0.8}B_{0.2}O₃ (B=Cu,Co,Ni) and BaCoO₃ at the microwave



8 Fig. S5. Microwave heating behavior of Cu-ZSM-5 and MeOx-Cu-ZSM-5 in the MCRM at the

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⁹ microwave power of 300 W^{S3}



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Fig. S6. SEM images of BaMnO₃ (a,b) and BaCoO₃ (c,d)

The SEM images (Fig. S6) of BaMnO₃ and BaCoO₃ indicates that the primary particles
were ca. 100 nm in size and formed agglomerates larger than 1.0 μm, which are very
resemble to other nanoscaled perovskites reported previously.^{S4,S5}

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8 S3. References:

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