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2	Supplementary Information for
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4	Bridge-type Mn-O-Mn sites promoted catalytic methane oxidation and carbonate
5	desorption over Mn-based oxides
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#### 20 1 Experimental Section

## 21 1.1 Details of catalyst preparation method

- 22 KMnO<sub>4</sub> (A.R.) and MnSO<sub>4</sub>·H<sub>2</sub>O (A.R.) were purchased from Aladdin, Shanghai, China.  $\alpha$ -
- 23 MnO<sub>2</sub> and  $\delta$ -MnO<sub>2</sub> were synthesized by controlling of KMnO<sub>4</sub>/MnSO<sub>4</sub> molar ratio with different
- 24 reaction times and temperatures.
- 25 1.25 g KMnO<sub>4</sub> and 0.53 g MnSO<sub>4</sub>·H<sub>2</sub>O for  $\alpha$ -MnO<sub>2</sub> preparation;
- 26 3.38 g MnSO<sub>4</sub>·H<sub>2</sub>O and 4.58 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> for  $\gamma$ -MnO<sub>2</sub> preparation;
- 27 1.50 g KMnO<sub>4</sub> and 0.28 g MnSO<sub>4</sub>·H<sub>2</sub>O for  $\delta$ -MnO<sub>2</sub> preparation.

28 Certain amounts of KMnO<sub>4</sub> and MnSO<sub>4</sub>·H<sub>2</sub>O were dissolved in 80 mL deionized water with magnetic stirring for about 30 min to form homogeneous suspension. Then the liquids were 29 30 instantly transferred into 100 mL Teflon-lined stainless-steel autoclaves and sealed. The 31 autoclaves were put into an oven to maintain the temperature at 160 °C for 12 h for  $\alpha$ - and  $\delta$ -MnO<sub>2</sub> preparation and at 90 °C for 24 h for γ-MnO<sub>2</sub> preparation. After cooling drown naturally to room 32 33 temperature, the resulting MnO<sub>2</sub> precipitates were collected, filtered, and washed with deionized water. All of the MnO<sub>2</sub> precipitate products were dried at 80 °C for 2 h and calcined at 360 °C for 34 35 2 h.

#### 36 1.2 Catalyst characterization

All prepared different MnO<sub>2</sub> catalysts were characterized using X-ray diffractometry (XRD), scanning electron microscope (SEM, TESCAN MIRA LMS), high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha analyzer), Raman spectroscopy (HORIBA Scientific LabRAM HR Evolution, Japan), and O<sub>2</sub> temperature-programmed desorption (O<sub>2</sub>-TPD, Tilon, LC-D200M, Ametek, USA).

## 43 1.3 Calculations

44 The turnover frequency of  $CH_4$  conversion on the catalyst (*TOF*, µmol m<sup>-2</sup> min<sup>-1</sup>) was 45 defined in Equation S1:

$$46 TOF = \frac{F \cdot [CH_4]_{in} \cdot x}{60 \cdot m \cdot S_{BET}} (S1)$$

47 where, *F* is the total gas flow rate in L min<sup>-1</sup>. *m* in g is the weight of the catalyst used in the 48 quartz tube reactor.  $[CH_4]_{in}$  and *x* are CH<sub>4</sub> concentration (µmol L<sup>-1</sup>) in the gas at the inlet of the 49 quartz tube reactor and CH<sub>4</sub> conversion, respectively.  $S_{BET}$  is the specific area of the catalyst, in 50 m<sup>2</sup> g<sup>-1</sup>.

51 The activation energy ( $E_a$ , kJ mol<sup>-1</sup>) of CH<sub>4</sub> oxidation was calculated based on the Arrhenius 52 equation obtained as follows:

53 
$$-r_{co} = k[CH_4]^{\alpha} \cdot [O_2]^{\beta}$$
 (S2)

54 where, *k* is a rate constant. [CH<sub>4</sub>] and [O<sub>2</sub>] are concentrations of CH<sub>4</sub> and O<sub>2</sub>, respectively.  $\alpha$  and 55  $\beta$  are constants.  $\alpha$  is generally 1.0,  $\beta$  equals 0 since O<sub>2</sub> concentration is higher enough than that of 56 CH<sub>4</sub><sup>1,2</sup>. Thus,

$$\frac{d[CH_4]}{[CH_4]} = -k \cdot dt \tag{S3}$$

$$\ln (1 - x) = -k \cdot t \tag{S4}$$

$$t = \frac{V_{catal}}{V_{gas}} = \frac{V_{catal}}{\frac{V_{gas}^{0}}{T^{0}} \cdot T}$$
(S5)

59

$$k = -T ln(1-x) \left[ \frac{V_{gas}^{0}}{T^{0}} \right] = A e^{-\frac{E_{a}}{RT}}$$
(S6)

60

$$lnk = \ln\left[-Tln(1-x)\right] + \ln\left[\frac{V_{gas}^{0}}{T^{0}}\right] = -\frac{E_{a}}{RT} + A$$
(S7)

61

62 where,  $V_{catal}$  is the volume of the catalyst in the quartz tube reactor. *t* and *T* are reaction time and 63 temperature, respectively.  $V_{gas}^0$  is the gas flow rate at reaction temperature  $T_0$ .

## 64 1.4 Normalization of peak intensity

65 The collected infrared spectra at different temperatures were normalized for relatively 66 quantitative analysis. The normalization is based on the absolute values of the strongest peak 67 height ( $P_{i max}$ ) of a positive peak and lowest peak height ( $P_{i min}$ ) of a negative peak using Equations 68 S8 and S9, respectively.

69

$$N_i = \frac{P_i}{P_{i max}}$$
(S8)

$$N_i = \frac{P_i}{|P_{i\,min}|} \tag{S9}$$

- $N_i$  represents the normalized value of the absorption peak *i* at the corresponding temperature;
- $P_i$  represents the peak height of the absorption peak *i* at the corresponding temperature.

## 74 Reference:

- A.-P. Jia, G.-S. Hu, L. Meng, Y.-L. Xie, J.-Q. Lu and M.-F. Luo, *Journal of Catalysis*,
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- J.-Q. Lu, C.-X. Sun, N. Li, A.-P. Jia and M.-F. Luo, *Applied Surface Science*, 2013, 287,
  124-134.

# 81 2 Supporting Figures



83 Fig. S1. Experimental setup of the operando TPR-DRIFTS-MS system.



86 Fig. S2. Normalization curve of  $M^+$ - $O_2^-$  and  $M^{2+}$ - $O_2^{2-}$  under  $CH_4/Ar$  atmosphere.





Gas atmosphere	Composition (%)	Total gas flow rate
		(mL/min)
CH <sub>4</sub> /Ar	CH <sub>4</sub> : 2.37%, Ar: balance	38
CH <sub>4</sub> +O <sub>2</sub> /Ar	CH <sub>4</sub> : 2.37%, O <sub>2</sub> :10%, Ar: balance	38
O <sub>2</sub> /Ar	O <sub>2</sub> : 5.26%, Ar: balance	38
CO <sub>2</sub> /Ar	CO <sub>2</sub> : 2.37%, Ar: balance	38

95 Table S1 Composition of the gases fed to the reaction chamber.