Supporting Information

Insights into the roles of superficial lattice oxygen in formaldehyde oxidation on birnessite

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1. Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a Smartlab X-ray diffractometer with Cu Kα radiation (λ=0.15405 nm). Raman spectra were recorded with a Horiba HR800 Confocal Raman spectrometer with 532 nm excitation. The determination of specific surface area and pore volumes involved the utilization of N_2 adsorption and desorption isotherms, which were conducted using a Micromeritics ASAP 2460 instrument. The morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi S-4800). High-resolution transmission electron microscopy (HRTEM) was carried out on a Tecnai, G2, F20. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo-Scientific K-Alpha. Oxygen-temperature programmed desorption (O_2-TPD) and hydrogen-temperature programmed desorption (H_2-TPR) were performed on an AutoChem II 2920.

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectra were acquiring using a Thermo iS10 instrument equipped with an MCT detector. The spectra were recorded by accumulating 128 scans, and a resolution of 4 cm^{-1} was used

during the recording process. Prior to the experiment, a 50 mg sample underwent in situ heating in an Ar atmosphere at 400 ºC for 30 min. Subsequently, the sample was cooled to the reaction temperature. Each temperature was scanned for 10 min while MnO_2-3K was exposed to $HCHO/O_2/Ar$ in humidity.

2. MBTH method

The gas leaving the reaction system was directed through a solution of 3-methyl-2-benzothiazolonehydrazone, which served as an adsorbent to capture unconverted HCHO, then the ammonia iron(III) sulfate solution was added to color the adsorbed solution and the colored solution was then subjected to measurement using a UV-Vis spectrometer [1, 2]. The tested relationship between absorbance (y) and HCHO content (x) is shown in Fig. S1 using least square method, which is used to determine the concentration of HCHO in the inlet and outlet. Furtherly, it should be noted that the detection limit of MBTH method for HCHO concentration is 0.056 µg (GB/T 18204.2-2014).
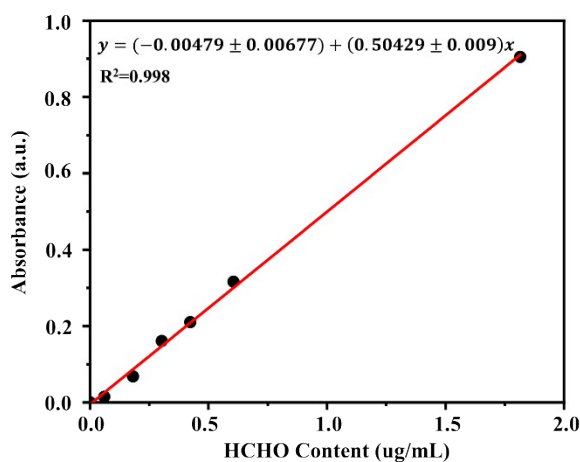

Fig. S1. The standard curve of MBTH method

3. Computational methods:

The density functional theory (DFT) calculations were performed by using the Vienna Ab-initio Simulation Package (VASP) [3,4]. MnO_2 (100) surface was used to build the slab and each slab consisted of four layers with 4 x 1 supercell. In the geometry optimization, the half of slab atoms were fixed and others were relaxed. The exchange–correlation interactions were described by generalized gradient approximation (GGA) [5] with the Perdew–Burke–Ernzerhof (PBE) functional [6]. Spin-

polarization was included in all the calculations and a damped van der Waals correction was incorporated using Grimme's DFT-D3(BJ) scheme to better describe the non-bonding interactions [7]. The cut-off energies for plane waves were set to be 500 eV, and the residual force and energy on each atom during structure relaxation were converged to 0.005 eV Å-1 and 10-5 eV, respectively. The Brillouin-zones were sampled with a k-point mesh of 2×3×1. The vacuum layer was ~15 Å to remove the slab interaction between the z direction.

Gibbs free energies for each gaseous and adsorbed species were calculated at 300 K, according to the expression

$$G = EDFT + ZEP + \int CvdT - TdS$$

where EDFT is the electronic energy calculated with VASP, ZPE is the zero-point energy, $\int CvdT$ is the enthalpy contribution and TdS is the entropy contribution. Standard ideal gas methods were employed to compute ZPE and TdS from temperature, pressure, and the calculated vibrational energies. The details of ZPE, $\int CvdT$, TdS were listed in Table S1.

Table S1. The details of ZPE, $\int CvdT$, and TdS

Adsorbed species on $MnO_2(100)$	$\int C_vdT$ (eV)	E_{ZPE} (eV)	(300 K) TS (eV)
$CH_2O(g)$	0.1048	0.69012	0.68153
$CO_2(g)$	0.09857	0.30403	0.6668
$H_2O(g)$	0.1035	0.55284	0.58801
*CH_2O	0.04389	0.73993	0.08124
*CHO+*OH	0.08246	0.82186	0.13891
*CHOOH	0.08417	0.90885	0.15376
*COOH+*OH	0.11428	0.9592	0.20741
*H_2CO_3	0.07933	1.01233	0.13507

4. Kinetic reaction measurement:

The apparent activation energy (Ea) (J/mol) was calculated by Eqs. (1) and (2) [8]:

$$lnr = -\frac{E_a}{RT} + lnA \qquad (1)$$

$$r = \frac{x \times f_{HCHO}}{m_{cat}}$$

(2)

Where x is the conversion of HCHO, m_{cat} is the mass of the catalyst (g), f_{HCHO} is the flow rate of HCHO ($\mu mol \cdot s^{-1}$), r is the reaction rate of HCHO ($\mu mol \cdot g^{-1} \cdot s^{-1}$), R is the universal gas constant, and T is the reaction temperature (K).

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