Supplementary Materials

Unveiling the Intrinsic Role of Water in the Catalytic Cycle of Formaldehyde Oxidation: A Comprehensive Study Integrating Density Functional Theory and Microkinetic Analysis

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Table S1. The comparison of apparent energy ($E_{apparent}$) at 400 K and the energy of barrier (E_{bar}) of the rate-determing step of Al_1/C_2N and other reported catalysts.

Catalysts	$E_{apparent}$ (eV)	
	Model predictions	**Experimental data**
LMO	1.00 (J. Ding et al., 2022)	0.94 (Xu et al., 2021) [a]
Sr-LMO	0.80 (J. Ding et al., 2022)	0.77 (Xu et al., 2021) [a]
Sn-LMO	0.80 (J. Ding et al., 2022)	
Ag-LMO	0.96 (J. Ding et al., 2022)	
$MnCe_{x-1}O_{2x-1}$ (111)	1.12 (W.Song et al., 2022)	
$MnCe_{x-1}O_{2x}$ (111)	1.60 (W.Song et al., 2022)	
$Mn_2Ce_{x-2}O_{2x}$ (111)	1.84 (W.Song et al., 2022)	
$Mn_3Ce_{x-3}O_{2x}$ (111)	2.54 (W.Song et al., 2022)	
Al_1/C_2N	1.30 (this work)	

Catalysts	E_{bar} (eV) of rate-determing step	
	Model predictions	**Condition**
Pd/Co_3O_4	0.90 (J. Deng et al., 2022)	Without H_2O
Co_3O_4 (defect)	1.37 (J. Deng et al., 2022)	Without H_2O
Co_3O_4 (perfect)	0.87 (J. Deng et al., 2022)	With H_2O
Co_3O_4 (defect)	0.51 (J. Deng et al., 2022)	With H_2O
Al_1/C_2N	0.86 (this work)	With H_2O

[a] Experimental condition: temperature = 110 ◦C, HCHO: O_2 = 1: 2000

[1] Journal of Hazardous Materials 422 (2022) 126931
[2] Appl. Catal. B 287, 119955.
[3] Journal of Hazardous Materials 425 (2022) 127985
[4] Catalysis Today 339 (2020) 210–219
[5] Chemical Engineering Journal 355 (2019) 540–550

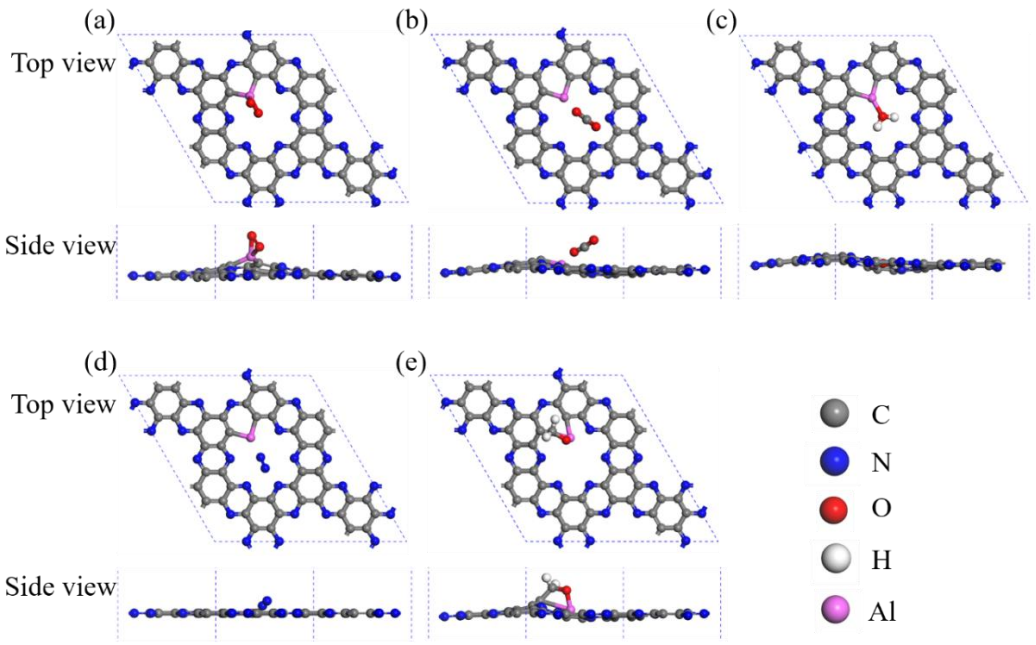
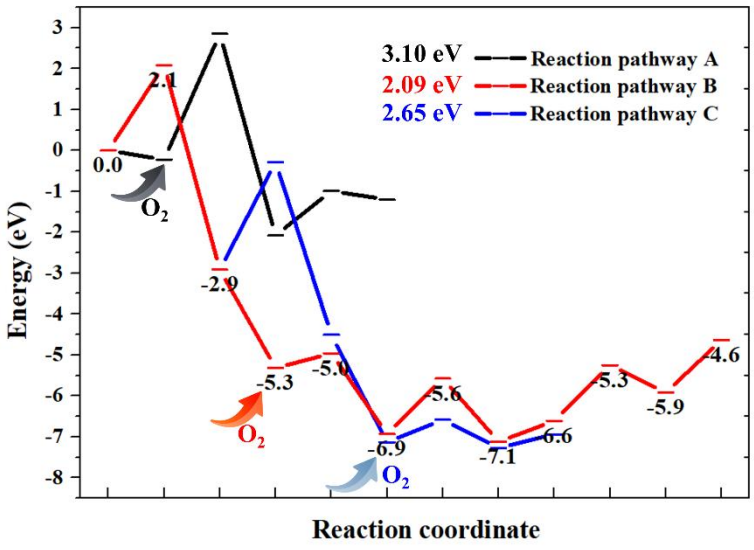


Fig. S1 The most stable configurations of (a) O_2, (b) CO_2, (c) H_2O, (d) N_2, and (e) HCHO adsorbed on Al_1/C_2N.



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48 **Fig. S2 Three direct oxidation pathways of HCHO on Al_1/C_2N.**

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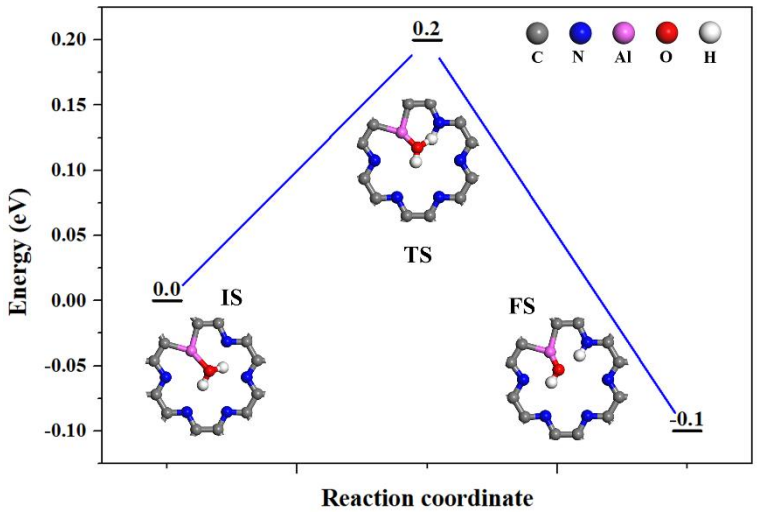
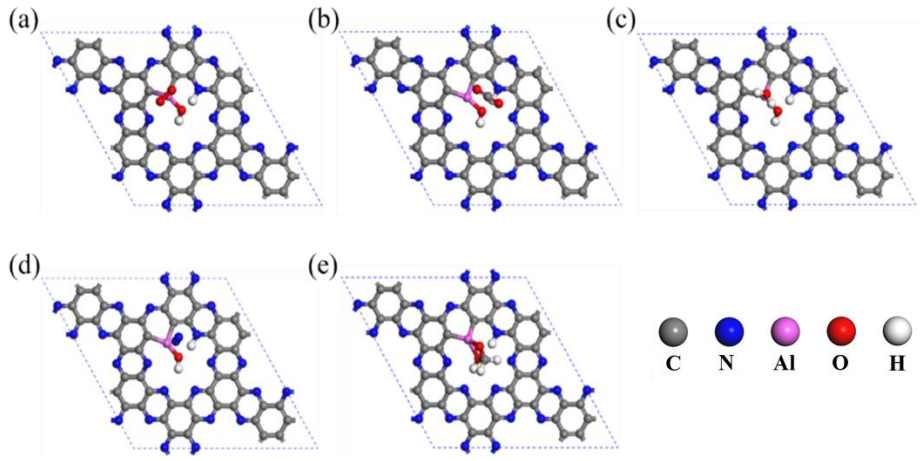


Fig. S3 The dissociating reaction of H_2O on Al_1/C_2N.



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55 **Fig. S4 Most stable configurations of (a) O_2, (b) CO_2, (c) H_2O, (d) N_2 and (e) HCHO adsorbed**

56 **on hydrated Al_1/C_2N.**

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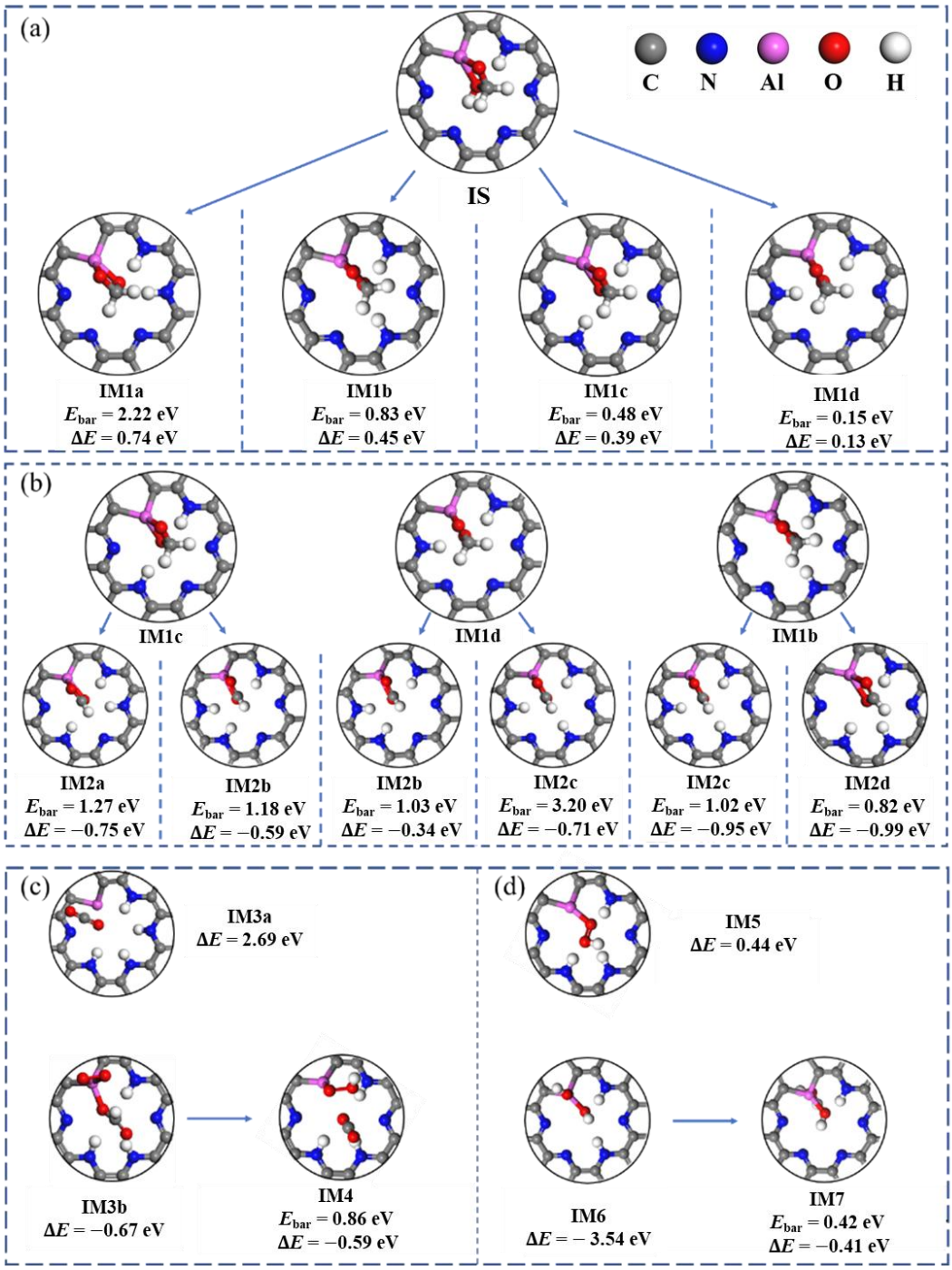

Fig. S5 The energy barrier (E_{bar}) and reaction energy (ΔE) of each elementary reaction of HCHO degraded on hydrated Al_1/C_2N.

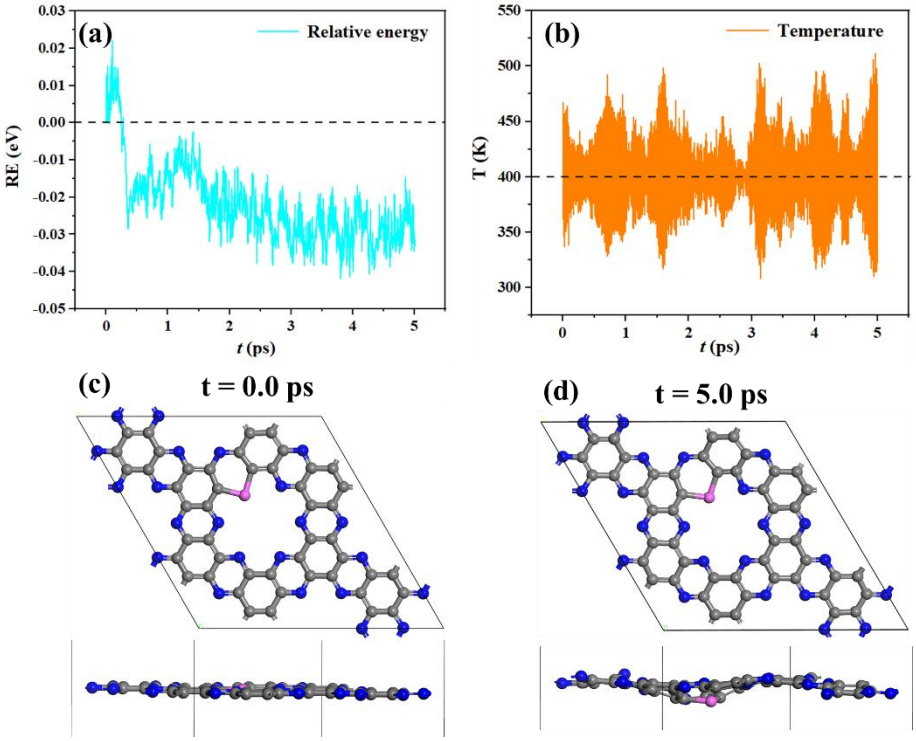

Fig. S6 Evolution of (a) relative energy (RE) and (b) temperature (T) of the Al_1/C_2N with NVT AIMD simulation time and the geometric structures of the Al_1/C_2N at simulation times (c) t = 0 ps and (d) t = 2.5 ps. The simulation temperature is 400 K.

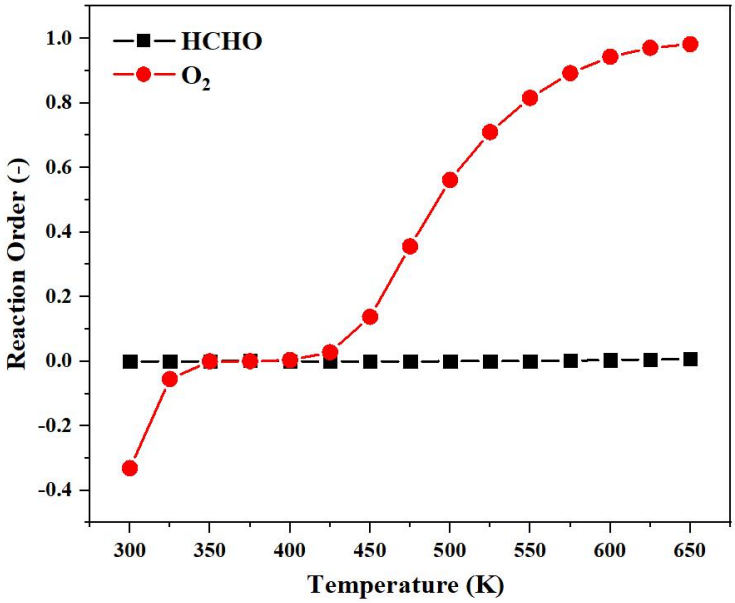

Fig. S7 The reaction order of HCHO oxidation on Al_1/C_2N.

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