

# Electronic Supporting Information for

## **Low cost, highly dispersed Ce/Na-ZSM-5 catalysts close to atomic dispersion for enhancing formaldehyde oxidation**

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## Experimental section

### Catalysts preparation

Ce/Na-ZSM-5 catalysts was prepared by an impregnation method. Na-ZSM-5 (Si/Al=30) was first uniformly dispersed into the 1M NaOH solution for 2 h. After filtration and dried, the sample was uniformly dispersed into the  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  aqueous solution (0.1, 0.05, 0.01, 0.005 M) for 2 h and then washed with deionized for several time. After filtration and dried, the sample was finally calcined at 500 °C for 2 h with a heating rate of 5 °C /min in air. The Ce loading of catalysts with 0.005M, 0.01M, 0.05M and 0.1M  $\text{Ce}^{3+}$  aqueous solution impregnated measured by the inductively coupled plasma-optical emission spectrometry (ICP-OES) were determined as 2.6 %, 4.7 %, 7.0 % and 8.7 %, respectively (Table S1). As a result, the catalysts above were denoted as 2.6 wt.% Ce/Na-ZSM-5, 4.7 wt.% Ce/Na-ZSM-5, 7 wt.% Ce/Na-ZSM-5 and 8.7 wt.% Ce/Na-ZSM-5, respectively. The Cu/Na-ZSM-5, Co/Na-ZSM-5, Ni/Na-ZSM-5 and Fe/Na-ZSM-5 were synthesized with the similar method, except for using  $\text{CuSO}_4$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$ ,  $\text{NiSO}_4$  and  $\text{FeCl}_3$  as the precursors, respectively.

### Material characterization

Field-emission scanning electron microscopy (SEM, JSM-6330F) was carried out to characterize the morphology of the Ce/Na-ZSM-5 catalysts. FEI Tecnai G2 F30 transmission electron microscope with an acceleration voltage of 300 KV was used to acquire transmission electron microscopy(TEM) and scanning transmission electron microscopy(STEM) images. The aberration corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) was carried out on a JEM-ARM200F transmission electron microscope operated at 200kV. X-ray diffraction (XRD) measurements were performed using a Broker's D8 ADVANCE powder X-ray diffractometer with Cu K radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The specific surface area and pore structures of the samples were obtained according to  $\text{N}_2$  adsorption/desorption isotherms by BELSORP-max automatic surface analyzer. Before the measurement, the samples were degassed and maintained in a vacuum for 2h at 120

°C to eliminate the surface contaminants. Raman spectroscopy was recorded on a Fourier Transform Raman spectrometer (Nicolet NXR 9650) with a excitation wavelength of 1064nm. Metal loading was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) which conducted on a PerkinElmer Optima 8300. X-ray photoelectron spectroscopy (XPS) measurements were performed on a ESCALab250 XPS system with Al K $\alpha$  source and a charge neutralizer, and all the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventurous carbon. AutoChem II 2920 analyzer with a thermal conductivity detector was used to analyze the temperature-programmed reduction (TPR) of Ce/Na-ZSM-5 catalysts. The catalysts (100 mg) were loaded in a U-shaped quartz tube with an atmosphere of 10% H<sub>2</sub> in N<sub>2</sub> at a flow rate of 50 mL/min between 50 and 800 °C at a heating rate of 10 °C/min. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was measured on a Nicolet IS50 spectroscopy apparatus. The catalysts (10 mg) were placed in a ceramic crucible in a gas chamber. The total gas flow rate was maintained at 60 mL /min (100ppm HCHO /Ar:20%O<sub>2</sub>/Ar = 1:2). The spectra were recorded as an average of 128 scans with a resolution of 8 cm<sup>-1</sup> under reaction conditions. The CO<sub>2</sub> in the gas phase was determined with an online mass spectrometer (MS, Pfeiffer Omni-star GSD-301). The XANES and EXAFS data were analyzed by Athena software. The X-ray absorption near-edge structure (XANES)and extended X-ray absorption fine structure (EXAFS) for the Ce L3-edge were collected at the SPring-8 14b2, where a pair of channel-cut Si (111) crystals was used in the monochromator. The storage ring was working at the energy of 8.0 GeV with average electron current of 99.5mA. For Wavelet Transform analysis, the  $\chi(k)$  exported from Athena was imported into the Hama Fortran code.

### **HCHO catalytic oxidation test**

The catalytic oxidation of HCHO and adsorption test was performed in a quartz tubular (i.d. =7 mm) fixed-bed reactor under atmospheric pressure with a home-made setup. Approximately 0.3 g of the catalyst was packed in the reactor. A simulated air stream (N<sub>2</sub>/O<sub>2</sub> = 4, 100 ml/min) containing ~50 ppm HCHO and water vapor (~35%

relative humidity) was introduced as the reactants. Gaseous HCHO was generated by passing a stream of simulated air through a bubbler containing a HCHO solution (5 wt.% HCHO). The gas hourly space velocity (GHSV) is 20,000 ml/(h·g). HCHO concentration in the reactant or product gas stream was analyzed by phenol spectrophotometric method.<sup>1,2</sup> The gas stream containing trace HCHO was bubbled through 5 ml phenol reagent (C<sub>6</sub>H<sub>4</sub>SN(CH<sub>3</sub>)C: NNH<sub>2</sub>·HCl, Alfa Aesar) solution (1 × 10<sup>-4</sup> wt.%) for 30 s to collect HCHO by absorption. Then, 0.4 ml (1 wt.%) ammonium ferric sulfate (NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, Tianjin Fuchen Chemical Reagent Company) solution was added as the coloring reagent. After shaking for 5 s and staying for 15 min in the dark, HCHO concentration in the gas stream was then determined by measuring light absorbance at 630 nm with a spectrophotometer (UV-240, Shimadzu Co. Ltd., Japan). The conversion of HCHO was calculated based on its concentration change. HCHO conversion was calculated using the following equation.

$$HCHO \text{ conversion}(\%) = \left( 1 - \frac{[HCHO]_{out}}{[HCHO]_{in}} \right) \times 100\%$$

### DFT Calculations

On the basis of periodic DFT, all calculations were performed employing a generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerh (PBE) of exchange correction functional.<sup>3,4</sup> The wave functions were created by expanding plane waves with 500 eV energy cutoff. Geometry optimization was performed using a gamma-centered k-point of 2×2×1. The geometry optimization consistency tolerances were set at 1.0×10<sup>-6</sup> eV/atom for total energy and 0.02 eV/Å for force, respectively. The semiempirical dispersion corrected DFT-D3 approach was used to identify the van der Waals interactions. To avoid surface interaction, a wide vacuum gap of 15 Å has been chosen in the periodically repeated slabs. Electron localization functions were used to examine the bonding property of adsorbed molecules. CINEB method has been used for the transition state calculation. The free energy of species was calculated according to the standard formula:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

where  $\Delta E$  was the total energy,  $\Delta E_{ZPE}$  was the zero-point energy,  $T$  was the temperature, and  $\Delta S$  was the entropy, respectively.

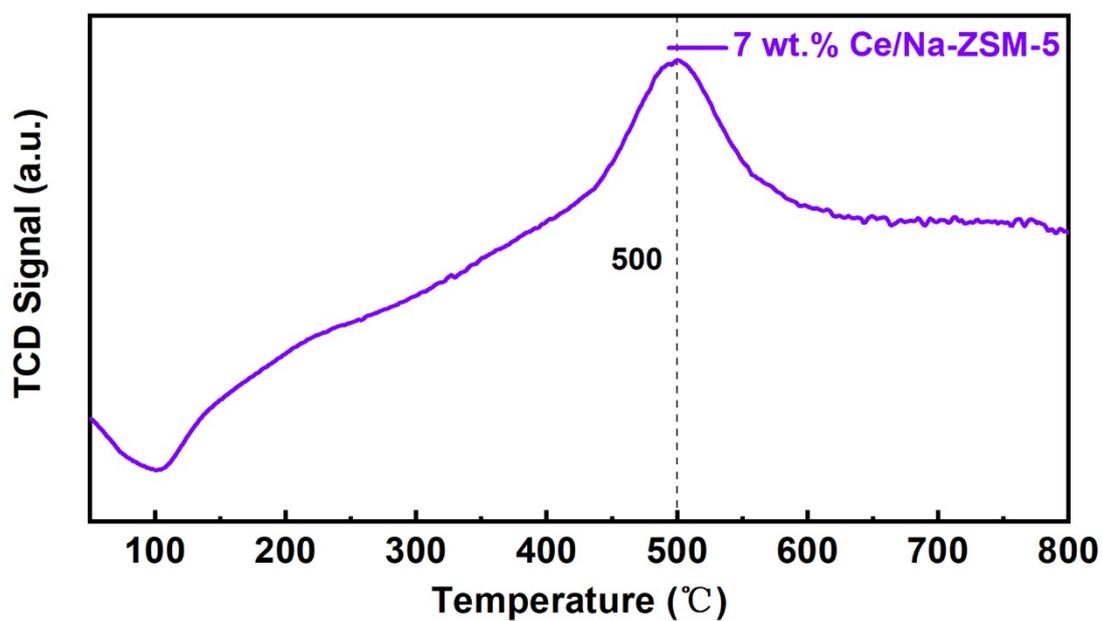


Fig. S1 H<sub>2</sub>-TPR profiles of 7 wt.% Ce/Na-ZSM-5.

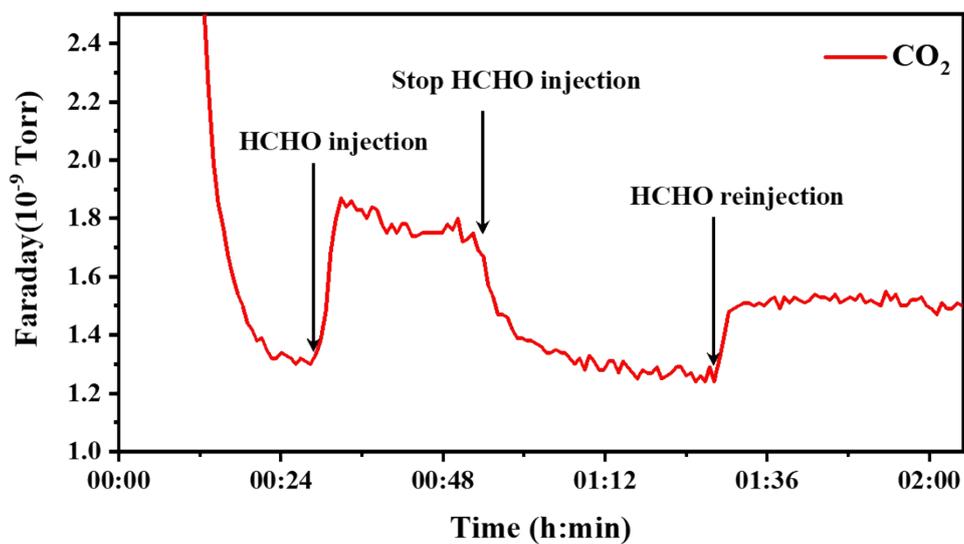
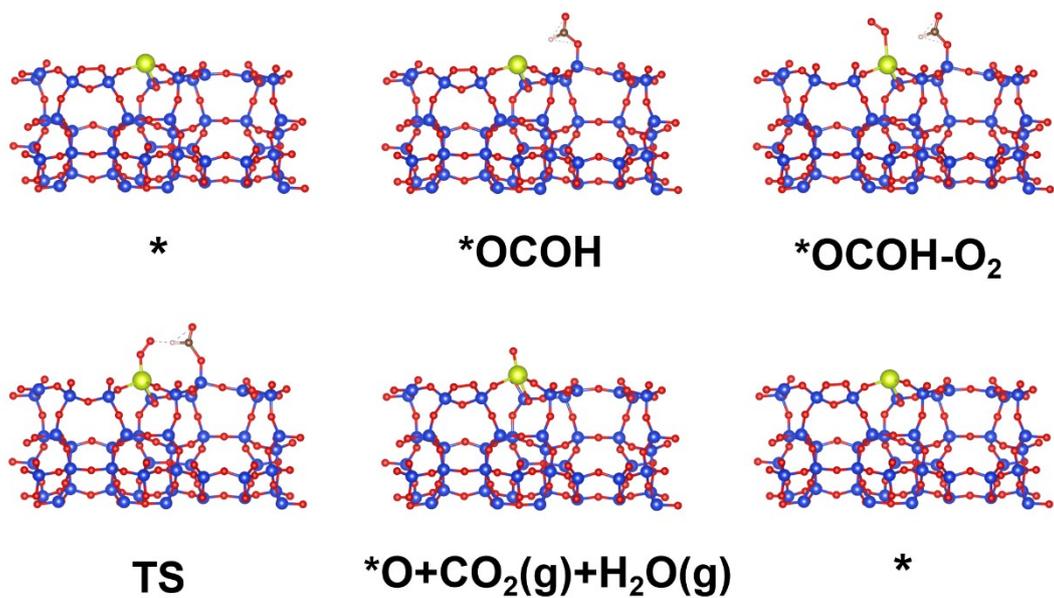
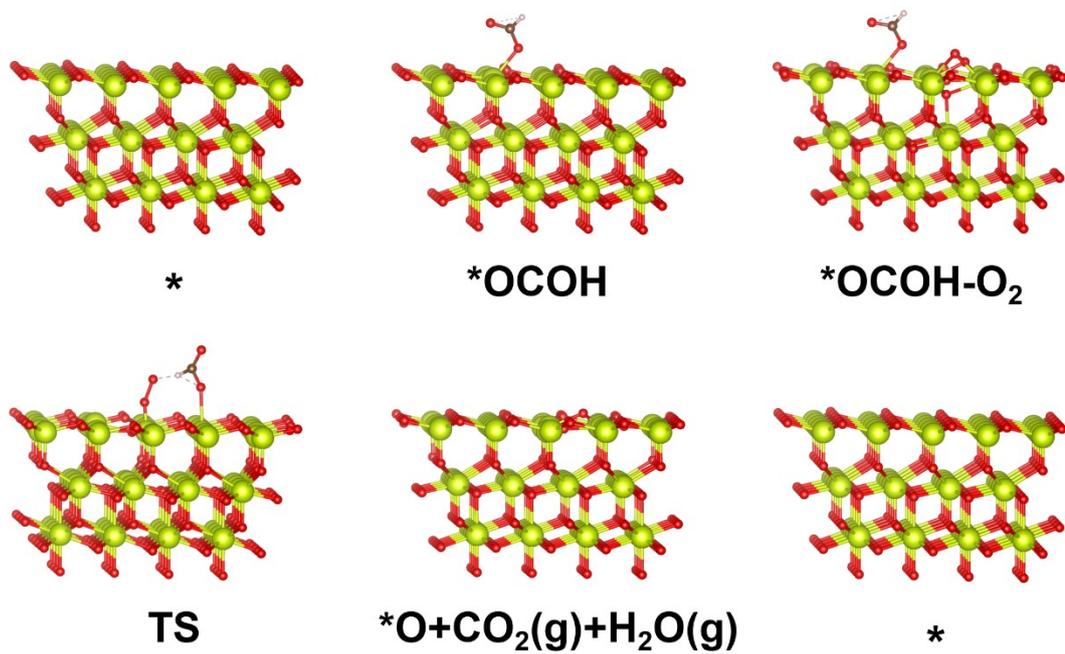


Fig. S2 Mass spectrometer spectra recorded from 7 wt.% Ce/Na-ZSM-5 at the relative molecular mass of 44 (CO<sub>2</sub>) for periods up to 2h.



**Fig. S3** Structure optimization of HCHO oxidation pathway on the surface of Ce/Na-ZSM-5 catalyst.



**Fig. S4** Structure optimization of HCHO oxidation pathway on the surface of CeO<sub>2</sub> catalyst.

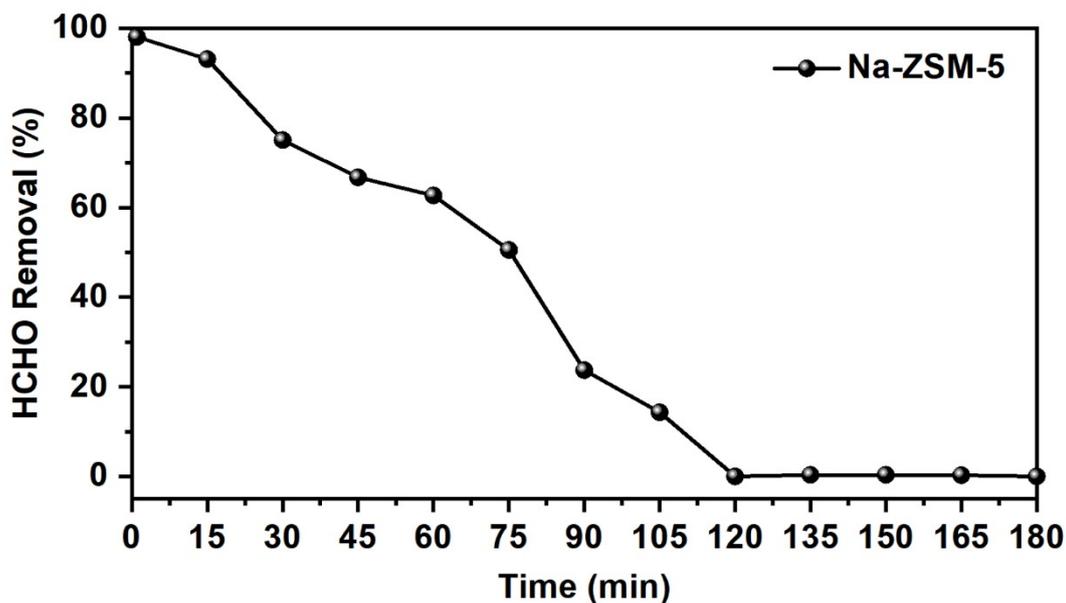


Fig. S5 HCHO removal efficiency of Na-ZSM-5 with time change at room temperature.

Table S1. Ce loading of Ce/ZSM-5 series samples.

Samples	Ce loading (wt.%)
Ce-0.005/Na-ZSM-5	2.6
Ce-0.01/Na-ZSM-5	4.7
Ce-0.05/Na-ZSM-5	7.0
Ce-0.1/Na-ZSM-5	8.7

0.005 of Ce-0.005/Na-ZSM-5 represents the molar concentration of the  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  aqueous solution.

Table S2 Physicochemical properties of Na-ZSM-5 and Ce/Na-ZSM-5 samples

Samples	$S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	D/nm	$V_p/\text{cm}^3\text{g}^{-1}$
Na-ZSM-5	360	2.33	0.21
2.6 wt. %Ce/Na-ZSM-5	312	2.94	0.23
4.7 wt. %Ce /Na-ZSM-5	305	3.09	0.24
7 wt. %Ce /Na-ZSM-5	336	3.80	0.32
8.7 wt. %Ce /Na-ZSM-5	319	2.79	0.22

**Table S3** XPS analysis results of Na-ZSM-5 and Ce/Na-ZSM-5 samples

Samples	Ce <sup>3+</sup> /Ce (%)	Ce <sup>4+</sup> /Ce (%)	O <sub>I</sub> /O (%)	O <sub>II</sub> /O (%)	O <sub>III</sub> /O (%)
Na-ZSM-5	\	\	1.4	3.4	95.2
Na-ZSM-5 (AT)	\	\	1.9	15.5	82.6
7 wt.% Ce/Na-ZSM-5 (NC)	47.4	52.6	14.3	6.7	79.0
7 wt.% Ce/Na-ZSM-5	39.8	60.2	12.5	5.3	81.2

AT represents Alkali Treatment; NT represents Not Calcined

**Table S4.** EXAFS fitting parameters at the Ce L3-edge for various samples ( $S_0^2=0.76$ )

Sample	Shell	CN <sup>a</sup>	R(Å) <sup>b</sup>	$\sigma^2(\text{Å}^2)^c$	$\Delta E_0(\text{eV})^d$	R factor
CeO <sub>2</sub>	Ce-O	8*	2.37*	0.0098 ± 0.0029	6.0 ± 1.3	0.02
	Ce-O-Ce	12*	3.87*	0.0025 ± 0.0015		
CePO <sub>4</sub>	Ce-O	7.3 ± 2.4	2.56 ± 0.02	0.0055 ± 0.0051	7.4 ± 1.2	0.02
	Ce-O-P	8.2 ± 2.3	3.24 ± 0.02	0.0029 ± 0.0019		
7 wt.% Ce/Na-ZSM-5	Ce-O	3.7 ± 0.9	2.18 ± 0.03	0.0086 ± 0.0063	-4.9 ± 4.9	0.02
	Ce-Si	6.1 ± 1.5	2.75 ± 0.03	0.0098 ± 0.0062		

<sup>a</sup>CN, coordination number; <sup>b</sup>R, distance between absorber and backscatter atoms; <sup>c</sup> $\sigma^2$ , Debye-Waller factor to account for both thermal and structural disorders; <sup>d</sup> $\Delta E_0$ , inner potential correction; R factor indicates the goodness of the fit.

## References

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