**Supplementary Information**

# Distribution of polychlorinated organic by-products during the hydrolysis oxidation of chlorinated volatile organic pollutants over Pd-Ni-based catalysts

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### 2.3 Catalytic performance evaluation

The gas stream from the reactor was passed through a six-way valve into an Agilent 6890 gas chromatograph, which was equipped with a DB-624 capillary column (30 m × 0.32 mm × 1.8 μm) and was used as an analytical tool for the determination of 1,2- DCB and organic by-products using an FID detector. During the detection process, the col-umn oven temperature was first held at 50 °C for 1 minute, then ramped up to 140 °C at a rate of 10 °C per minute, and finally maintained for 5 minutes. Method detection limits (MDLs) for representative chlorinated aromatic by-products including Benzene, Chlorobenzene, and Dichlorobenzene were determined in accordance with the U.S. EPA Method 40 CFR Part 136 (signal-to-noise ratio, S/N = 3). Under ambient temperature and pressure (25 °C, 101.325 kPa), the MDL ranges of the target analytes in gas-phase samples were determined to be $1.5\times10^{-2}$~$6.0\times10^{-2}$ ppm, $1.0\times10^{-2}$~$4.5\times10^{-2}$ ppm and $1.0\times10^{-2}$~$3.33\times10^{-2}$ ppm, respectively.

The concentrations of $CO_2$, CO, and HCl at the outlet were analyzed online using an FTIR spectrometer (MKS, MultiGas™2030). The generation of $Cl_2$ was measured by bubbling the outlet gas stream into 0.0125 M NaOH solution for 20 minutes. The con-centration of $Cl^-$ (produced from $Cl_2$) was determined using an ultraviolet-visible spec-trophotometer (Purkinje, TU-1810PC, China) with N,N-diethyl-p-phenylenediamine (DPD) as the indicator.

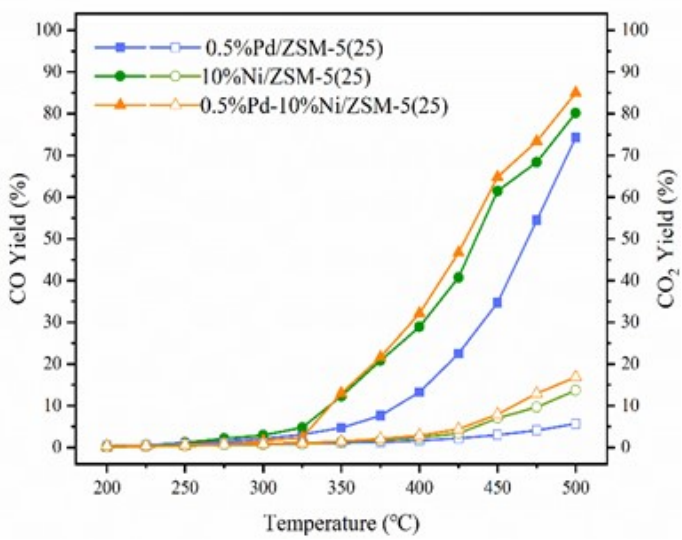


**Fig. S3.1** Variation of CO yield (left vertical axis) and $CO_2$ yield (right vertical axis) with temperature during hydrolysis oxidation of 1,2-DCB.

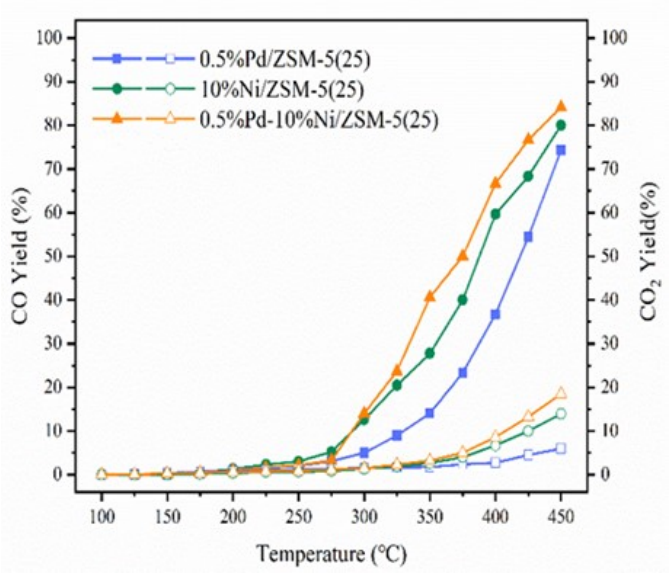

**Fig. S3.2** Variation of CO yield (left vertical axis) and $CO_2$ yield (right vertical axis) with temperature during hydrolysis oxidation of CB.

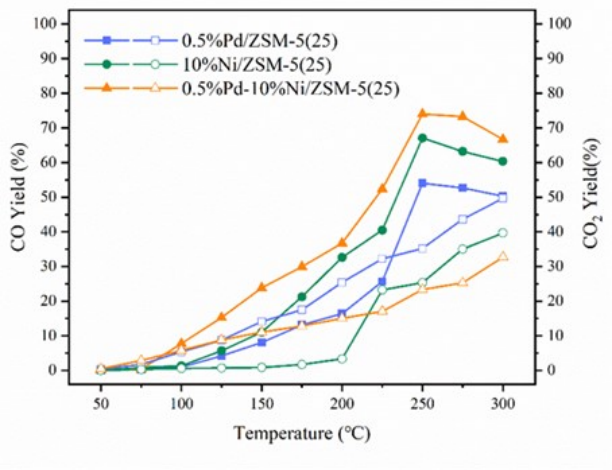


**Fig. S3.3** Variation of CO yield (left vertical axis) and $CO_2$ yield (right vertical axis) with temperature during hydrolysis oxidation of *o*-chlorophenol.