

Supporting Information

Efficient removal of tetracycline hydrochloride over Co-doped metal-organic framework MIL-125(Ti) derivate by Fenton-like catalysis

Yiqiong Yang, Caihong Fang, Heng Chen, Xingru Chen, Xueling Li and Longhui

Nie*

(School of Materials and Chemical Engineering, Hubei University of Technology,

Wuhan 430068, China)

* Author to whom any correspondence should be addressed. E-mail:

nielonghui@mail.hbut.edu.cn (L. Nie)

1. Experimental Section

1.1 Chemical reagents

Methanol (Macklin), DMF (Keshi), 1,4-benzenedicarboxylic acid (BDC, Macklin), isopropyl titanate (IV) (TTIP, Aladdin), cobalt chloride hexahydrate (Sinopharm) and tetracycline hydrochloride (Macklin) were analytically pure. All commercially reagents were used in the experiments directly without further treatment.

1.2 Characterization

Scanning electron microscopy (SEM, ZEISS GeminiSEM 300, Germany) was used to analyze the morphology and elemental distribution of the samples with working MIL-400. voltage of 1.0 kV. X-ray diffractometer (XRD, Empyrean, Netherlands) was used for phase analysis. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA, working conditions: scanning range: $2\theta = 5^\circ \sim 85^\circ$, voltage: 45 kV, current: 40 mA, $\lambda = 0.15406$ nm) was used to analyze the elemental compositions and valence states of the samples. BET analyzer (BET, BSD-660S A6, China) was used to determine the specific surface area and pore structure of the samples, and the samples were degassed at 200 °C for 2 h before testing. The functional groups of the samples were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, USA). The determination of total organic carbon (TOC) was carried out by a TOC-L analyzer (Shimadzu) by a combustion method. Before the TOC measurement, Na_2NO_2 was used to quench the remained PMS. Electron paramagnetic resonance (EPR, EMX10/12, Bruker, Germany) spectra were used to identify the reactive free radicals.

The electrochemical impedance spectroscopy (EIS) of Co-Ti and Co-Ti-400 samples was measured on an electrochemical workstation (PGSTAT204, Metrohm Autolab) with a three-electrode system using an open-circuit voltage of 0.8 V. The 0.1 M sodium sulfate aqueous solution was used as the electrolyte solution. The platinum electrode was used as the counter electrode, the saturated Ag/AgCl was used as the reference electrode, and the 100 μ L catalyst mixture solution (containing perfluorosulfonic acid DuPont membrane solution, ethanol, and catalyst) was coated on the FTO glass and dried at 60 $^{\circ}$ C to serve as the working electrode.

The intermediates formed in TCH oxidation were analyzed by LC-MS technique (Agilent 1100 high-pressure liquid chromatography equipped with TSQ Quantum Ultra AM of mass spectrometry, Thermofisher Scientific, USA). The HPLC separation was performed using a Welch ultimate XB-C18 analytical column (100 \times 2.1 mm, 3 μ m, Agilent Technologies) in 90% mobile phase A (0.1% formic acid in water) + 10% mobile phase B (acetonitrile) with 0.3 mL min^{-1} of flow rate. The injection quantity was 4 μ L, and the column temperature was maintained at 23 $^{\circ}$ C. The working conditions for MS were set as follows: ion source: HESI II, spray voltage: 3.0 kV, heater temperature: 450 $^{\circ}$ C, capillary temperature: 350 $^{\circ}$ C.

1.3 Reusing performance of Co-Ti-400

The used catalyst Co-Ti-400 was regenerated by absolute ethyl alcohol and DI water three times to evaluate its reusability, respectively. The generated sample was reused four times under the same experimental conditions ($t = 30^{\circ}\text{C}$, $\text{pH} = 4$, $C_0(\text{TCH})$

= 70 mg.L⁻¹).

2. Results

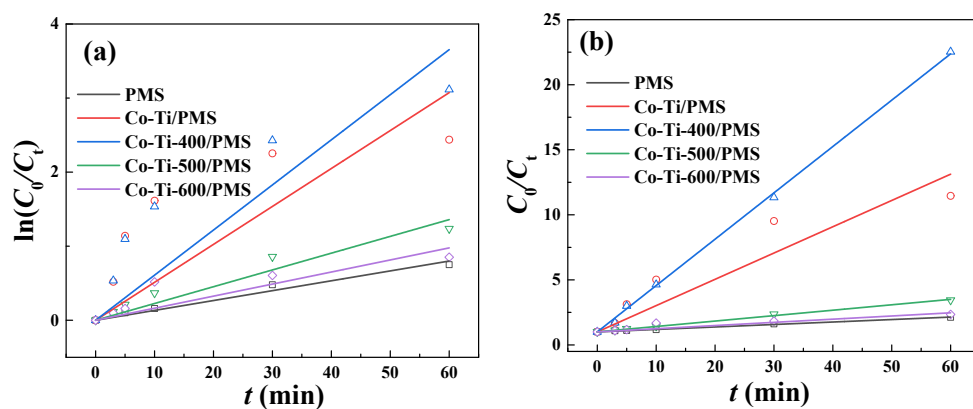


Fig. S1 Pseudo-first-order kinetics (a) and pseudo-second-order kinetics (b) for TCH degradation in the different systems.

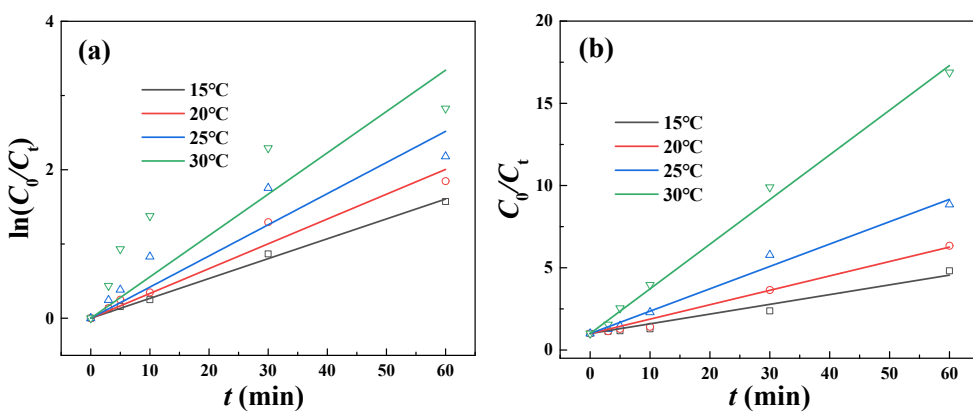


Fig. S2 Pseudo-first-order kinetics (a) and pseudo-second-order kinetics (b) for TCH degradation over Co-Ti-400 at different temperature.

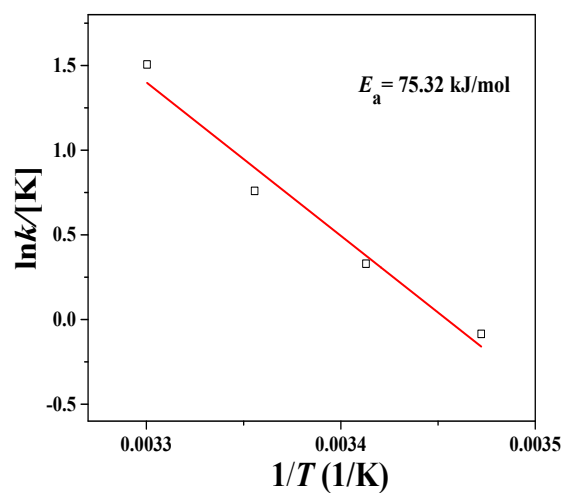


Fig. S3 the Arrhenius plot for activation energy on the catalytic activity of the Co-Ti-400 sample

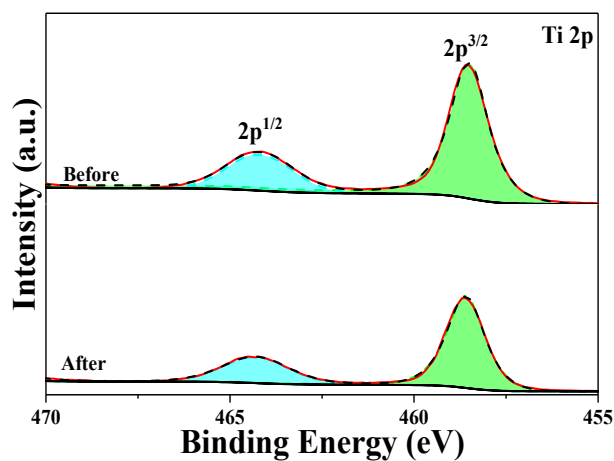


Fig. S4. High-resolution XPS spectra of Ti 2p for Co-Ti-400 before and after reaction.

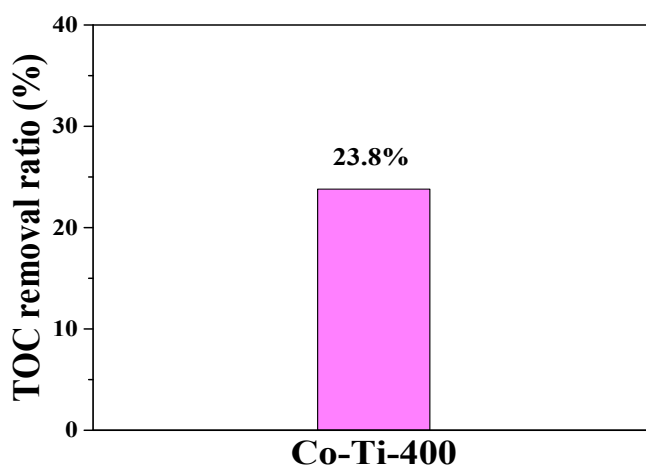


Fig. S5. TOC removal in the presence of Co-Ti-400/PMS.

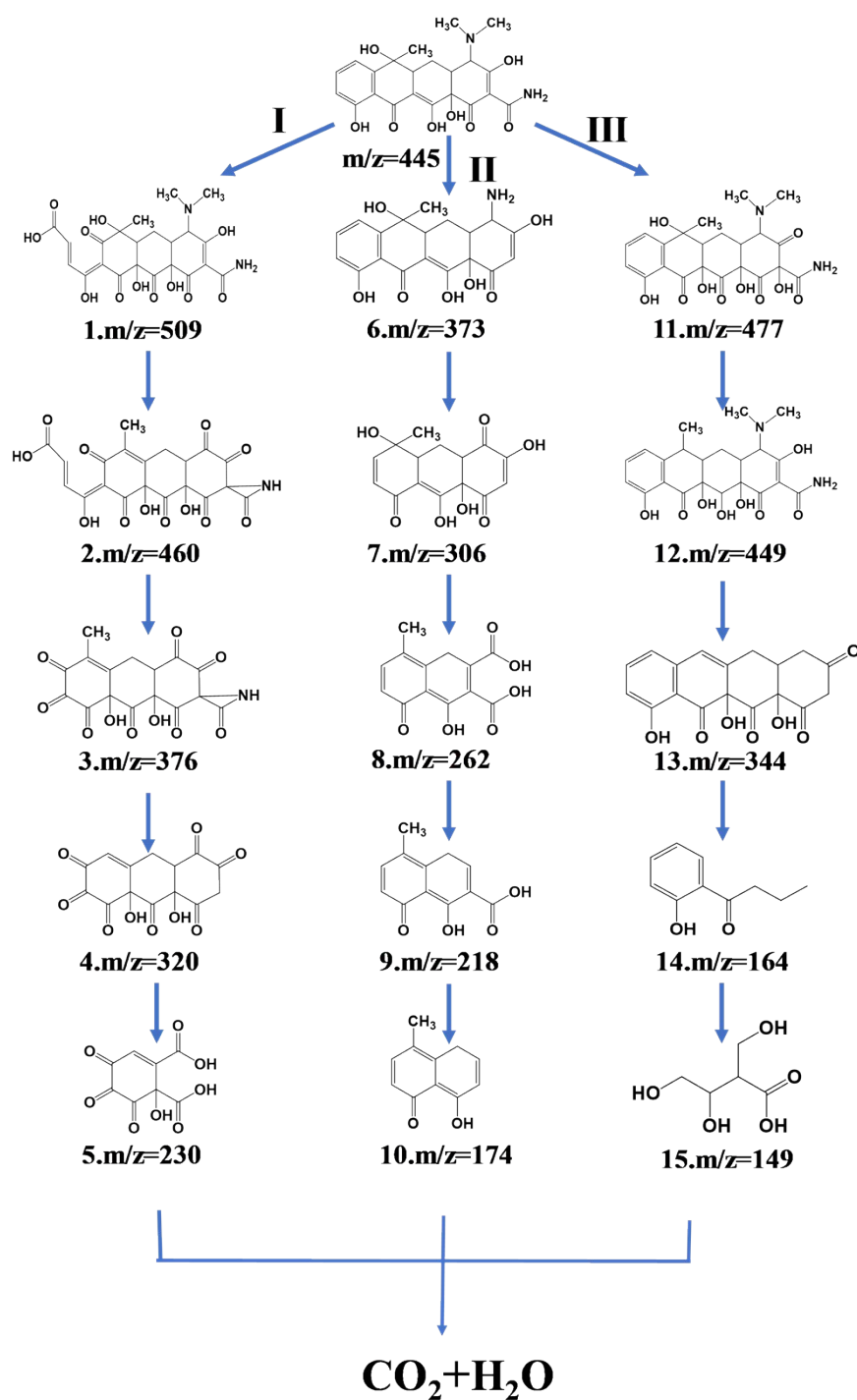


Fig. S6. The proposed catalytic degradation mechanism of TCH over Co-Ti-400.

Table S1 Kinetics parameters from the pseudo-first-order and pseudo-second-order kinetics models for different samples

Sample	Pseudo-first-order kinetics	Pseudo-second-order kinetics
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	k_1 (min^{-1})	R^2	k_2 ($\text{L}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	R^2
PMS	0.013	0.9847	0.27	0.9997
Co-Ti	0.051	0.7996	3.33	0.9460
Co-Ti-400	0.061	0.8838	5.90	0.9995
Co-Ti-500	0.023	0.9678	0.62	0.9993
Co-Ti-600	0.0163	0.8825	0.3707	0.9858

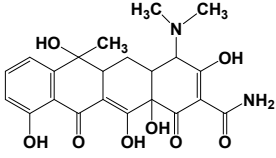
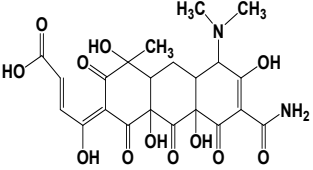
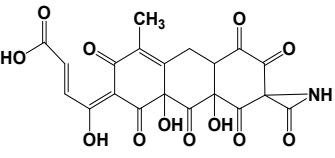
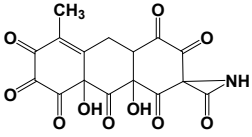
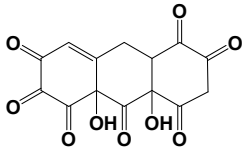
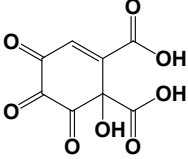
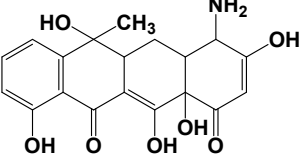
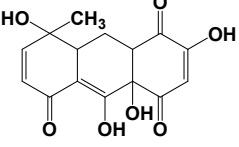
Table S2 Kinetics parameters from the pseudo-first-order and pseudo-second-order kinetics models for Co-Ti-400 at different temperatures

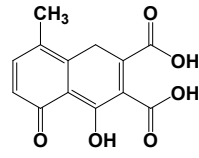
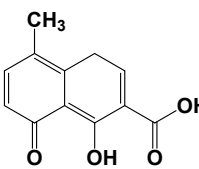
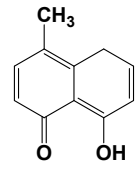
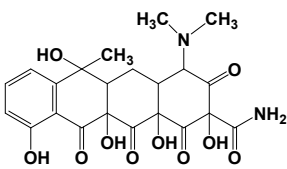
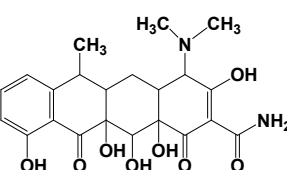
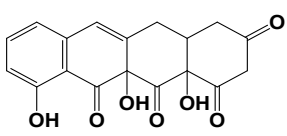
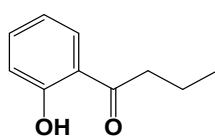
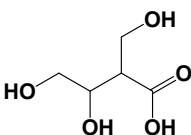
t ($^{\circ}\text{C}$)	Pseudo-first-order kinetics		Pseudo second-order kinetics	
	k_1 (min^{-1})	R^2	k_2 ($\text{L}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	R^2
15	0.027	0.9975	0.92	0.9901
20	0.033	0.9775	1.39	0.9957
25	0.041	0.9344	2.14	0.9946
30	0.056	0.8873	4.51	0.9978

Table S3. The contents of oxygen species of O 1s in Co-Ti [1] and Co-Ti-400.

element	Oxygen species	Co-Ti	Co-Ti-400
O 1s	O_{latt} (%)	14.5	40.7
	O_{surf} (%)	9.4	5.1
	H_2O (%)	10.7	4.4

Table S4. Possible degradation intermediates identified by LC-MS

Compounds	<i>m/z</i>	Proposed structure
TC	445	
1	509	
2	460	
3	376	
4	320	
5	230	
6	373	
7	306	
8	262	

		
9	218	
10	174	
11	477	
12	449	
13	344	
14	164	
15	149	

Reference

- [1] L.H. Nie, Y.Q. Yang, C.H. Fang, H. Chen, S.T. Xin, Co-doped metal-organic framework MIL-125(Ti) derivate for efficient adsorption of tetracycline hydrochloride from water, *Appl. Surf. Sci.* 640 (2023) 158390.

