

In situ pyrolysis of Mn-doped MOF-74 metal-organic framework derived MCNO_x catalysts for enhanced low-temperature catalytic performance of toluene

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Experimental Setup

The experimental system for toluene degradation by plasma synergistic catalysis consists mostly of the following components:

(1) Gas distribution system: The gas distribution system supplies the reaction gas for the experiment. The injection pump injects liquid toluene into a three-port flask, which is positioned in an 85 °C constant temperature water bath. The dry air exiting the cylinder enters the three-port flask and combines with the volatile toluene vapor to generate a toluene gas stream (toluene gas concentration is about 200 ppm). The toluene concentration is determined by the speed of the injection pump and the gas flow.

(2) Corona discharge plasma reaction system: plasma discharge is achieved using a self-made high-voltage DC power source with a discharge voltage range of 0-50 kV and a current range of 0-5 mA. The plasma reactor is a self-constructed concentric tube construction. The outer electrode is a 39 mm diameter stainless steel round tube with a length of 120mm, while the inner electrode is a 2 mm diameter stainless steel round rod with the same length. The outer electrode's surface is a sealed clear quartz tube, having air inlets and outlets at each end.

(3) Catalyst Performance Evaluation System: The catalytic reaction system's main components are the resistance heating furnace, the temperature controller, and the quartz tube reactor. The catalyst's performance was investigated using a fixed bed

quartz reaction tube. To reduce the effect of heat dispersion and guarantee optimal gas-catalyst contact, the experiment blended 1g of powder catalyst with quartz sand in a 1:3 ratio, which was then packed inside a quartz tube measuring 7mm in inner diameter. The catalyst region was then secured with quartz cotton, and the filled quartz tube was placed in a resistance furnace for heating, with the test temperature accurately regulated by a temperature controller.

(4) Tail gas detection system: The concentration of toluene in the effluent gas is detected by gas chromatography equipped with hydrogen flame ionization detector (FID). A gas chromatography equipped with a (TCD) thermal conductivity detector and a methane reforming furnace was used to detect the CO₂ concentration in the effluent gas. In order to ensure the catalytic reaction to reach a stable state, samples were measured after staying for 30min under various reaction conditions.

Catalyst preparation

The specific synthesis of CoNi-MOF-74 method is as follows: initially, 2,5-dihydroxy terephthalic acid is dissolved into a 75 mL solution of DMF, ethanol, and H₂O at a ratio of 1:1:1. Subsequently, precise quantities of Co (NO₃)₂·6H₂O and Ni (NO₃)₂·6H₂O are added to this solution, and the mixture is sonicated for 30 minutes until the solid components are completely solubilized. The resulting solution is then transferred to a 100mL reaction kettle, and the reaction proceeds at 110 °C for 24h. Upon the cooling of the reaction kettle to room temperature, the solution is centrifuged to isolate the solid components, washed thrice with ethanol and deionized water, and subsequently dried in a vacuum at 90 °C. The synthesized CoNi-MOF-74 precursor was calcined in a muffle furnace at 350 °C for 3 h in N₂ gas atmosphere at a ramp rate of 5 °C/min, after which the sample undergoes carbonization to form the CoNi-MOF-74 metal oxide catalyst. For comparison, pure nickel cobalt oxide, denoted as CoNiOx, was prepared by a similar calcination process using Co (NO₃)₂·6H₂O and Ni (NO₃)₂·6H₂O as precursors.

Specific surface area and pore size distribution analysis

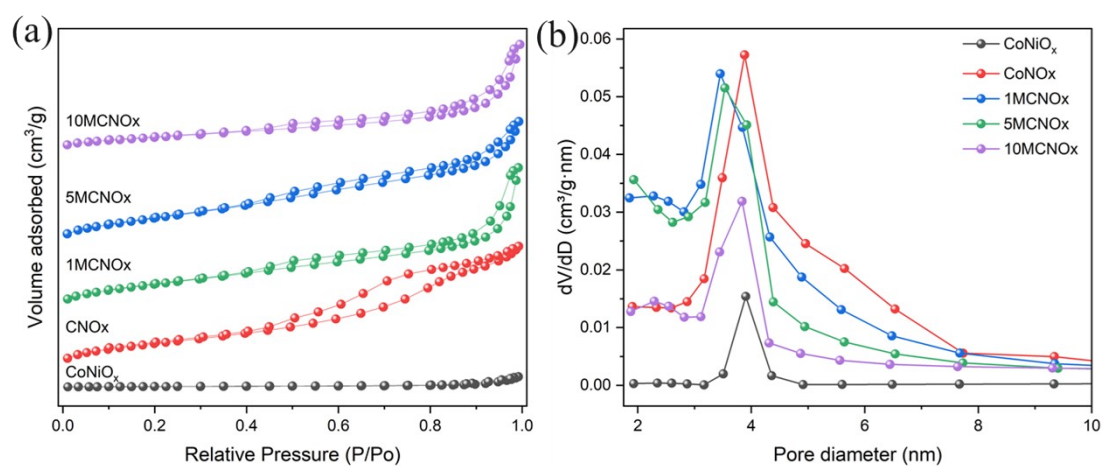


Fig.S1 Sample nitrogen adsorption-desorption isotherm (a) and pore size distribution (b)

Table S1 BET surface area, total pore volume and pore diameter of the sample

Catalyst	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{total}}/(\text{cm}^3 \cdot \text{g}^{-1})$	Pore Diameter $D_v(d)/(\text{cm}^3 \cdot \text{g}^{-1})$
CoNiOx	17	0.0151	4.6788
CoNi-MOF	161	0.2337	5.4507
1%MnCoNi-MOF	161	0.2309	5.1746
5%MnCoNi-MOF	161	0.2615	6.4629
10%MnCoNi-MOF	81	0.1905	8.2363

Raman spectrum analysis

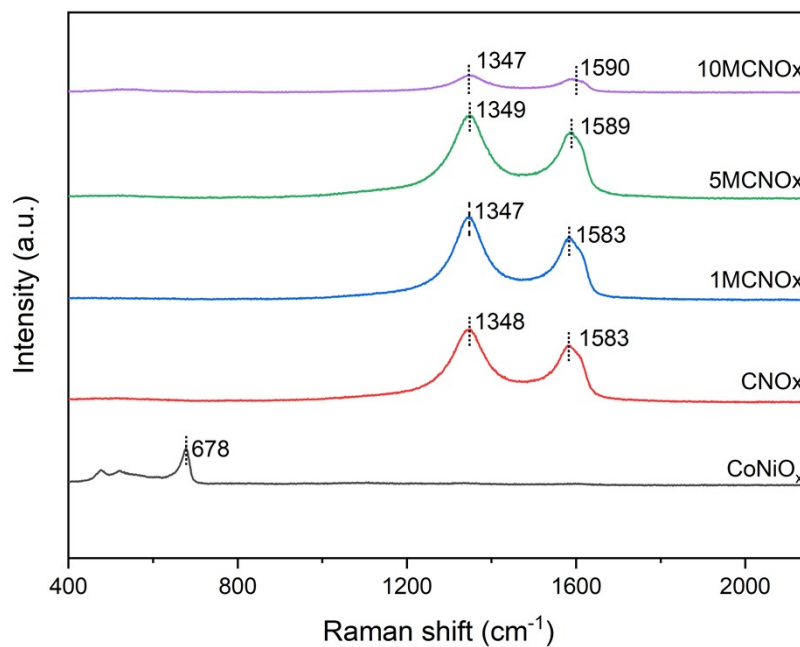


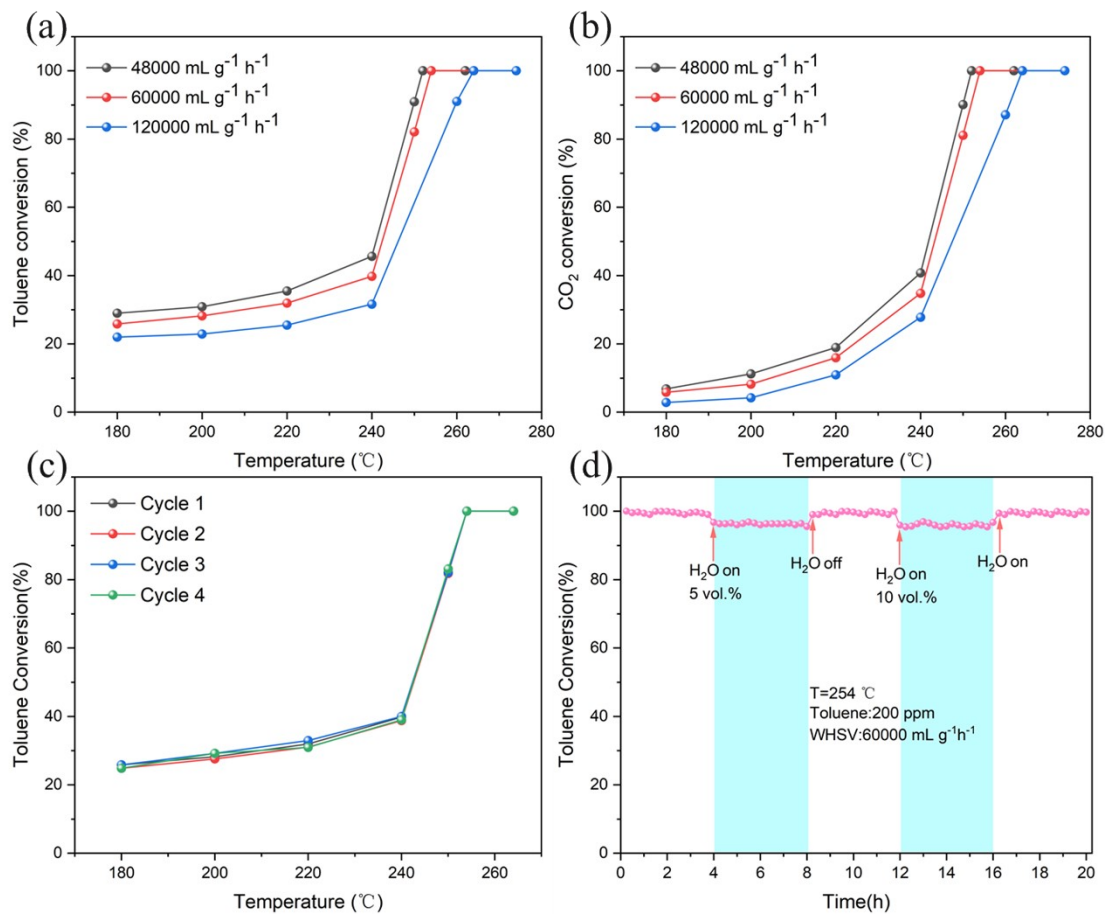
Fig.S2 Catalyst sample Raman mapping

Evaluation of catalytic activity

Table.S2 Reaction temperature functions of toluene over the five catalysts

Catalyst	Thermal catalysis technique (T/°C)		Plasma catalysis technology (T/°C)	cooperative
	T50	T90	T50	T90
CoNiOx	309	323	285	300
CoNi-MOF	290	305	267	283
1%MnCoNi-MOF	268	282	246	262
5%MnCoNi-MOF	263	271	242	251
10%MnCoNi-MOF	269	283	247	264

prepared



Toluene catalytic oxidizer investigation

Fig.S3 5MCNO_x catalysts at different SVs for (a) toluene degradation efficiency, (b) and CO₂ conversion, (c) reusability, and (d) stability