Supporting information

Fabrication of multi-dimensional $CoFeO_x$ catalyst with enhanced o-dichlorobenzene catalytic oxidation performan

Shixing Wu[a, b], Haijun Zhao[b,c], Zhicheng Tang[b,c*], Jiyi Zhang[a*]

([a] School of Petroleum and Chemical, Lanzhou University of Technology, Lanzhou 730050, China.

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, and National Engineering Research Center for Fine Petrochemical Intermediates, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China.

c. Yantai Zhongke Research Institute of Advanced Materials and Green Chemical Engineering, Shandong Laboratory of Yantai Advanced Materials and Green Manufacturing, Yantai, 264006, China.)

*Corresponding author.

E-mail address: tangzhicheng@licp.cas.cn (Z. Tang), zhangjiyi@lut.edu.cn (J. Zhang).

Experimental section

Catalyst characterizations

BET-related data were obtained by using an ASAP 2010 specific surface area analyzer at -196 ^{o}C. The crystalline phase analysis of the catalysts was performed on a Rigaku D/max-rb diffractometer using a CuK electrode (0.154 nm) with an instrument scan speed of 0.5^{o}/min and a scan angle range of 10^{o} to 90^{o}. Raman spectra were scanned in the range of 100 cm^{-1} to 900 cm^{-1}. Scanning electron microscope (SEM) images of three samples were obtained by a JSM-6701F cold field emission scanning electron microscope. The microstructure of the catalysts was observed by emission transmission electron microscopy (TEM). Infrared spectra were tested with a Nicolet Nexus 870 Fourier transform infrared spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed with a VGESCALAB 210, using Mg Kα as the X-ray source, and the binding energy of the catalyst was corrected by C1s (284.6 eV) energy pairs. The H_2-TPR test was performed on a fully automated multifunctional adsorption device (DAS-7000) with 0.03 g of catalyst in a quartz tube reactor. Pretreatment in N_2 atmosphere at 300 ^{o}C for 60 min. Then, the H_2/N_2 atmosphere (40 mL/min) was ramped up from 50 to 900 ^{o}C (10 ^{o}C/min). In the O_2-TPD test, 0.15 g of catalyst was placed in a quartz tube reactor and pretreated at 300 ^{o}C under N_2 atmosphere for 1 h, followed by adsorption under N_2/O_2 atmosphere for 45 min, followed by purging under He atmosphere for 10 min (40 mL/min), and then heated at 40 to 900 ^{o}C at a rate of 10 ^{o}C/min. For the NH_3-TPD test, the difference from the O_2-TPD test is the pretreatment under N_2 atmosphere followed by adsorption under NH_3

atmosphere for 45 min and a final purge with N_2 for 10 min, followed by a purge with nitrogen at 40 mL/min for 10 min and heating from 40 to 900 °C at a rate of 10 °C/min.

Catalytic activity measurements

The catalyst was pressed and sieved (40-60 mesh). First, 0.4 g of catalyst and 0.4 g quartz sand were mixed and tested in a fixed bed continuous flow microreactor. The reactor introduces O_2/N_2 (5 vol %) through a heated chamber, stores a certain amount of o-DCB (99.9%), maintains it at 30 °C and mixes it with another containing O_2/N_2 (5 vol %) in a mixer at 180 °C to control the o-DCB gas time-space velocity (GHSV) and concentration. The gas stream passes through a catalytic unit and reacts with a reactor heated by an electric furnace. The reacted gas was analyzed on a chromatograph (Agilent GC-6820) equipped with TCD and FID. The device was allowed to stabilize in operation for at least 30 min before testing. The conversion efficiency of o-DCB was calculated by the following equation:

$$x = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

Where x is the conversion of o-DCB, C_{in} and C_{out} are the inlet and outlet concentrations of o-DCB in the gas phase.

Fig. S1 XPS spectra of 2D/1D CoO_x/$CoFeO_x$ (a), 2D $CoFeO_x$ (b), 2D/1D $CoFeO_x$/CoO_x (c) and u-2D/1D $CoFeO_x$/CoO_x (d) catalysts.

Fig. S2 XPS spectra of the Co 2p (a), O 1s (b), Fe 2p (c) and Cl 2p (d) on u-2D/1D $CoFeO_x$/CoO_x catalyst.

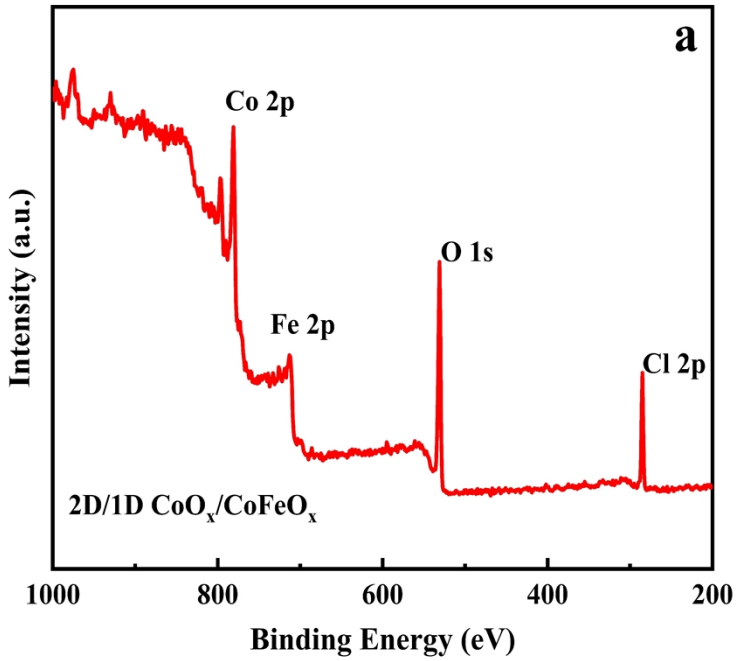
Fig. S3 O_2-TPD profiles of the 2D/1D CoO_x/$CoFeO_x$, 2D $CoFeO_x$ and 2D/1D $CoFeO_x$/CoO_x.

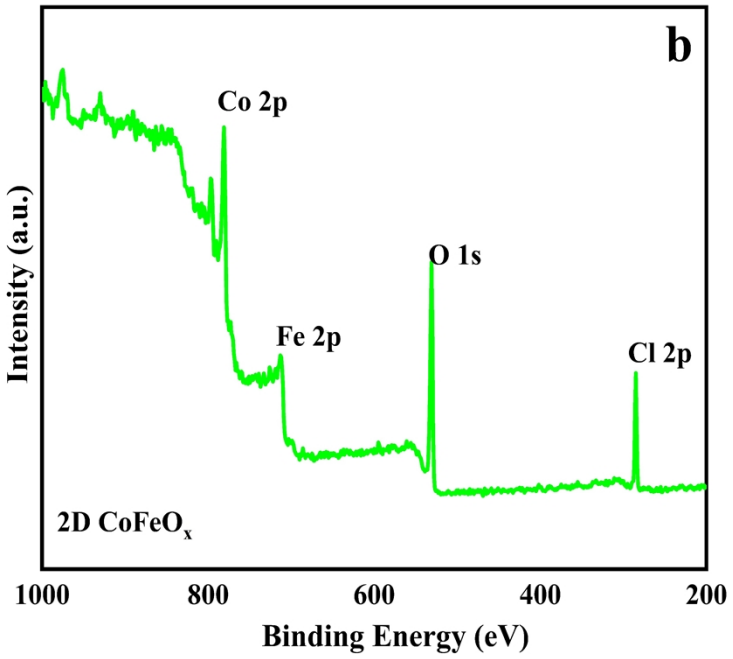
Fig. S4 Selectivity of CO_2 and HCl on 2D/1D $CoFeO_x$/CoO_x catalyst.

Fig. S5 Arrhenius curves of the 2D/1D CoO_x/$CoFeO_x$, 2D $CoFeO_x$ and 2D/1D $CoFeO_x$/CoO_x.

Fig. S6 The relations of r and TOF versus O_{sur} catalyst.

Table S1 Reaction activity dynamic parameters of o-DCB elimination on $CoFeO_x$ catalysts.


a
Co 2p
O 1s
Fe 2p
Cl 2p
Intensity (a.u.)
2D/1D CoO$_x$/CoFeO$_x$
1000
800
600
400
200
Binding Energy (eV)


b
Co 2p
O 1s
Fe 2p
Cl 2p
Intensity (a.u.)
2D CoFeO$_x$
1000
800
600
400
200
Binding Energy (eV)

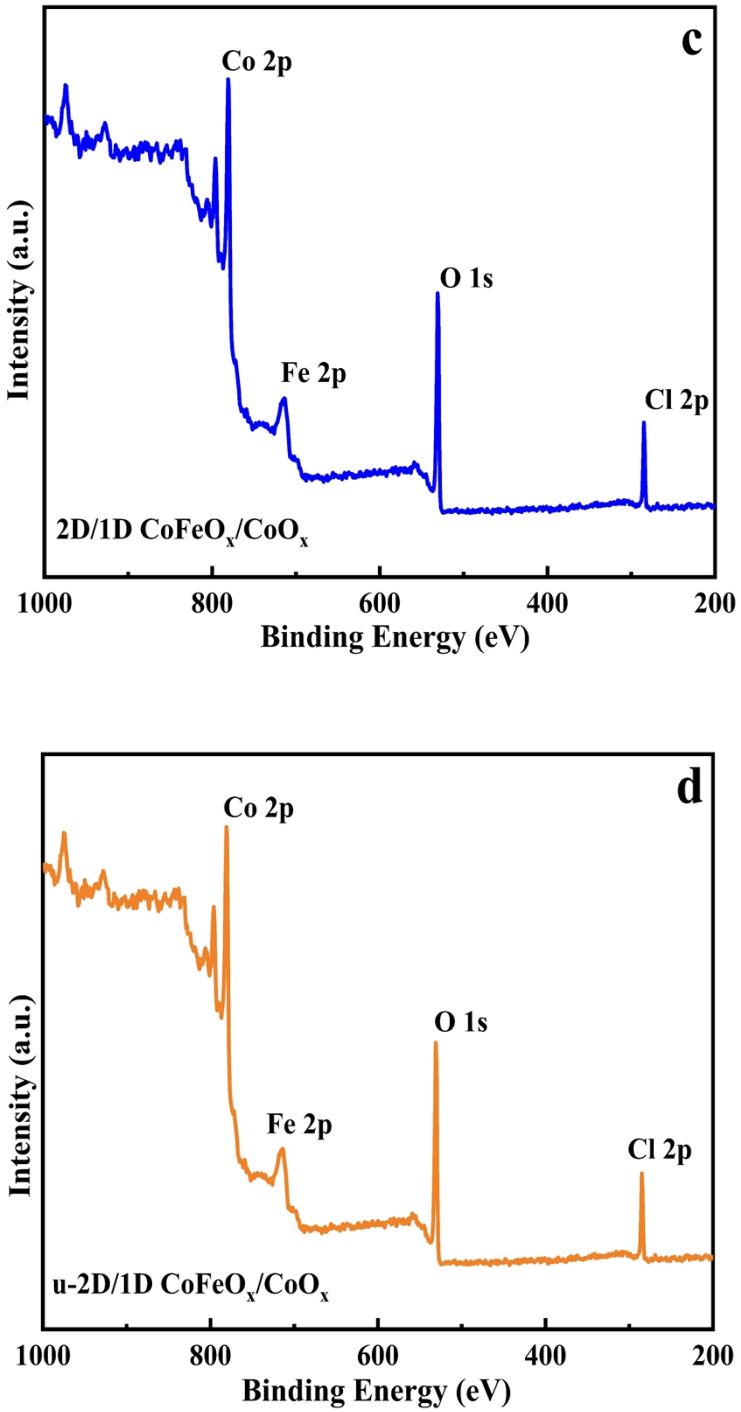


Fig. S1 XPS spectra of 2D/1D CoO_x/$CoFeO_x$ (a), 2D $CoFeO_x$ (b), 2D/1D $CoFeO_x$/CoO_x (c) and u-2D/1D $CoFeO_x$/CoO_x (d) catalysts.

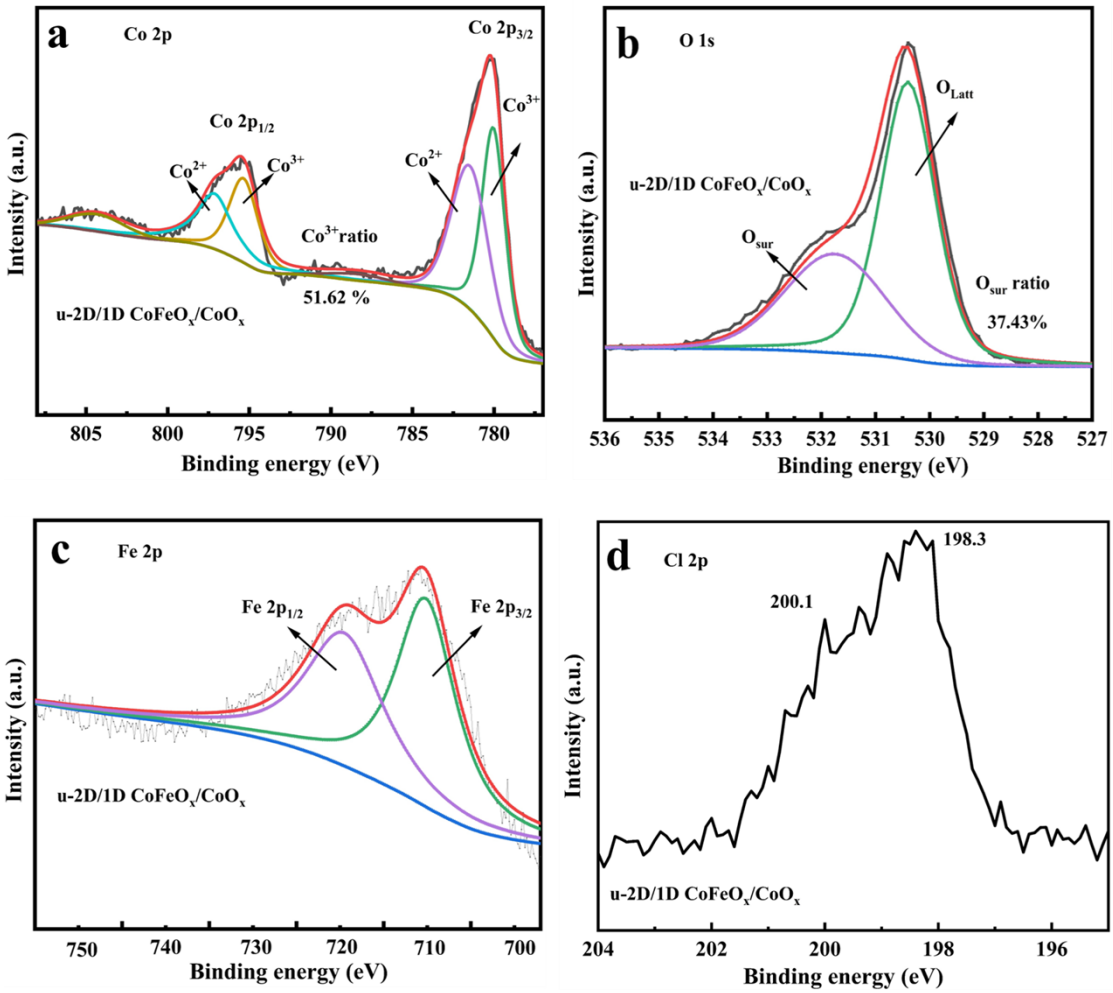


Fig. S2 XPS spectra of the Co 2p (a), O 1s (b), Fe 2p (c) and Cl 2p (d) on u-2D/1D $CoFeO_x/CoO_x$ catalyst.

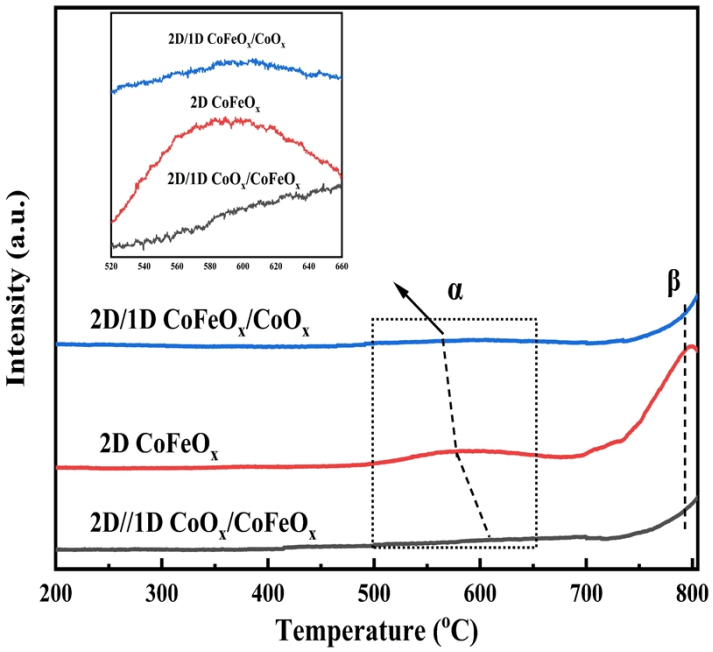


Fig. S3 O_2-TPD profiles of the 2D/1D $CoO_x/CoFeO_x$, 2D $CoFeO_x$ and 2D/1D $CoFeO_x/CoO_x$.

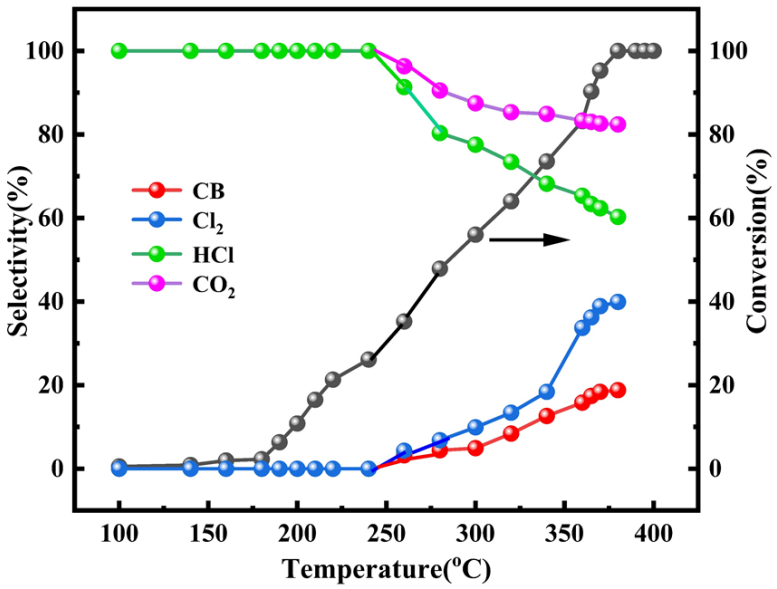


Fig. S4 Selectivity of CO_2 and HCl on 2D/1D $CoFeO_x/CoO_x$ catalyst.

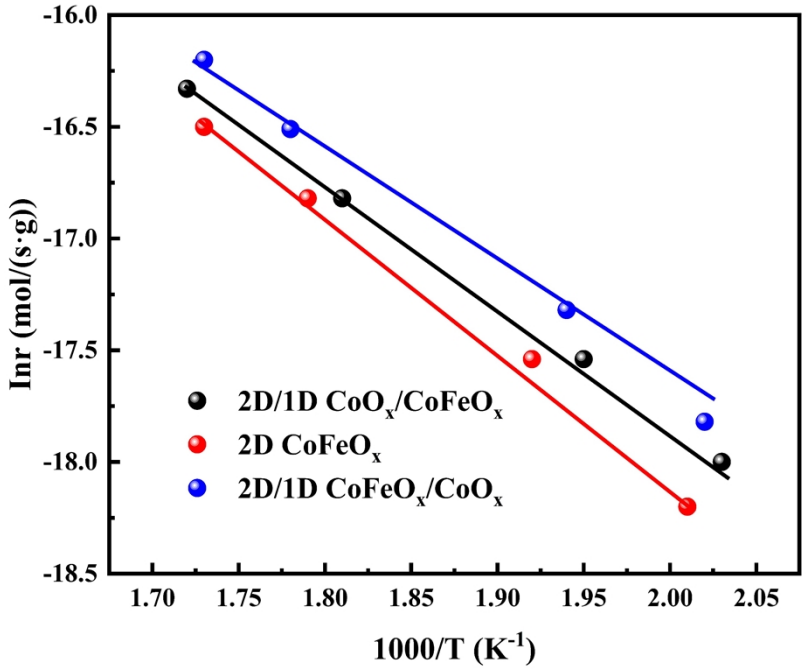


Fig. S5 Arrhenius curves of the 2D/1D $CoO_x/CoFeO_x$, 2D $CoFeO_x$ and 2D/1D $CoFeO_x/CoO_x$.

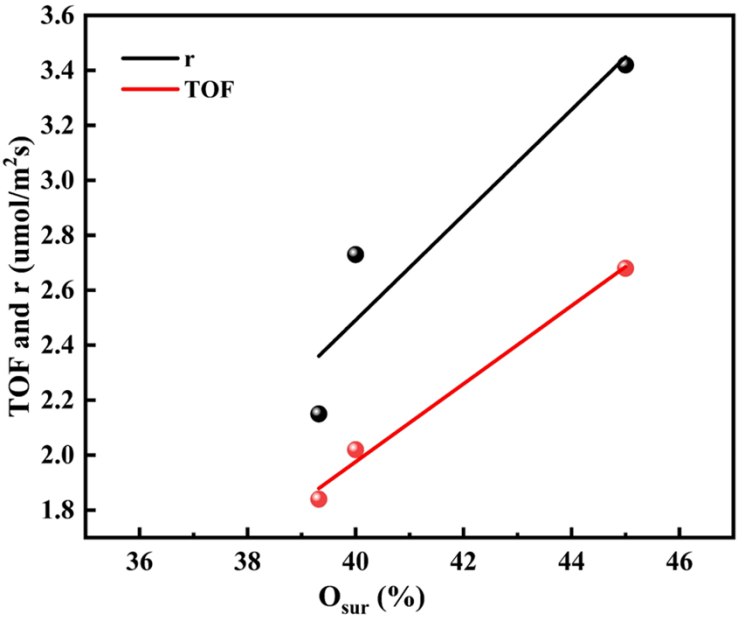


Fig. S6 The relations of r and TOF versus O_{sur} catalyst.

Table S1 Reaction activity dynamic parameters of o-DCB elimination on $CoFeO_x$ catalysts.

Catalysts	E_a (kJ/mol)	r (umol/m^2s)	TOF_{Co} (umol/m^2s)
2D/1D CoO_x/$CoFeO_x$	44.78	2.73	2.02
2D $CoFeO_x$	50.96	2.15	1.84
2D/1D $CoFeO_x$/CoO_x	40.08	3.42	2.68