Supplementary Information

A novel method of shortening the pathway between surface reactive oxygen species and organic receptors under surface lattice metal atom substitution over HZSM-5SM-5 for intensifying catalytic oxidation CH_2Cl_2

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(1) Chemicals

$Cu(NO_3)_2\cdot 3H_2O$ (99.99 wt.%), $Co(NO_3)_2\cdot 6H_2O$ (99.99 wt.%), $KMnO_4$ (99.5 wt.%), $K_2Cr_2O_7$(99.5 wt.%) were obtained from Sigma-Aldrich (America). Tetrapropylammonium hydroxide (TPAOH, 25 wt.%) was provided by Weng Jiang Chemical Testing Co., Ltd (Guangzhou ,China). NaOH (≥96 wt.%), $Mn(NO_3)_2$ (50 wt. %) were provided by Zhanyun Chemical Co., Ltd (Shanghai ,China).

(2) Catalyst characterization

The amounts of metal atoms were obtained by ICP-OES using a Agilent ICPOES730 analyzer.

X-ray powder diffraction (XRD) patterns were obtained from a D8 ADVANCE powder X-ray diffractometer system (BRUKER, Germany) with nickel-filtered Cu-Ka radiation (40 kV and 40 mA).

The surface morphology of the prepared catalyst was observed by scanning electron microscopy (SEM) using a HITACHI SU8020 microscope (HITACHI, Japan) and the elemental composition was obtained by Energy Dispersive Spectrometer (EDS) mapping.

Transmission electron microscopic (TEM) were conducted using a JEM 1200EX electron microscope (JEOL, Japan) operating at 120 kV.

N_2 physical adsorption–desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2460 analyzer (Micromeritics, USA). The total surface area was estimated from the BET method. The external surface area, micropre surface area and micropore volume were estimated by the t-plot method. The mesopore volume was obtained by the total pore volume minus the micropore volume. The total volume was derived at P/Po = 0.99.

The ^{29}Si MAS-NMR spectra of the powdered samples were recorded at room temperature on a Bru-ker AVANCEIIIHD 500MHZSM-5 NMR spectrometer. The spectrometer frequency was 130.33 MHZSM-5, and aluminium chloride was used as an external reference material

Ultraviolet visible diffuse reflectance (DRS UV-Vis) spectra were recorded by a HIMadZU-1601PC spectrometer, with a scanning range of 200-800 nm and a barium sulfate support.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded by a Nicolet IS10 spectrometer with the resolution of 4cm^{-1} in the range of 400-4000 cm^{-1}.

The Pyridine-IR (Py-IR) signals were collected through a Thermo Nicolet 380 analyzer in the range of 400-4000 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) analyses were provided by a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer (Micromeritics, USA) with Al Kα radiation as an exciting X-ray source.

The amount and strength of the acid sites on the catalyst surface were obtained by temperature-programmed desorption (TPD) of ammonia on a Micromeritics Auto Chem II 2920 analyser (Micromeritics, USA), and the temperature ranged from 100 °C to 700 °C at a heating rate of 10 °C/min under a N_2 atmosphere. The desorbed ammonia gas was monitored on-line by thermal conductivity (TCD). Moreover, the desorption curve of ammonia gas was plotted. The desorption peaks at the temperature range of 100-200 °C, 200-300 °Cand 300-500 °C corresponded to the desorption of NH_3 from weak acid sites, medium strong acid sites and strong acid sites, respectively.

Temperature-programmed reduction of hydrogen (H_2-TPR) and temperature-programmed desorption of oxygen (O_2-TPD) were performed on a Micromeritics Auto Chem II 2920 analyser instrument (Micromeritics, USA) equipped with a TCD detector. Before the experiments, the catalysts for H_2-TPR were heated at 200 °C for 2 h, and the catalysts for O_2-TPD were heated at 300 °C for 2 h in N_2 atmosphere; after that, they were all cooled to 50 °C with N_2 (30 ml/min). Additionally, for H_2-TPR, the catalyst was reduced from 50 °C to 850 °C at a heating rate of 10 °C/min under 5% H_2/N_2 (30 ml/min). For O_2-TPD, the catalyst was treated with 5% O_2/N_2 (30 ml/min) for 30 min, and then purged by N_2 flow for 30 min to stabilize the baseline. Next, the catalyst is heated by programmed from 50 to 850 °C at a heating rate of 10 °C/min under N_2 flow (30 ml/min). During the O_2-TPD and H_2-TPR test, the water vapour produced was condensed in a cold trap filled with liquid nitrogen. The temperature was 77k.

Table S1

The aera percentages and ratios of Q^3 and Q^4 signal peaks of ^{29}Si MAS-NMR curves on the prepared samples.

Samples	Q^3(%)	Q^4(%)	Q^3/Q^4 ratio
Si-HZSM-5	3.29	96.71	0.034
Fe-HZSM-5	8.21	91.79	0.089
Co-HZSM-5	7.60	92.40	0.082
Cr-HZSM-5	4.58	95.42	0.048
Mn-HZSM-5	7.94	92.06	0.086
Cu-HZSM-5	4.94	95.06	0.052

Table S2

The catalytic activity of some catalysts for DCM.

Catalysts	Airspeed	T_{90}	References
HZSM-5	$15000h^{-1}$	350℃	[1]
9%Cr/HZSM-5	$15000h^{-1}$	330℃	[1]
1%Cr-O/HZSM-5	$15000h^{-1}$	330℃	[2]
Mn-Co@Z	$30000h^{-1}$	420℃	[3]
CeO_2-CrOx-S	$15000h^{-1}$	360℃	[4]
0.01 Pt/HZSM-5	$15000h^{-1}$	320℃	[5]
V_4/TiO_2	12000ml/g·h	>400℃	[6]
Mn_4/TiO_2	12000ml/g·h	>400℃	[6]
$Pd_{0.12}Mn_4/TiO_2$	12000ml/g·h	>400℃	[6]
HZSM-5	40000ml/g·h ($80000h^{-1}$)	(＞500℃)	This work
0.5%Cr-HZSM-5	40000ml/g·h ($80000h^{-1}$)	405℃	This work
0.5%Mn-HZSM-5	40000ml/g·h ($80000h^{-1}$)	360℃	This work

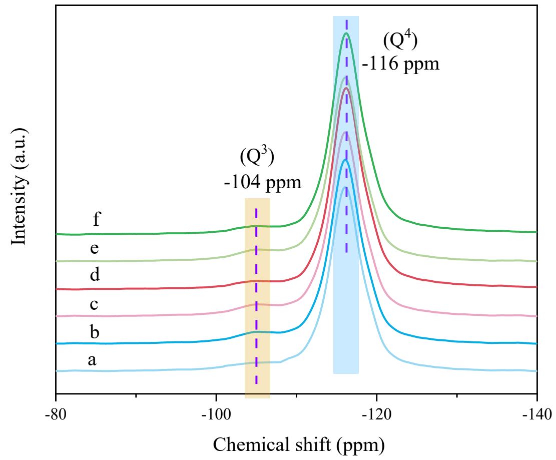

Fig. S1. The ^{29}Si MAS-NMR spectra of (a) Si-HZ, (b) Fe-HZ, (c) Co-HZ, (d) Cr-HZ, (e) Mn-HZ, (f) Cu-HZ.

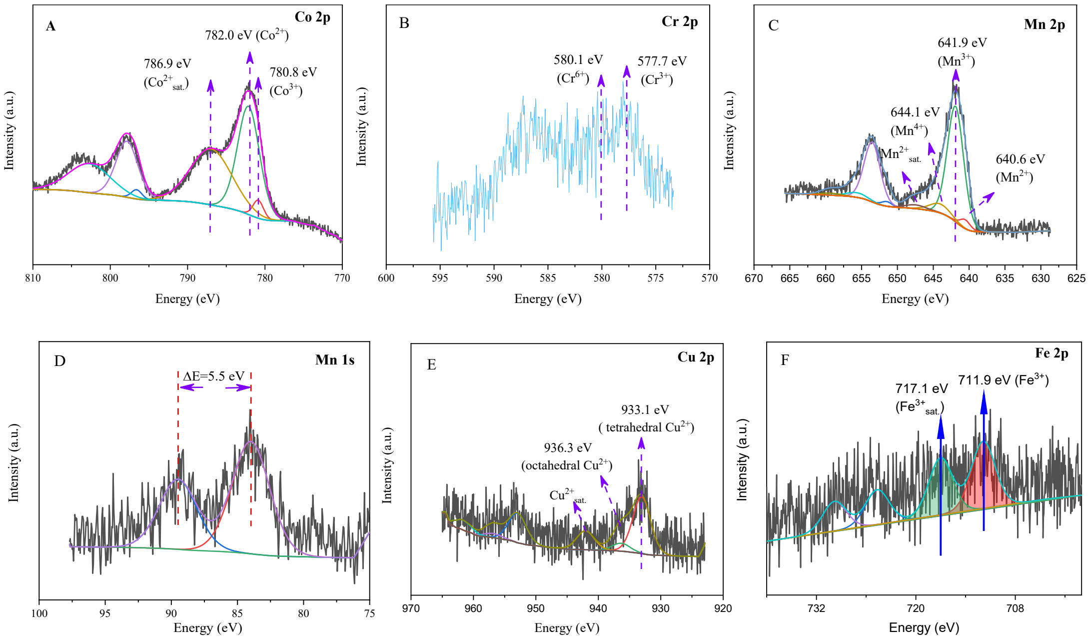

Fig. S2. XPS spectra of (A) Co 2p of Co-HZSM-5, (B) Cr 2p of Cr-HZSM-5, (C) Mn 1s of Mn-HZSM-5, (D) Mn 2p of Mn-HZSM-5, (E) Cu 2p of Cu-HZSM-5 and (F) Fe-HZSM-5.

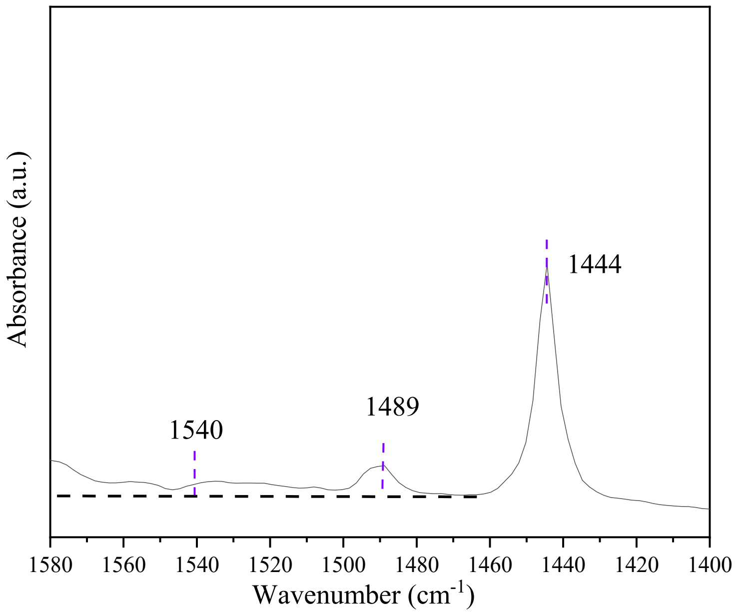

Fig. S3. Py-IR profiles of Si-HZSM-5.

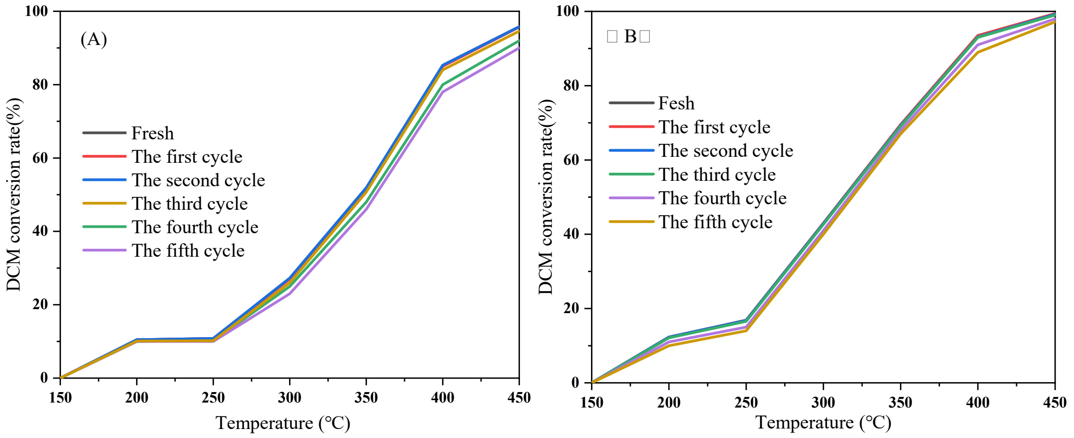

Fig. S4. The reuse catalytic performance of (A) Cr-HZSM-5and (B)Mn-HZSM-5.

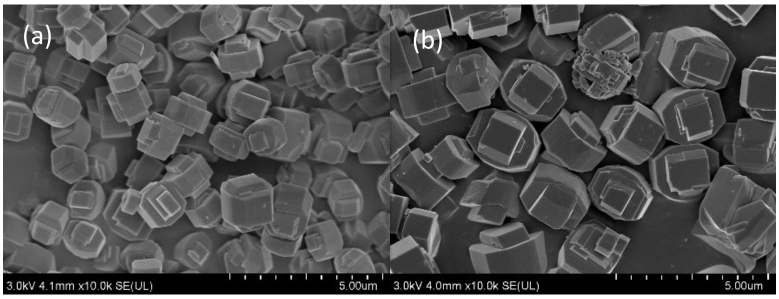

Fig. S5. The SEM of Cr-ZSM-5 (a)before and (b)after the reuse studies.

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