

**Co-Cr bimetallic oxide derived from layered double hydroxides with high
catalytic performance for chlorinated aromatics oxidation**

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Table S1 Comparison of rate and Ea with literatures

Catalyst	T ₉₀	Rate	Ea	Condition	Ref
	/ °C	/ μmol min ⁻¹ m ⁻²	kJ/mol		
Ce _{0.5} Ti _{0.5}	375	0.053 at 275 °C	95.7	1000 ppm DCB ^a , GHSV = 30000 mL g ⁻¹ h ⁻¹	1
3.6% V ₂ O ₅ /TiO ₂	360	0.084 at 275 °C		500 ppm DCB GHSV = 53000 mL g ⁻¹ h ⁻¹	2
Cr _{0.1} Ti _{0.9}	296	0.237 at 275 °C	66.0	1000 ppm DCB GHSV = 30000 mL g ⁻¹ h ⁻¹	3
		0.050 at 225 °C			
0.6Ru/Co ₃ O ₄	303	0.151 at 250 °C		1000 ppm DCB GHSV = 30000 mL g ⁻¹ h ⁻¹	4
Co ₉ Mn ₁	347	0.033 at 250 °C	88.3	1000 ppm DCB GHSV = 15000 mL g ⁻¹ h ⁻¹	5
FeMn ₂₀	400			50 ppm DCB, GHSV = 88,000 mL g ⁻¹ h ⁻¹	6
FeCa ₁₀	400		21.6	50 ppm DCB, GHSV = 88,000 mL g ⁻¹ h ⁻¹	7
Co ₃ Cr	288	0.170 at 250 °C	87.3	1000 ppm DCB GHSV = 60000 mL g ⁻¹ h ⁻¹	This work

^a 1, 2-dichlorobenzene

References

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Calculation of Rate

Rate at 250 °C based on the converted mole number of 1, 2-dichlorobenzene per minutes per square shown in Table 2 and S1. Reaction condition: feed, 100 mL min⁻¹; 1000 ppm 1, 2-dichlorobenzene, 10 vol. % O₂ and N₂ in balance; catalyst: 100 mg

For example

For Co₃O₄:

DCB conversion at 250 °C: 5.3%, S_{BET}: 30 m²/g

Rate = DCB concentration × feed × conversion / (22.4 × m_{cat} × S_{BET}) = 1000 × 100 × 10⁻³ × 5.3 × 10⁻² / (22.4 × 0.1 × 30) = 0.08 μmol·min⁻¹·m⁻²

Characterization of Co₃Cr mixed oxides synthesized by different methods and their performance for 1, 2-dichlorobenzene combustion:

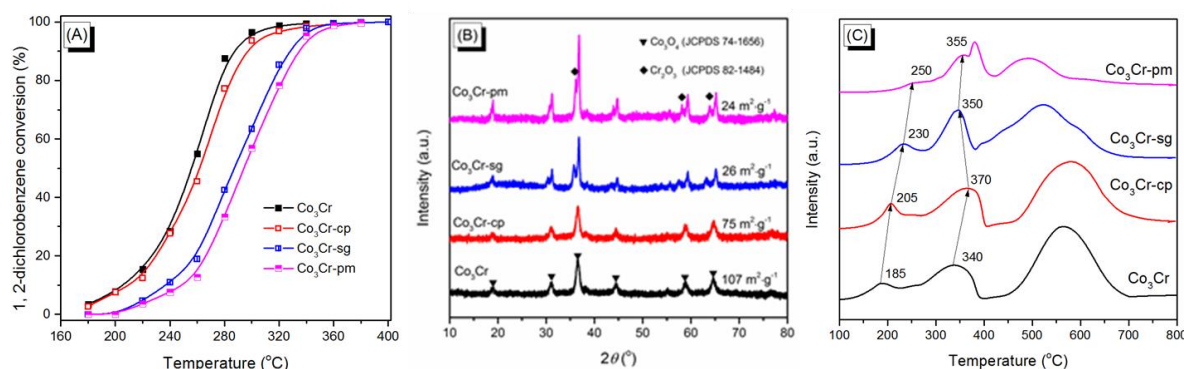


Fig. S1 The activity test for 1, 2-dichlorobenzene combustion (A), the XRD pattern (B) and the H₂-TPR profiles (C) of CoCr mixed oxides with Co/Cr=3 (mole) synthesized by different methods. Gas composition: 1000 ppm 1, 2-dichlorobenzene, 10 vol. % O₂ and N₂ balance; GHSV: 60,000 mL g⁻¹ · h⁻¹; catalyst amount: 100 mg.

Methods: The Co₃Cr was synthesized by a hydrotalcite derived methods as discribed in the present paper. The Co₃Cr-cp was synthesized by a co-precipitation method using ammonium hydroxide (NH₄OH) as the precipitator and the final pH was maintained at about 9.0. The Co₃Cr-sg was prepared from a sol-gel method using using citric acid as a chelating agent. The Co₃Cr-pm was just obtained from the calcination of their physical mixtures, before calcination, the metal nitrate precursors mixed through a grinding process with grinding duration of 5 min. All the prepared samples was calcinated at 400 °C for 4h with the same ramping rate of 2 °C per minute.

Results and Discussion: The activity test for combustion of 1, 2-dichlorobenzene with 1000 ppm in the flow gas under GHSV=60000 mL g⁻¹ · h⁻¹ illustrated that CoCr mixed oxides synthesized from different methods showed a high activity, of which, T₉₀ (temperature for 90% conversion) could be obtained before 400 °C, indicating that the CoCr mixed oxide itself was an active catalyst for 1, 2-dichlorobenzene combustion. However, the apparant activity of each catalyst was quite different, among them, the Co₃Cr showed a highest activity with T₉₀ of 288 °C, which was higher or comparable to Ru/Co₃O₄ with high efficient for 1, 2-dichlorobenzene abatement [Table S1, Ref. 4]. The different performance of each catalyst for 1, 2-dichlorobenzene combustion might be ascribed for the existence of metal oxides (Fig. 1S B , pure spinel phase for Co₃Cr and Co₃Cr-cp, coexistence of Co₃O₄ and Cr₂O₃ for Co₃Cr-sg and Co₃Cr-pm), different specific surface area (Fig. 1S B) and different redox properties (Fig. 1S C)

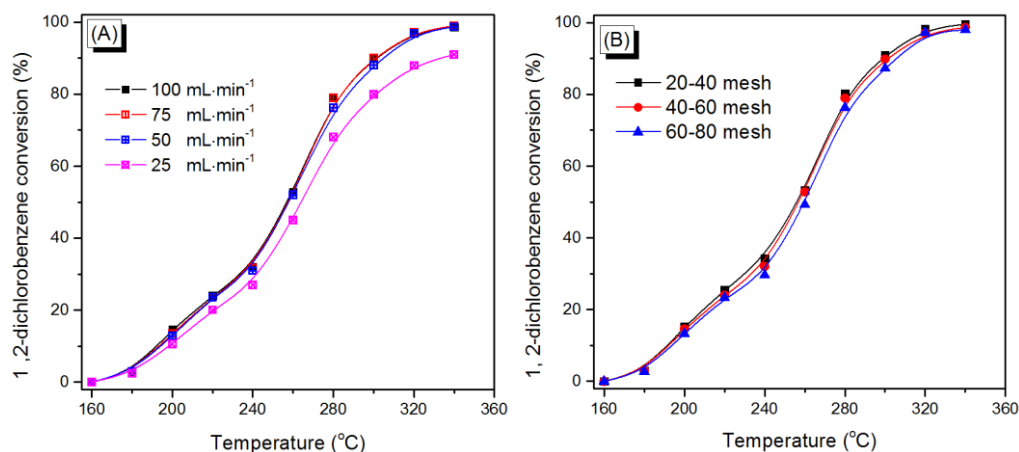


Fig. S2 Effect of gas flow on 1, 2-dichlorobenzene oxidation over Co_5Cr (A); gas composition: 10 vol. % O_2 and N_2 balance; 1, 2-dichlorobenzene liquid flow: $30 \mu\text{L h}^{-1}$; GHSV: $60,000 \text{ mL g}^{-1} \cdot \text{h}^{-1}$; gas flow: $25\text{-}100 \text{ mL min}^{-1}$. Effect of particle size of Co_5Cr catalyst on 1, 2-dichlorobenzene oxidation (B); gas composition: 1000 ppm 1, 2-dichlorobenzene, 10 vol. % O_2 and N_2 balance; GHSV: $60,000 \text{ mL g}^{-1} \text{ h}^{-1}$; catalyst amount: 100 mg.

Discussion: As shown in Fig. S2A, changing the gas flow rate from 50 mL min^{-1} to 100 mL min^{-1} , the conversion of 1, 2-dichlorobenzene was kept essentially the same, meaning that there was no external mass transfer resistance for 1, 2-dichlorobenzene oxidation. However, when the flow rate lower to 25 mL min^{-1} , indicating that the external mass transfer had a negative impact on 1, 2-dichlorobenzene oxidation, especially for the high temperature range. Similarly, changing the particle size from 20-80 mesh, the conversion of 1, 2-dichlorobenzene changed a little, meaning that the internal diffusion resistance could be eliminated. Totally, the given conditions for 1, 2-dichlorobenzene oxidation in the manuscript could effectively eliminate the internal diffusion and external mass transfer resistances.

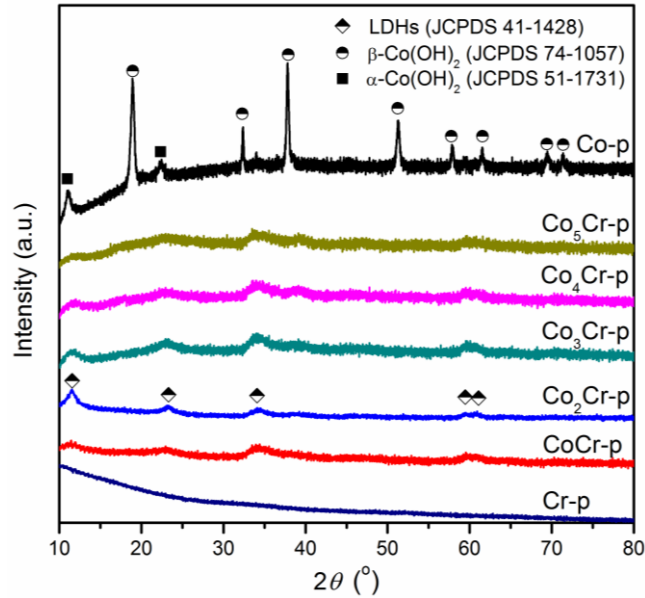


Fig. S3 XRD patterns of as-synthesized precursors

Discussion: The XRD patterns of synthesized precursors were shown in Fig. S3. The patterns presented some different characteristics with the variation of Co/Cr ratio. The Co-p showed the coexistence of α -Co(OH)₂ (JCPDS 51-1731) with brucite-like structure and β -Co(OH)₂ (JCPDS 74-1057) under high basicity [Z.P. Xu and H.C. Zeng, Interconversion of Brucite-like and Hydroxalcalcite-like Phases in Cobalt Hydroxide Compounds, *Chem. Mater.*, 1999, **11**, 67-74]. With the addition of Cr, the Co_xCr-p (x=1~5) showed a typical LDHs structure, but the intensity of the peaks changed with the variation of Co/Cr ratio. As reported, pure hydroxalcalcite phase generally could be obtained in a narrow range of $[M^{3+}]/([M^{3+}]+[M^{2+}])$ between 0.2~0.33. Otherwise, side products could be formed [X. D and D.G. Evans, Layered Double Hydroxides, 2006, **119**]. However, it was undeniable that even the Co/Cr ratio varied from 1 to 5 (the corresponding $[Cr^{3+}]/([Cr^{3+}]+[Co^{2+}])$ was 0.16~0.5), no other peaks were detected, indicating that the extra Co or Cr species presented amorphous structure or poor crystalline. The characteristic diffractions of Cr-p showed amorphous.

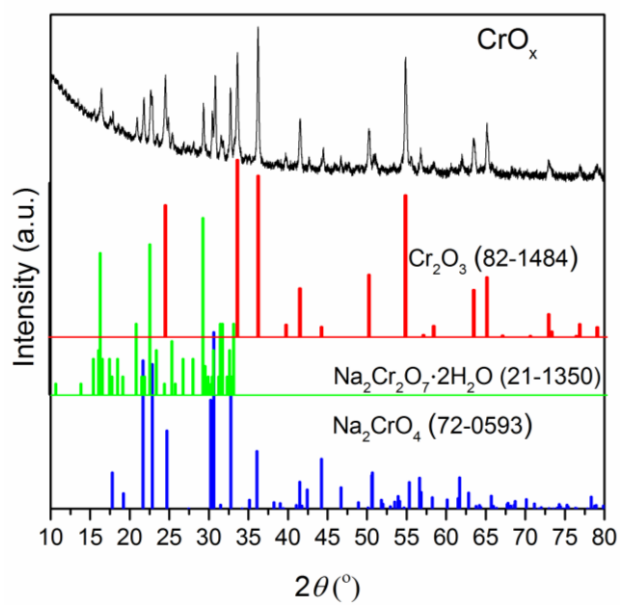


Fig. S4 XRD pattern of as-synthesized CrO_x

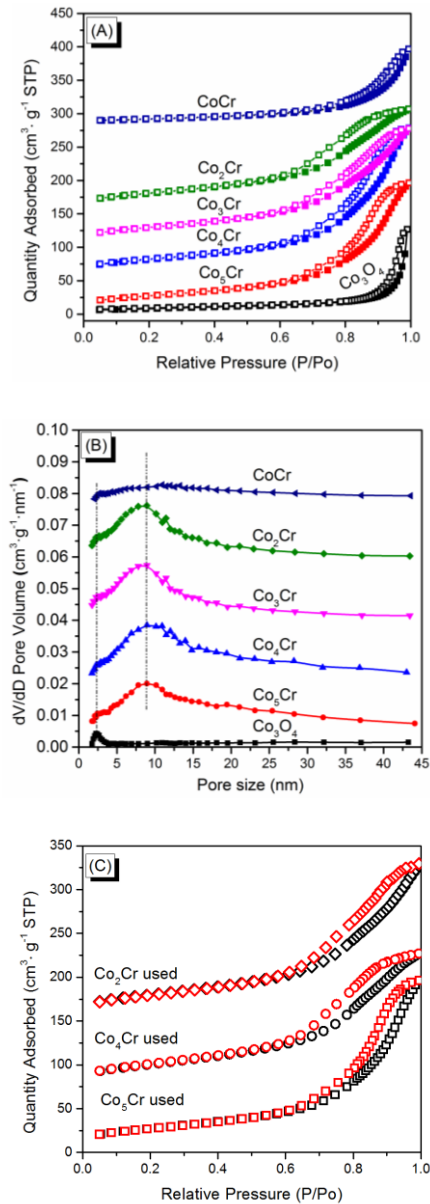


Fig. S5 N₂ sorption isotherms (A), pore size distributions (B) for fresh catalysts and N₂ sorption isotherms (C) for used catalysts

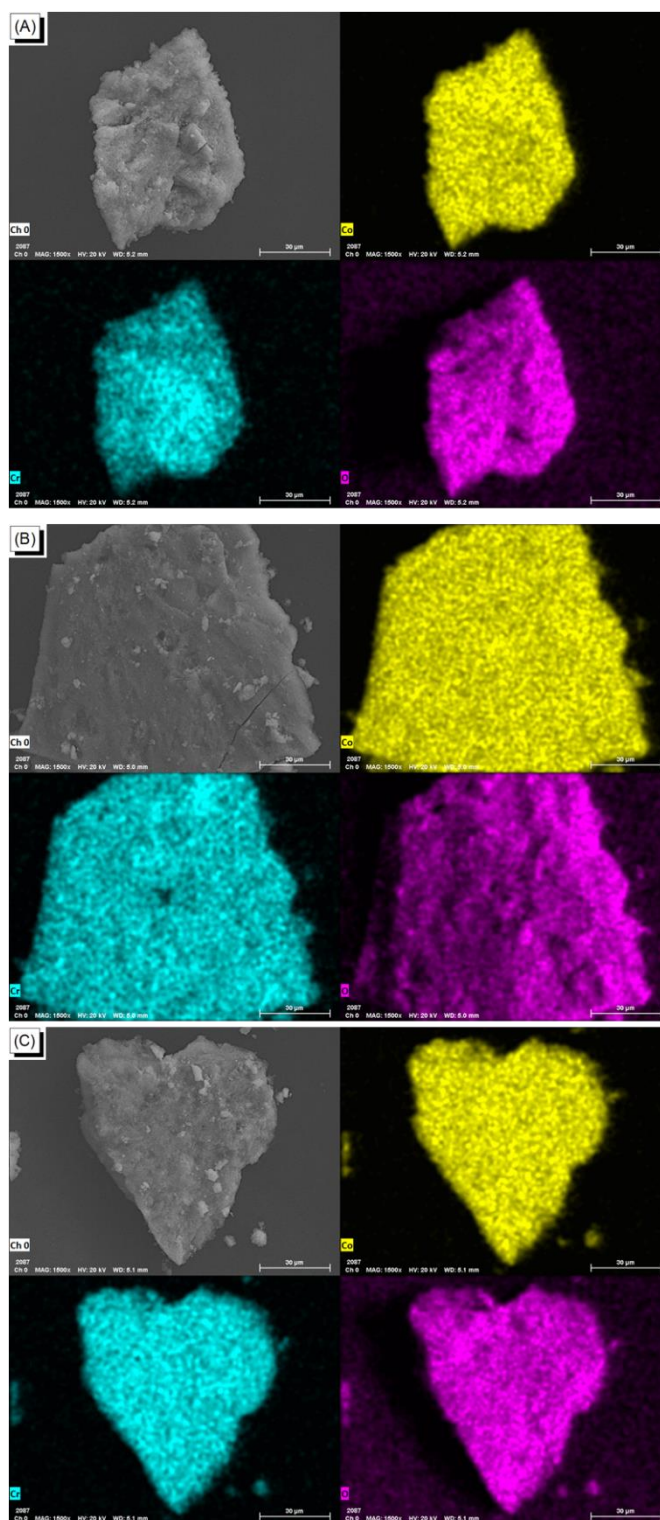


Fig. S6 The SEM images and elemental mappings of as-prepared samples: (A) Co₅Cr, (B) Co₃Cr and (C) CoCr.

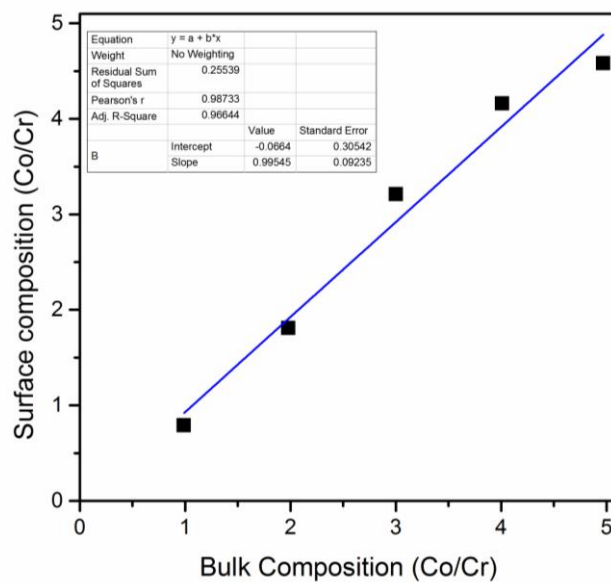


Fig. S7 Surface ratio of Co/Cr as a function of bulk composition of Co-Cr mixed oxides.

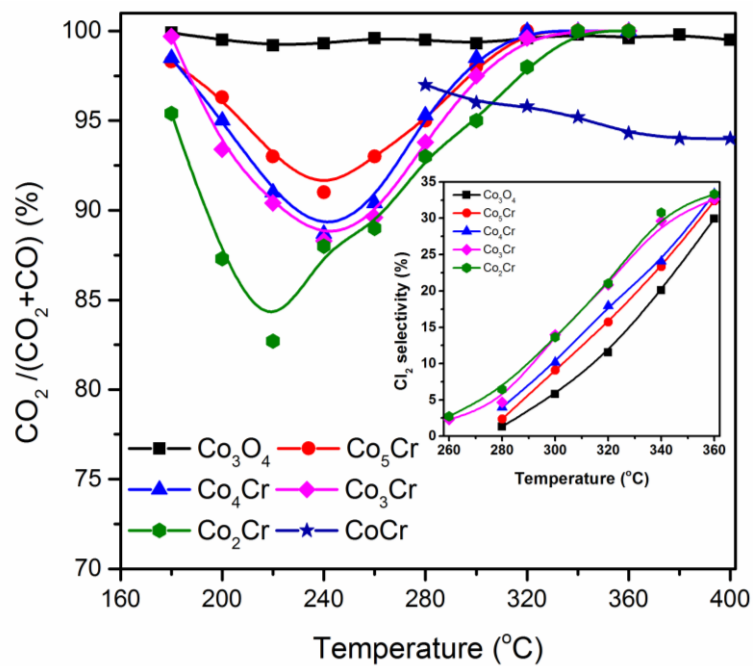


Fig. S8 The CO₂ to CO_x (CO₂+CO) and selectivity of Cl₂ on cobalt based catalysts. Gas composition: 1000 ppm 1, 2-dichlorobenzene, 10 vol. % O₂ and N₂ balance; GHSV: 60,000 mL g⁻¹ · h⁻¹; catalyst amount: 100 mg.

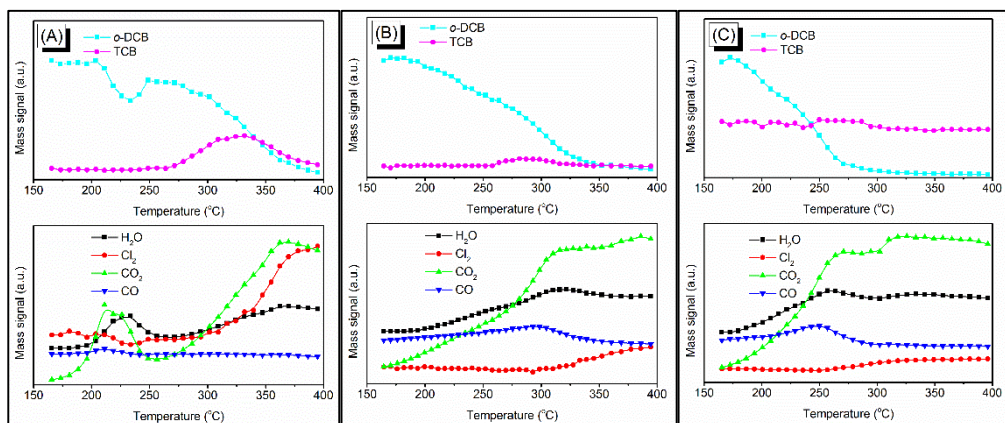


Fig. S9 Temperature-programmed surface oxidation reaction curves (TPSR) of 1, 2-dichlorobenzene (*o*-DCB) combustion over Co_3O_4 (A), Co_5Cr (B) and Co_2Cr (C); Gas composition: 1000 ppm, 1, 2-dichlorobenzene (*o*-DCB), 10 vol. % O_2 and Ar balance; GHSV = 30,000 $\text{mL g}^{-1} \text{h}^{-1}$; catalyst amount: 100 mg.

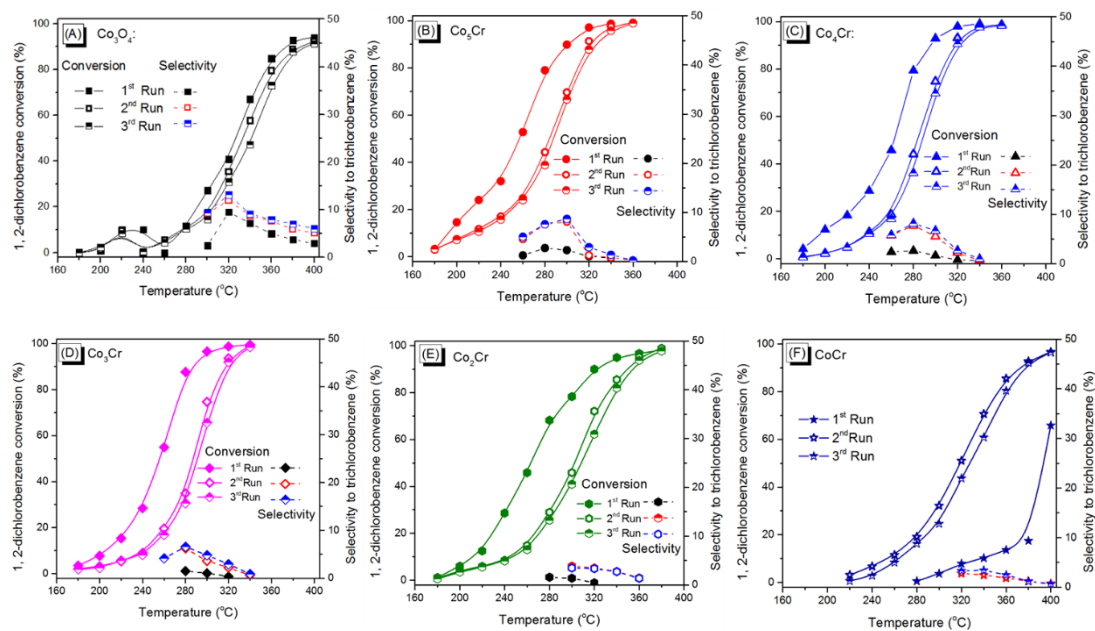


Fig. S10 Recycling experiments for 1, 2-dichlorobenzene oxidation and 1, 2, 4-trichlorobenzene selectivity over as-prepared catalysts. Gas composition: 1000 ppm 1, 2-dichlorobenzene, 10 vol. % O₂ and N₂ balance; GHSV: 60,000 mL g⁻¹ · h⁻¹; catalyst amount: 100 mg.

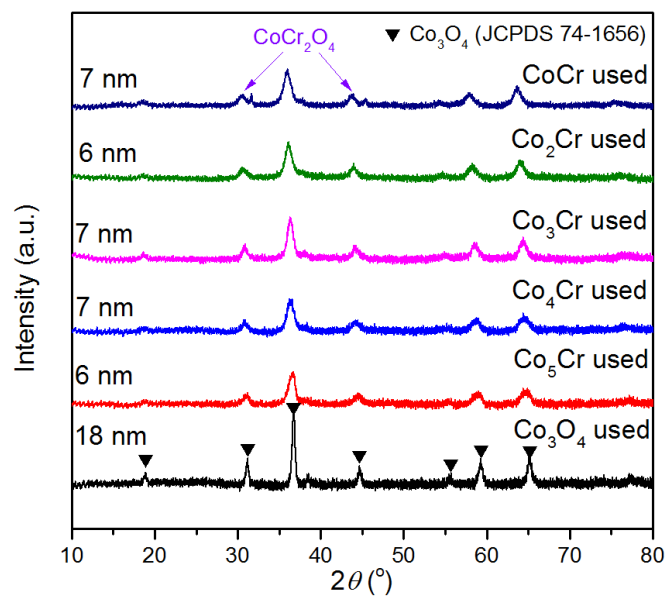


Fig. S11 The XRD patterns of used catalysts after recycling tests.

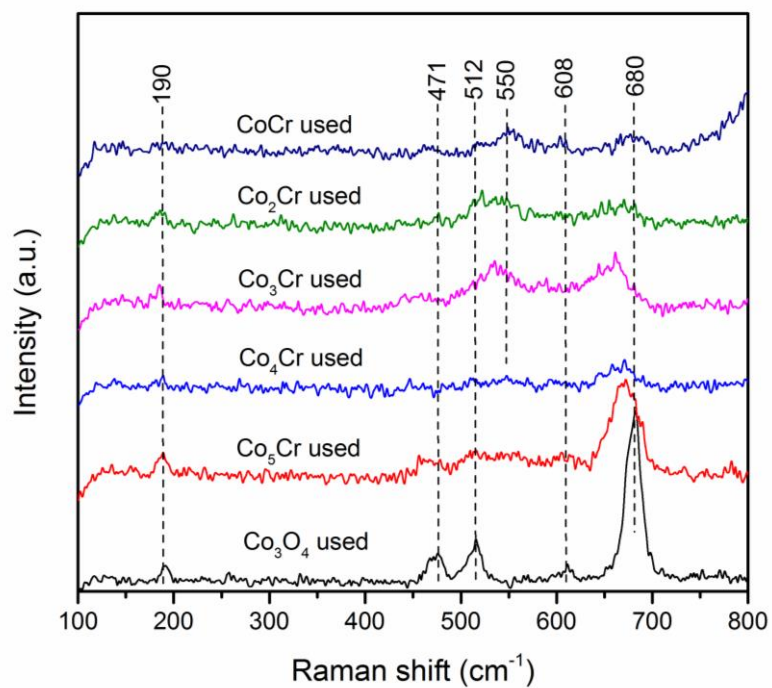


Fig. S12 The Raman spectra for used catalysts after recycling tests.

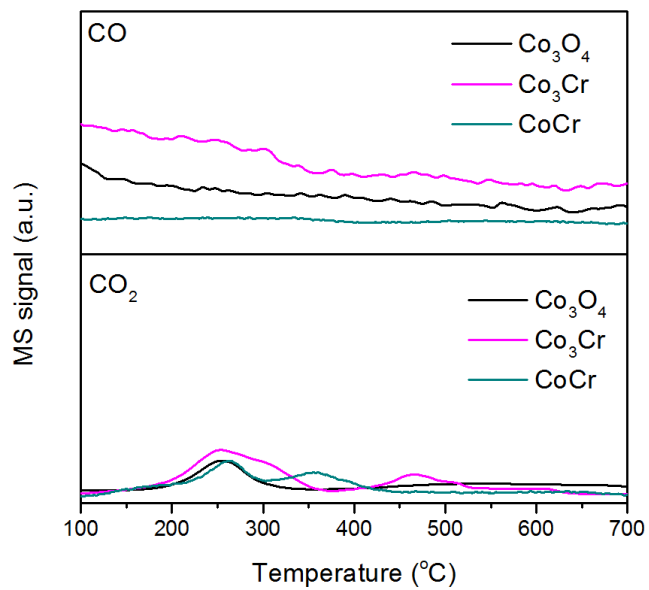


Fig. S13 O₂-TPO-MS profiles for CO₂ and CO of the used Co₃O₄, Co₃Cr and CoCr catalysts after stability test.

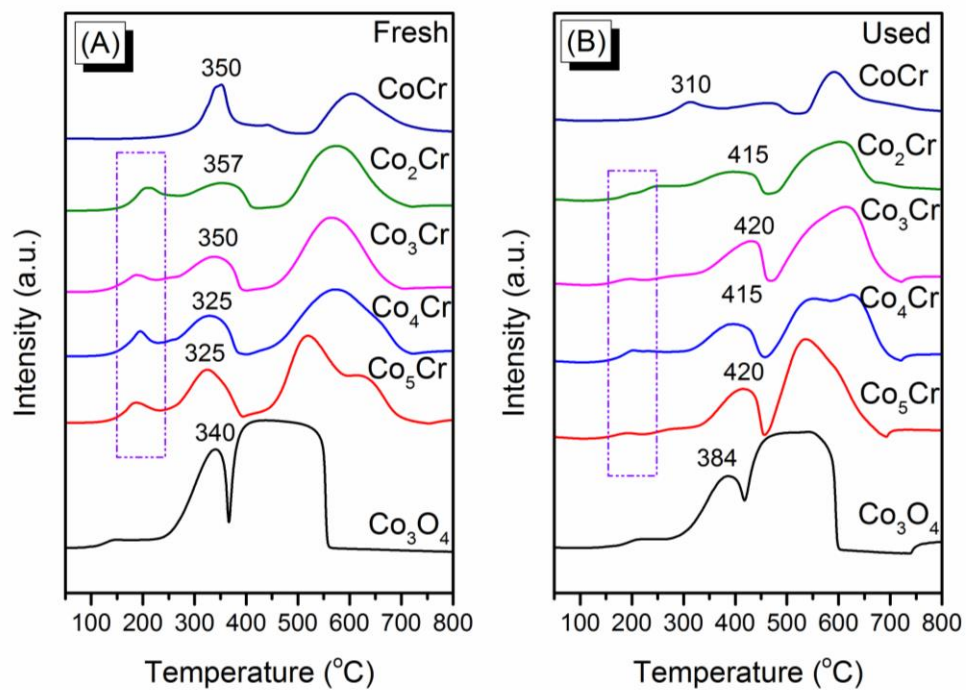


Fig. S14 The H₂-TPR profiles of fresh and used catalysts.

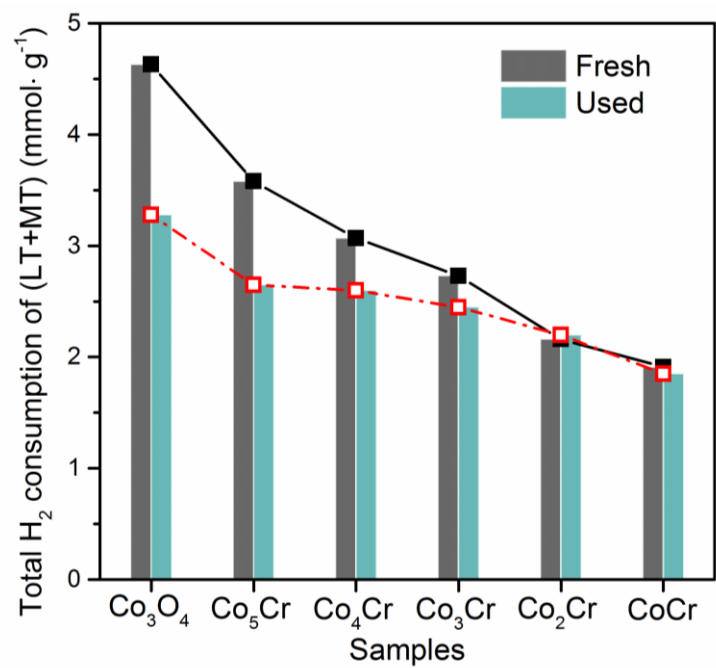


Fig. S15 The total H₂ consumption for fresh and used catalysts.

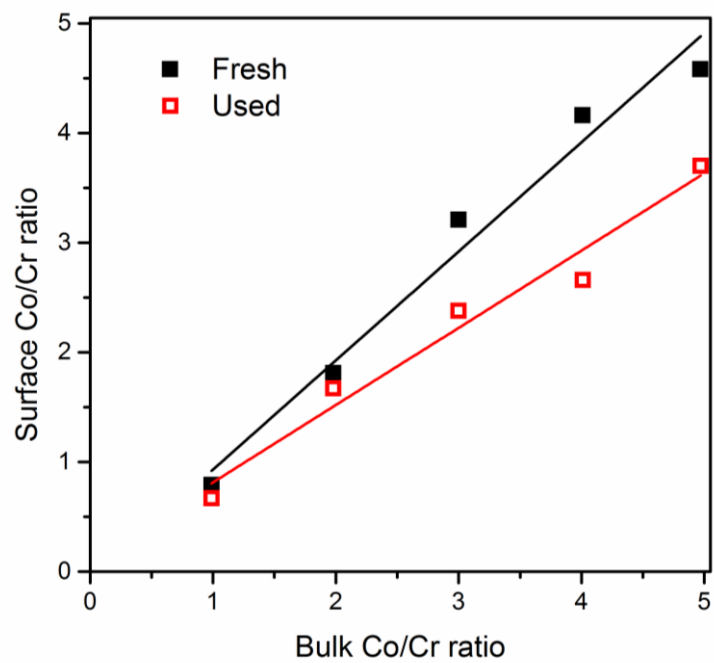


Fig. S16 Surface Co/Cr ratio relevant to their bulk ratio for fresh and used catalysts

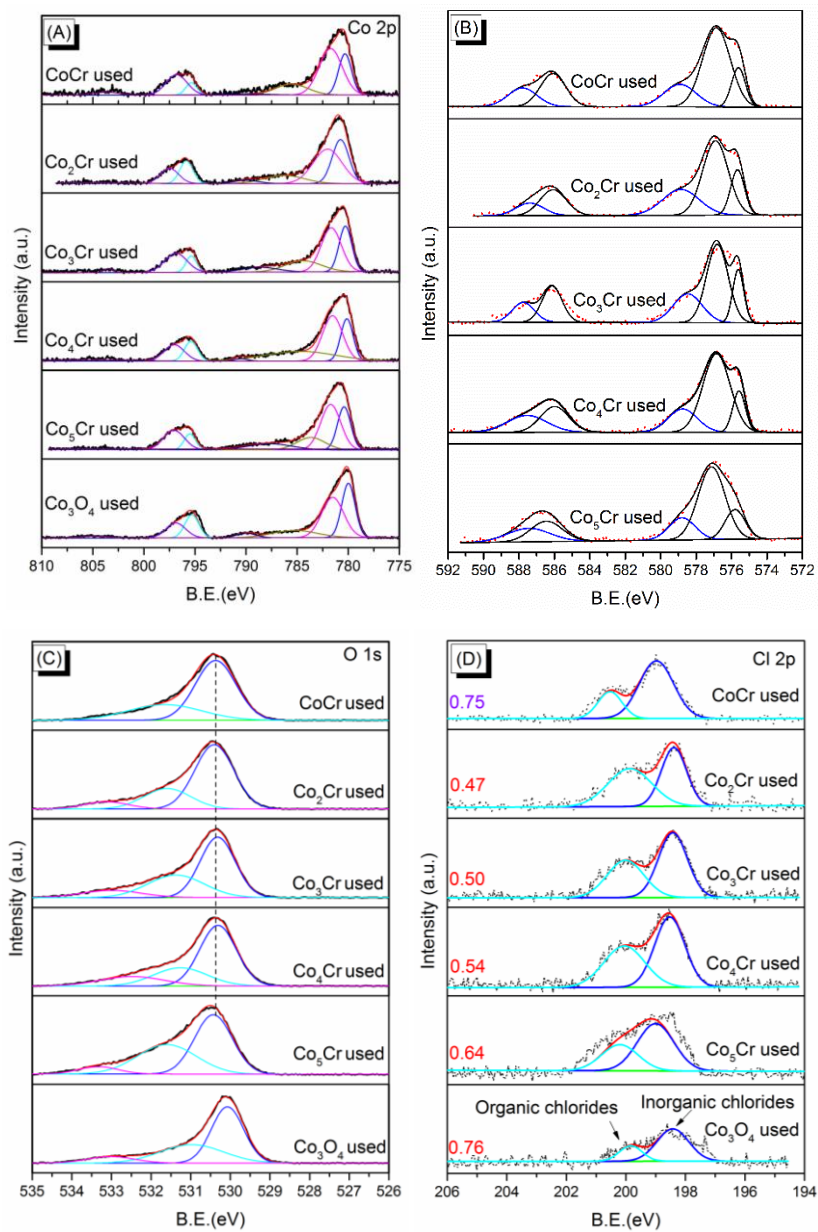


Fig. S17 XPS spectra of Co 2p, Cr 2p, O 1s and Cl 2p for used samples.

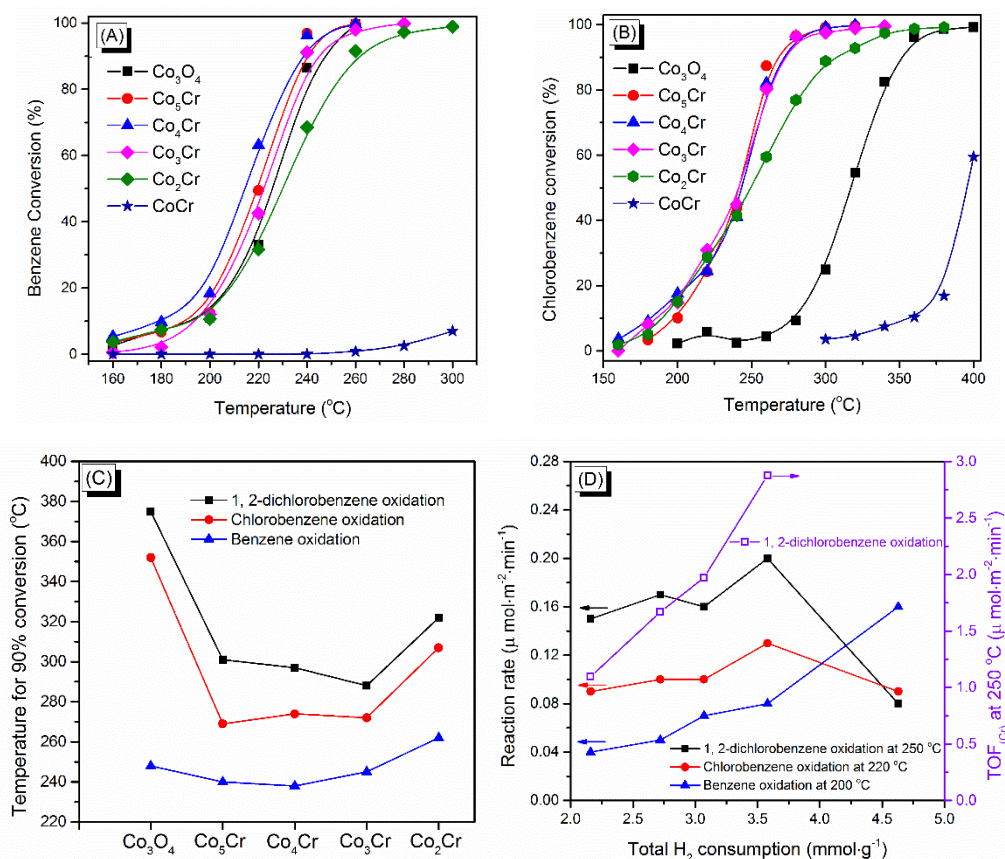


Fig. S18 Catalytic combustion of benzene (A), chlorobenzene (B) and T_{90} for benzene/Chlorobenzene/1, 2-dichlorobenzene oxidation versus total H_2 consumption (C) over cobalt based catalysts, Reaction rate at designated temperature for aromatics oxidation and $TOF_{(Cr)}$ for 1, 2-dichlorobenzene oxidation at 250 °C versus total H_2 consumption (D). Conditions: 1000 ppm VOCs, 10 vol. % O_2 and N_2 balance; GHSV = 60000 mL $g^{-1} h^{-1}$.

Discussion: The light off curves for aromatics oxidation, the T_{90} for aromatics oxidation, reaction rate at designated temperature and $TOF_{(Cr)}$ (the value based on the rate per square meter normalized by Cr% on surface obtained from XPS data) at 250 °C for 1, 2-dichlorobenzene versus total H_2 consumption was also presented in Fig. S18. The T_{90} for chlorinated aromatics showed no obvious association to total H_2 consumption confirmed that the reducibility of the cobalt based catalysts was not the only one factor for the apparent activity. The $Rate_{200}$ for benzene oxidation showed a positive correlation with the total H_2 consumption, indicating that the oxidation of benzene was more depended on the reducibility of the catalysts (Fig. S18D). However, for the chlorinated aromatics combustion, the $Rate_{220}$ or $Rate_{250}$ showed a distinct tendency. Fig. S18D also showed $TOF_{(Cr)}$ at 250 °C as a function of H_2 consumption over Co/Cr=2-5, the $TOF_{(Cr)}$ increased with the raise of Co/Cr ratio, meaning that Co_3O_4 species with high reducibility showed high activity for 1, 2-dichlorobenzene oxidation.

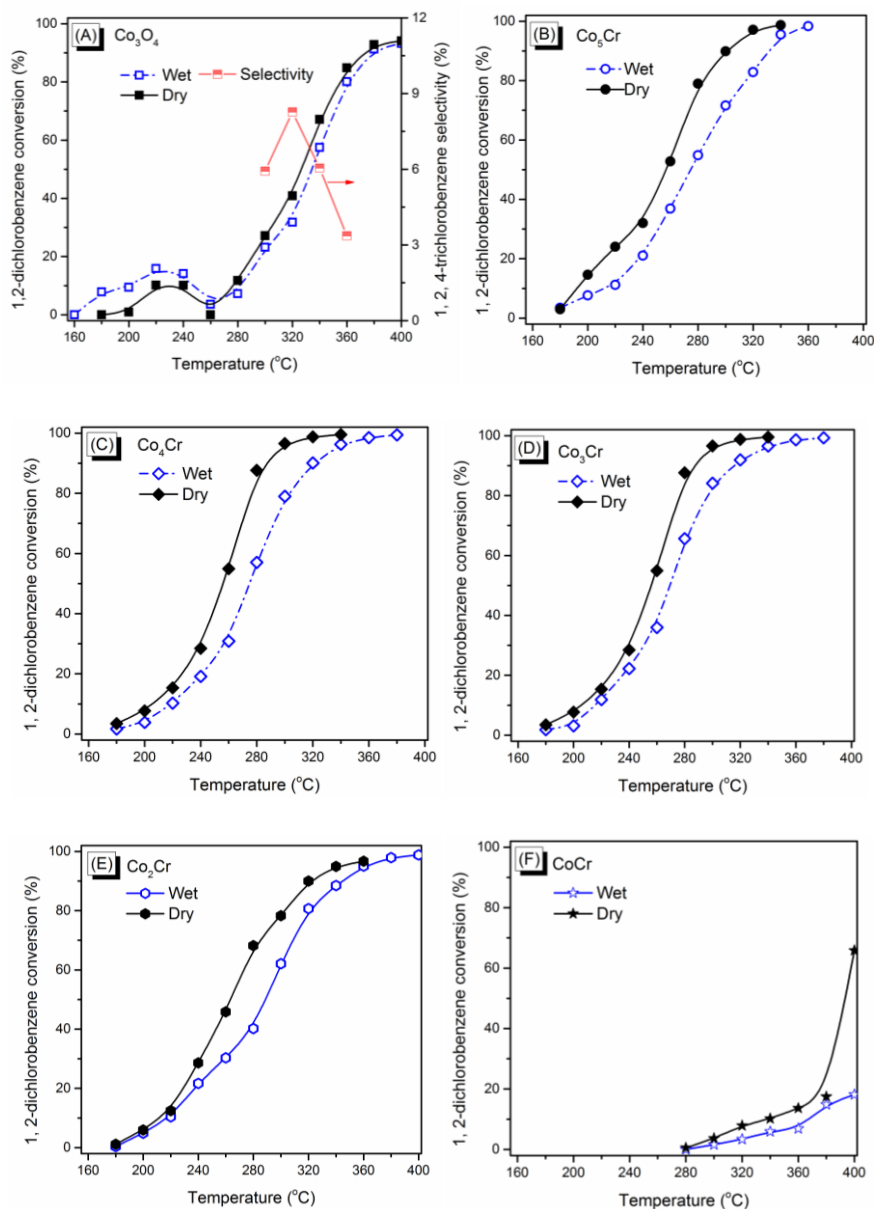


Fig. S19 The effect of water on 1, 2-dichlorobenzene catalytic combustion over synthesized catalysts (A: Co_3O_4 , B: Co_5Cr , C: Co_4Cr , D: Co_3Cr , E: Co_2Cr , F: CoCr); Gas composition: 1, 2-dichlorobenzene 1000 ppm+ 3 vol. % water (only using for wet condition); 10 vol. % O_2 and N_2 balance; GHSV = $60000 \text{ mL g}^{-1} \text{ h}^{-1}$.