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Supporting Information

The effect of Ru on the activity of Co₃O₄ catalysts for chlorinated aromatics oxidation

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Characterization

The powder X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku D/Max-rC powder diffractometer using Cu Ka radiation (40 kV and 100 mA). The diffractograms were recorded in the 2θ range of 10-80 °C with a 2θ step size of 0.01° and a step time of 10 s. The nitrogen adsorption and desorption isotherms were measured at -196 °C on an ASAP 2400 system in static measurement mode. Samples were out-gassed at 160 °C for 4 h before the measurement. Specific surface area was calculated using BET model. The chemical compositions of the prepared catalysts were determined by ICP-AES with the instrument model of Vanan 710. Before measurement, the metal oxides were dissolved using a mixture of inorganic acids (H₂SO₄, HNO₃ and HF). The transmission electron microscopy (TEM) images of powder samples were recorded on a JEM-1400 instrument operated at 120 kV. Highresolution transmission electron microscopic (HRTEM) images were taken on a JEM-2100 microscope that operated at 200 kV. The XPS measurements were made on a VG ESCALAB MK II spectrometer by using Mg Ka (1253.6 eV) radiation as the excitation source. Charging of samples was corrected by setting the binding energy of adventitious carbon (C1s) at 284.6 eV. Powder samples were pressed into selfsupporting disks, loaded into a sub-chamber, and evacuated to 10⁻⁹ mbar maintaining 4 h, prior to the measurements at 25 °C. Raman spectra were recorded on Via Reflex Laser Raman instrument, equipped with a CCD (charge coupled device) detector. The excitation source was the 514.5 nm line of Ar ion laser. The laser power was set at 3 mW. All data or results obtained from characterization tests were repeated basically

three times. H₂-temperature programming reduction (H₂-TPR) was investigated by heating catalysts (20 mg) in H₂ (5 vol%)/Ar flow (30 ml min⁻¹) at a heating rate of 10 °C min⁻¹ from 50 to 750 °C. The hydrogen consumption was monitored by a gas chromato- graphs (GC) equipped with thermo-conductivity detector. Before H₂-TPR analysis, the sample was heated for 60 min in Ar flow at 300 °C. EXAFS measurements at Pt L3-edge in both transmission (for Pt foil) and fluorescence (for samples) mode were performed at the BL14W1. The electron beam energy was 3.5 GeV and the stored current was 230 mA (top-up). A 38-pole wiggler with the maximum magnetic field of 1.2 T inserted in the straight section of the storage ring was used. XAFS data were collected using a fixed-exit double-crystal Si(111) monochromator. A Lytle detector was used to collect the fluorescence signal, and the energy was calibrated using Pt foil. The photon flux at the sample position was 2.6×10¹² photons per second. The raw data analysis was performed using IFEFFIT software package according to the standard data analysis procedures. The spectra were calibrated, averaged, pre-edge background subtracted, and post-edge normalized using Athena program in IFEFFIT software package. The Fourier transformation of the k3-weighted EXAFS oscillations, $k_3 \cdot \chi(k)$, from k space to R space was performed over a range of 3.5-11.5 Å⁻¹ to obtain a radial distribution function. And data fitting was done by Artemis program in IFEFFIT.

Raman



Fig. S1 Raman spectra of Ru/Co₃O₄ catalysts with various Ru loadings; a, Co₃O₄; b, 0.1%; c, 0.2%; d, 0.4%; e, 0.6%; f, 1.0%; g, 2.0%.

EXAFS Analyses



Fitting results of the Co K-edge EXAFS spectra of Co_3O_4 , $0.6Ru/Co_3O_4$ and $1.0Ru/Co_3O_4$. Fig. S2 EXAFS analyses at the Ru K-edg and Co K-edg.

The activity of 1.0Ru/SiO₂



Fig. S3 The activity of 1.0Ru/SiO₂ for 1,2-DCB oxidation; gas composition: 1000 ppm 1,2-DCB, 10% O₂ and N₂ balance; GHSV=30,000 ml·g⁻¹·h⁻¹.

Calculation of R_{Ru} based on the rate at 250 °C subtracting the contribution from Co_3O_4 normalized by Ru content on the surface

(XPS)

Rate=conversion \times 1,2-DCB concentration \times flow /(22.4 \times catalyst content \times surface area)

R_{Ru}=(Rate obtained over Ru/Co₃O₄- Rate obtained over Co₃O₄)/Ru content on surface

Reaction condition: 1,2-DCB concentration=1000 ppm O₂ concentration =10% flow=100 ml/min catalyst content=0.2 g

Rate = conversion $\times 1000 \times 10^{-6} \times 100 \times 10^{-3} / (22.4 \times 0.2 \times \text{surface area})$

Catalysts	$S_{BET}\!/\ m^2\!\cdot\!g^{1}$	Ru Content/ %	Conversion/ %	R_{Ru} / umol·m ⁻² ·min ⁻¹
Co ₃ O ₄	25	0.00	7.6	0
0.1Ru/Co ₃ O ₄	26	0.32	10.8	3.4
0.2Ru/Co ₃ O ₄	34	0.62	16.3	6.5
0.4Ru/Co ₃ O ₄	35	0.83	21.2	9.8
0.6Ru/Co ₃ O ₄	34	1.10	23.0	9.4
1.0Ru/Co ₃ O ₄	32	1.80	28.0	5.9
2.0Ru/Co ₃ O ₄	28	2.40	31.4	6.6

Table S1 R_{Ru} at 250 °C over Ru/Co₃O₄ with various Ru loadings (umol·m⁻²·min⁻¹)

The activity for benzene and chlorobenzene over Ru/Co₃O₄ catalysts



Fig. S4 The conversion curves of benzene (A) and chlorobenzne (B) over Ru/Co₃O₄catalysts; gas composition: reactant ,1000 ppm, 10% O₂ and N₂ balance; GHSV=30,000 ml·g⁻¹·h⁻¹.

The distribution curves of Cl_2 during 1,2-DCB oxidation over Ru/Co_3O_4 catalysts



Fig. S5 The distribution curves of Cl_2 during 1,2-DCB oxidation over Ru/Co₃O₄ catalysts; gas composition: 1000 ppm 1,2-DCB, 10% O₂ and N₂ balance; GHSV=30,000 ml·g⁻¹·h⁻¹.



The effect of O₂ concentration on the production of 1,2,4-TCB

Fig. S6 The production of 1,2,4-TCB for 1,2-DCB catalytic oxidation over Co_3O_4 catalysts; gas composition: 1000 ppm 1,2-DCB, and $0.0 \sim 20\%O_2$, N₂ balance; GHSV=30,000 ml·g⁻¹·h⁻¹.

1,2-DCB conversion curves almost keep constant



 $\label{eq:Fig.S7} \begin{array}{ll} \mbox{The conversion curves of 1,2-DCB over Ru/Co_3O_4 catalysts; gas composition: reactant, $1000 \mbox{ ppm}, 10\% \mbox{ }O_2$ and N_2 balance; $GHSV=30,000 \mbox{ }ml\cdot g^{-1}\cdot h^{-1}$. \end{array}$

Characterization for the used Ru/Co₃O₄ catalysts





Fig. S8 XPS spectra of Co 2p, O 1s and Cl 2p for Ru/Co₃O₄ samples.





Fig. S9 H_2 -TPR profiles of used Ru/Co₃O₄ samples.

XPS data for the used catalysts in wet feed

Sample	Atom %	- Co ³⁺ /Co ²⁺	O _{sur} /O _{lat}	O _{OH} /O _{lat}
Co ₃ O ₄	0.46	1.61	0.41 (-0.04) ^a	0.27 (+0.17) ^a
0.2Ru/Co ₃ O ₄	0.69	1.45	0.45 (-0.14)	0.33 (+0.18)
2.0Ru/Co ₃ O ₄	1.02	1.33	0.36 (-0.17)	0.28 (+0.17)

Table S2 XPS data for the used catalysts in wet feed

^a The values within brackets mean the difference between the fresh and the used catalysts.

FT-IR spectra of CO adsorption on 1.0Ru/Co₃O₄



Fig. S10 FT-IR spectra of CO adsorption on $1.0 \text{Ru}/\text{Co}_3\text{O}_4$ in 1200-2400 cm⁻¹ region at room temperature during the treatment with the stream of 5% CO balanced by Ar.

In situ DRIFT for adsorption of 1,2-DCB over 1.0Ru/SiO₂



Fig. S11 *In situ* DRIFT for adsorption of 1,2-DCB over 1.0Ru/SiO₂ in 1200-2000 cm⁻¹ region from 50 to 400 °C after the treatment with the stream of 1000 ppm 1,2-DCB balanced by Ar.