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Supporting Information

Catalytic Activity, Water Resistance and Stability of Hematite Nanomaterials in

Oxidative Removal of Polychlorinated Aromatic Hydrocarbons Can Be

Simultaneously Enhanced through Facet Engineering

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1. GENERAL INFORMATION

1.1. Catalyst Characterizations

Power X-ray powder diffraction (XRD) patterns of the samples were recorded on a Rigaku D/max-2500 cooled to room temperature within the 20 range of 10-70°, using Cu K α radiation (40 kV and 100 mA). Scanning electron microscopy (SEM, Shimadzu SS-550, 10 kV) and high-resolution transmission electron microscopy (HRTEM, TECNAI G² F20, 200 kV) were utilized to observe the morphologies of the samples. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD spectrometer with an Al K α X-ray source (hv = 1,486.6 eV). N₂ adsorption-desorption isotherms were recorded on an ASAP 2020/TriStar 3000 sorption analyzer and the specific surface area was calculated through Brunauer-Emmett-Teller (BET) method. Contact angle experiments were conducted by a Kino SL250 instruments.

To characterize the nature of the acid sites of the samples, pyridine-adsorbed Fourier transform infrared (Py-FTIR) spectra were collected with a PerkinElmer 2000 FTIR spectrophotometer with a resolution of 2 cm⁻¹. The catalysts were pressed into self-supporting thin discs of about 25 mg/cm² and 0.1 mm thick. The discs were placed in an IR cell which allowed thermal treatments. The catalyst samples were first pretreated in a vacuum at 350 °C for 1 h. Then the samples were cooled down to room temperature, and the spectra of the clean catalyst were collected and utilized as the background. Finally, pyridine was introduced by opening the valve of the vessel containing the substance at 25 °C for several seconds, and Py-FTIR spectra were collected. And evacuation was then performed at room temperature.

 O_2 temperature-programmed desorption (O_2 -TPD) was conducted to explore the difference of surface oxygen species for the samples by AutoChem1 II 2920. Firstly, 100 mg of the sample was loaded to a fixed-bed U-shaped quartz microreactor, successively pretreated in O_2 (30

mL/min) for 1 h and He (30 mL/min) for 2 h at 300 °C, then cooled to 50 °C. Secondly, the sample was successively filled with a (10 vol% O_2 + 90 vol% He) flow of 30 mL/min for 1 h and He (30 mL/min) for 1 h. Finally, the sample was heated at a ramp of 10 °C/min from 50 to 800 °C with a He flow of 30 mL/min. H₂ temperature-programmed reduction (H₂-TPR) was conducted to explore the reducibility of the samples by the Plus Chemisirption System of ChemiSorb 2720. Firstly, 100 mg of the sample was loaded to a fixed-bed U-shaped quartz microreactor, pretreated in Ar (30 mL/min) at 300 °C for 1 h, and cooled to 25 °C. Then, the sample was filled with a (10 vol% H_2 + 90 vol% Ar) flow of 30 mL/min for 0.5 h and heated at a ramp of 10 °C/min from 25 to 800 °C. H₂O temperature-programmed desorption (H₂O-TPD) was conducted to explore the H_2O adsorption behaviors of the samples by AutoChem1 II 2920. Firstly, 100 mg of the sample was loaded to a fixed-bed U-shaped quartz microreactor, successively pretreated in 10 vol% O₂ + 90 vol% He (30 mL/min) for 1 h and He (30 mL/min) for 2 h at 400 °C, then cooled to 25 °C. Secondly, the sample was successively filled with a (5 vol% H₂O + 95 vol% He) flow of 30 mL/min for 1 h and He (30 mL/min) for 1 h. Finally, the sample was heated at a ramp of 10 °C/min from 25 to 800 °C with a He flow of 30 mL/min.

1.2. Kinetic Studies

The concentrations effect of the reactants on the oxidation rate of *o*-DCB was investigated in the range of 225-300 °C with fixed amount of 200 mg catalyst. The total flow rate of the gaseous mixture flowing through the catalytic reactor was 60 mL/min, and the concentration of *o*-DCB was varied by changing *o*-DCB flow rate from 0.5 to 2.5 mL/min. Each *o*-DCB catalytic oxidation test conducted in kinetic study was under isothermal operation.

The removal of *o*-DCB (X) and yield of $CO_x(Y)$ can be calculated by the following equations:

$$X(\%) = (1 - \frac{C_{\text{out}}}{C_{\text{in}}}) \times 100\%$$
(1)

$$Y(\%) = \frac{C_{co_x}}{6 \times C_{in}} \times 100\% (x = 1, 2)$$
(2)

where C_{in} is the initial concentration of *o*-DCB, C_{out} is the *o*-DCB concentration in the outlet gas, and C_{COx} is the total concentration of CO₂ and CO after reaction.

The rate of catalytic oxidation of o-DCB (labelled as CB in the following equation), r, can be expressed by the following equation:

$$r = -\frac{d[CB]}{dt} = k[CB]^n [O_2]^n$$
(3)

where [CB] and $[O_2]$ are the concentration of 1,2-dichlorobenzene and O_2 , respectively; *k* is the apparent rate constant of the reaction. Since $[O_2] \gg [CB]$, the Eq. (4) can be rewritten as follows:

$$r = -\frac{d[CB]}{dt} = k_{ap} [CB]^n \tag{4}$$

Suppose this reaction obeys a first-order rate law, combining Eq. (1) and Eq. (4), and solving the resulting differential equation leads to Eq. (5):

$$\ln[1/(1-X)] = k'_{ap}\tau \tag{5}$$

where τ is the space time (s), and is defined as the reciprocal of the space velocity. The apparent activation energy of the catalytic oxidation of 1,2-dichlorobenzene over the synthesized three catalysts was calculated, according to the Arrhenius equation (Eq. (6)):

$$\ln \frac{\dot{k_{ap1}}}{\dot{k_{ap2}}} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(6)

where k'_{ap1} and k'_{ap2} are the apparent rate constants at 498 K and 573 K, respectively, s⁻¹; E_a is the apparent activation energy, kJ/mol; and T_1 and T_2 are the reaction temperatures, K.

1.3. DFT Calculation Method and Models

Method. The electronic structures were calculated using DFT within the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.¹ The project-augment wave (PAW) scheme was used to describe the inner cores^{2,3} and the electronic wave functions were expended in a plane wave basis with the kinetic cut-off energy of 400 eV. A Monkhorst-Pack grid of size of 3×3×1 was used to sample the surface Brillouin zone.⁴ To analyze electron correlations in transition metal oxides, conventional DFT calculations based on the local density approximation and GGA were failed to predict the values of the band gap and band-gap states. Therefore, this paper used the DFT+U method⁵ to evaluate the on-site Coulomb interactions in the localized d orbital and exchange interactions, by adding an effective Hubbard-U parameter to express the repulsion between electrons on the same orbital. In our GGA+U calculations, the value of (U-J) parameter was determined to be 3.00 eV for the Fe atom.⁶ It was geometrically optimized to obtain the most stable configuration with the lowest energy. The transition state (TS) was located by three steps: firstly, nudged elastic band (NEB) method^{7,8} was employed to find out the likely one; secondly, atomic structures were relaxed using a quasi-Newton algorithm to make the forces on the atoms less than 0.05 eV/Å; and lastly, the frequency analysis was performed for a confirmation of the TS structure.

The adsorption energy for $[IS(p)] (\Delta E_{ads(p)})$ and $[IS(v)] (\Delta E_{ads(v)})$ configurations of *o*-DCB on α -Fe₂O₃ catalyst surface were defined as:

 $\Delta E_{ads(p)} = E_{IS(p)} - (E_{o-DCB} + E_{surface})$

$$\Delta E_{ads(v)} = E_{IS(v)} - (E_{o-DCB} + E_{surface})$$

where E_{o-DCB} and $E_{surface}$ respectively represent the energies of the *o*-DCB molecule and α -Fe₂O₃ surface. Since the system consisting of *o*-DCB and α -Fe₂O₃ surface is the starting point of the

dissociation process studied by DFT, the $E_{o-DCB} + E_{surface}$ is set as 0.

The C-Cl bond broken energy barrier (ΔE_{bar}) and reaction energy (ΔE_{rea}) can be defined as:

$$\Delta E_{bar} = E_{TS} - E_{IS(p)}$$

$$\Delta E_{rea} = E_{FS} - E_{IS(p)}$$

where $E_{IS(p)}$, E_{TS} and E_{FS} represent the energy in the initial state with a parallel configuration [IS(p)], transition state (TS) and final state (FS) of the system. Positive ΔE value represents the reaction process is endothermic reaction, on the contrary, a negative value is exothermic reaction.

Models. We considered four magnetic configurations for Fe atoms since there are four Fe atoms in a rhombohedral unit cell of α -Fe₂O₃, such as (+ + + +), (+ - + -), (+ - - +) and (+ + - -), where + and - designated up- and down-spin directions with respect to the z-axis. The total energy of antiferromagnetic arrangement (+ - - +) is the lowest, which consistent with the other theoretical works.^{9, 10} The optimized unit cell parameters of α -Fe₂O₃ (a = b = 5.052 Å, c = 14.057 Å) close to the experimental values (a = b = 5.038 Å, c = 13.772 Å). For (001), we chose the type of $-[Fe-O_3-Fe-]_n$ in this work because of relative stability as compared to those of -[Fe-Fe-O₃-]_n and -[O₃-Fe-O₃-]_n. A (2×2) super-cell containing nine atomic layers was built, and the slab was separated by a vacuum space of 15 Å. The first six layers were allowed to be relaxed while the other layers beneath the surface were frozen during the geometry optimizations. For (012), a (2×2) super-cell containing five atomic layers was built, and the slab was separated by a vacuum space of 15 Å. The first three layers were allowed to be relaxed during the geometry optimization processes. For (110), a (1×2) super-cell containing twelve atomic layers was built, and the slab was separated by a vacuum space of 15 Å. The first six layers were allowed to be relaxed while the other layers beneath the surface were frozen during the geometry optimizations.

	a-Fe ₂ O ₃	α -Fe ₂ O ₃	a-Fe ₂ O ₃
	NR-{110}	NP-{012}	NS-{001}
Crystal size (nm) ^[a]	17.6	29.2	22.8
Surface area $(m^2 g^{-1})^{[b]}$	34.2	46.9	35.8
$O_{sur}/(O_{latt}+O_{sur}+O_{ads}) \ ^{[c]}$	42 %	38 %	29 %

 Table S1. Characteristics of the as-prepared catalysts.

^[a] Crystal size obtained from XRD based on the (104) diffraction peak of α -Fe₂O₃ in Figure S1 using Scherrer equation;

^[b] Specific surface area calculated using the BET method;

^[c] Calculated based on XPS analysis.

	Commercial	α -Fe ₂ O ₃ NR-	a-Fe ₂ O ₃	a-Fe ₂ O ₃
	α-Fe ₂ O ₃	{110}	NP-{012}	NS-{001}
T _{50%} [a]	333 °C	229 °C	280 °C	294 °C
T _{90%} ^[a]	420 °C	265 °C	330 °C	357 °C
T _{90%} [b]	415 °C	285 °C	366 °C	377 °C

Table S2. Catalytic performance of the iron oxide catalysts for *o*-DCB oxidation.

Note: $T_{50\%}$ & $T_{90\%}$ stand for the temperature with 50% and 90% removal of *o*-DCB, respectively; ^[a] In dry condition;

^[b] In humid condition.

Catalyst			Test conditions		Performances		
Designation	Composition	Reactant	Conc. (ppm)	Space velocity	Removal efficiency (%)	Temperature (°C)	Reference
α-Fe ₂ O ₃ NR-{110}	α-Fe ₂ O ₃	o-DCB	50	$\frac{18,000 \text{ mL}}{\text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}}$	90	265	This work
Fe_xZr_{1-x} oxide catalysts	(Fe _{0.5} Zr _{0.5} -S) α -Fe ₂ O ₃ ; amorphous phase ZrO ₂	o-DCB	750	30,000 (h ⁻¹)	90	389	11
SO ₄ ²⁻ /Fe ₂ O ₃ catalysts	$(SO_4^2-/Fe_2O_3-II) \alpha$ -Fe_2O_3	o-DCB	750	30,000 (h ⁻¹)	90	368	12
Ca-doped FeO _x hollow microspheres	(FeCa10) α-Fe ₂ O ₃ ; Fe ₃ O ₄	o-DCB	50	88,000 (h ⁻¹)	100	400	13
Ti-doped iron oxides	(Fe ₁₈ Ti ₂ O _x) α -Fe ₂ O ₃ ; γ - Fe ₂ O ₃ ; anatase TiO ₂	o-DCB	100	22,000 (h ⁻¹)	100	350	14
Fe-Mn mixed oxide hollow microspheres	(FeMn20) α-Fe ₂ O ₃	o-DCB	50	88,000 (h ⁻¹)	100	400	15
$CaCO_3/\alpha$ -Fe ₂ O ₃ nanocomposites	(FeCa10) CaCO ₃ ; α-Fe ₂ O ₃	o-DCB	100	22,000 (h ⁻¹)	100	450	16
Fe-Ca-O _x /TiO ₂ catalysts	(TiFe5Ca70-S) α-Fe ₂ O ₃ ; calcite CaCO ₃ ; anatase TiO ₂	o-DCB	50	$18,000 \text{ mL} \\ g_{\text{cat}}^{-1} \cdot h^{-1}$	90	322	17

Table S3. Comparison of *o*-DCB oxidative degradation activities between α -Fe₂O₃ NR-{110} and literature-reported FeO_x catalysts.

Facet	$\Delta E_{ads(p)} (eV)$	$\Delta E_{ads(v)} (eV)$	$\Delta E_{bar} \left(eV \right)$	$\Delta E_{rea} \left(eV \right)$	$L_{C\text{-}Cl}\left(\mathring{A}\right) {}^{\left[a\right] }$
(110)	-0.85	-0.65	0.88	-0.70	2.362
(012)	-0.50	-0.42	1.00	-0.66	2.157
(001)	-0.50	-0.26	1.64	-0.36	2.193

Table S4. Calculated energies in the processes of *o*-DCB adsorption and breaking of a C-Cl, and length of C-Cl bond in TS on different facets of α -Fe₂O₃.

 $\ensuremath{^{[a]}}\xspace L_{C\text{-}Cl}$ represents the length of C-Cl bond in TS.



Figure S1. XRD spectra of α -Fe₂O₃ NR-{110}, NP-{012} and NS-{001}. The crystallite sizes of the synthesized catalysts were also evaluated from the (104) diffraction peak of α -Fe₂O₃ using Scherrer equation, and the values were 17.6, 29.2 and 22.8 nm for NR-{110}, NP-{012} and NS-{001}, respectively (Table S1). We observed that the rod-shaped α -Fe₂O₃ possessed the lower crystallite size than the other two catalysts.



Figure S2. SEM images of a) α -Fe₂O₃ NR-{110}, b) α -Fe₂O₃ NP-{012} and c) α -Fe₂O₃ NS-{001}.



Figure S3. Illustrated geometric structure of a) α -Fe₂O₃ NR-{110}; b) NS-{001}.



Figure S4. (a) O₂-TPD profiles of NR-{110}, NP-{012} and NS-{001} indicated the presence of $O_2^{-}sur (100-200 \text{ °C})^{18,19}$, $O_2^{2^{-}}sur (300-400 \text{ °C})^{20}$, $O_{sur}^{-} (400-500 \text{ °C})^{19}$, and $O_2^{-}latt (500-800 \text{ °C})^{18,20}$. (b) H₂-TPR profiles of NR-{110}, NP-{012} and NS-{001} showed two H₂ consumption stages caused by the reduction of Fe₂O₃ to Fe₃O₄ (300-500 °C) and Fe₃O₄ to FeO (500-700 °C).^{19,21} The initial lower reduction temperature in NR-{110} indicated it possessed greater low-temperature reducibility.^{22,23}



Figure S5. Plots of $\ln[1/(1-X)]$ vs space time (τ) at different temperatures over the prepared a) α -Fe₂O₃ NR-{110} ($E_a = 42.6 \text{ kJ mol}^{-1}$), b) α -Fe₂O₃ NP-{012} ($E_a = 43.2 \text{ kJ mol}^{-1}$) and c) α -Fe₂O₃ NS-{001} ($E_a = 44.1 \text{ kJ mol}^{-1}$) in dry condition (50 ppm *o*-DCB, 10% O₂, balance N₂, WHSV = 18,000 mL g_{cat}⁻¹·h⁻¹).



Figure S6. CO_x yields over different catalysts a) in dry condition and b) in humid condition (0.5% water) (50 ppm *o*-DCB, 10% O₂, balance N₂, WHSV = 18,000 mL g_{cat}⁻¹·h⁻¹), denoting that NR-{110} showed higher CO₂ yield. Error bars indicate variances of triplicates.



Figure S7. Contact angle of α -Fe₂O₃ NR-{110}, NP-{012} and NS-{001}.



Figure S8. H₂O-TPD profiles of NR-{110}, NP-{012} and NS-{001}, which exhibit one desorption peak originating from the physically adsorbed water.²⁴ The relatively lower desorption temperature in NR-{110} showed that it possessed weaker interaction with H₂O molecular than NP-{012} and NS-{001}.²⁵⁻²⁷



Figure S9. Stability of NR-{110}, NP-{012} and NS-{001} for *o*-DCB removal at 325 °C in dry condition. Experimental conditions: 50 ppm *o*-DCB, 0.5% water, 10% O₂, balance N₂, and WHSV = 18,000 mL $g_{cat}^{-1} \cdot h^{-1}$.

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