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# In-Depth Understanding of the Morphology Effect of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on Catalytic Ethane Destruction

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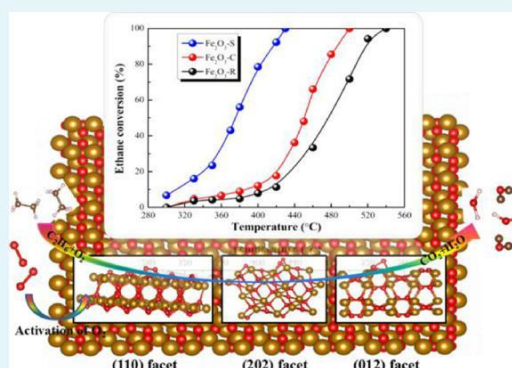
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\* Supporting Information

**ABSTRACT:** Shape effects of nanocrystal catalysts in different reactions have attracted remarkable attention. In the present work, three types of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> oxides with different micromorphologies were rationally synthesized via a facile solvothermal method and adopted in deep oxidation of ethane. The physicochemical properties of prepared materials were characterized by XRD, N<sub>2</sub> sorption, FE-SEM, HR-TEM, FTIR, in situ DRIFTS, XPS, Mössbauer spectroscopy, in situ Raman, electron energy loss spectroscopy, and H<sub>2</sub>-TPR. Moreover, the formation energy of oxygen vacancy and surface electronic structure on various crystal faces of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were explored by DFT calculations. It is shown that nanosphere-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibits much higher ethane destruction activity and reaction stability than nanocube-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and nanorod-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> due to larger amounts of oxygen vacancies and lattice defects, which greatly enhance the concentration of reactive oxygen species, oxygen transfer speed, and

material redox property. In addition to this, DFT results reveal that nanosphere-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has the lowest formation energy of oxygen vacancy on the (110) facet ( $E_{\text{Vo}}(110) = 1.97$  eV) and the strongest adsorption energy for ethane ( $-0.26$  eV) and O<sub>2</sub> ( $-1.58$  eV), which can accelerate the ethane oxidation process. This study has deepened the understanding of the face-dependent activities of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in alkane destruction.

**KEYWORDS:** Fe<sub>2</sub>O<sub>3</sub>, oxygen vacancy, ethane, catalytic oxidation, DFT calculation



## 1. INTRODUCTION

The emission of volatile organic compounds (VOCs) during industrial processes leads to great environment hazards such as ozone depletion and photochemical smog.<sup>1</sup> Furthermore, many VOCs are carcinogenic and toxic. It is difficult to destroy linear short-chain alkanes. Ethane is an inert alkane that vastly existed in natural gas (1.8–5 mol %) and currently mainly used as a fuel for industrial refining processes.<sup>2</sup> Catalytic combustion can be considered as one of the most effective approaches for the low-energy elimination of VOCs.<sup>3</sup> The Pt- and Pd-based materials are the most efficient catalysts for total oxidation of hydrocarbons currently, but the use of noble metal-free metal oxides offers considerable economic advantages.<sup>4</sup> Among them, CoO<sub>x</sub>, MnO<sub>x</sub>, and FeO<sub>x</sub> materials

constitute another choice to Pt/Pd-based catalysts. However, common CoO<sub>x</sub>, MnO<sub>x</sub>, and FeO<sub>x</sub> oxides are less active than the supported noble metal catalysts in most cases. Comparatively, the environment-friendly FeO<sub>x</sub> oxides possess much higher anti-sintering ability than the CoO<sub>x</sub> and MnO<sub>x</sub> materials, which suffer from catalytic deactivation at elevated temperatures, endowing FeO<sub>x</sub> oxides a kind of promising catalysts for inert alkane destruction, although the low-temperature activity of FeO<sub>x</sub> is more or less lower than that of CoO<sub>x</sub> and MnO<sub>x</sub> catalysts.<sup>5–7</sup> Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), based

on hexagonal close packing of oxygen with iron in two-thirds of the octahedral vacancies, is generally adopted as an heterogeneous catalyst due to its high resistance, low cost to deactivation, and environment-friendly properties.<sup>9</sup>

Controlling the morphology of the nanoparticles can influence their catalytic performance because the different topographies of the particles can expose different crystal faces.<sup>10</sup> It is known that facet engineering causes different chemical and physical properties in nanomaterials due to distortion of the electronic structures and various exposed atoms in crystal surfaces having different exposed faces. Many applications, for example, gas sensing, energy conversion and storage, and heterogeneous catalysis are very alive to surface structures. As such, the promise of high energy and reactivity in engineering surface structures and exposure-specific aspects is becoming a promising research direction.<sup>11</sup> Different kinds of nanomaterials with special forms and structures, for example, nanowires,<sup>12</sup> nanorods,<sup>13</sup> nanotubes,<sup>14</sup> nanobelts,<sup>15</sup> nano-plates,<sup>16</sup> and nanorings,<sup>17</sup> have been synthesized by various methods. Li et al.<sup>18</sup> compared the catalytic property of CeO<sub>2</sub> nanoparticles and CeO<sub>2</sub> nanorods in CO oxidation and found that the catalytic activity of CeO<sub>2</sub> nanorods is greater than nanoparticles because the exposed {110} and {100} planes have higher oxygen storage capacity. Similarly, Xie et al.<sup>19</sup> proposed that CeO<sub>2</sub> nanorods that exposed the {110} and {001} facets show a better CO conversion efficiency than CeO<sub>2</sub> with {111} facets. Qiu et al.<sup>20</sup> proposed that the propane adsorption energies on different crystal facets of MnO<sub>2</sub> are different ( $\alpha(310) > \gamma(120) > \beta(110) > \delta(001)$ ), which influence its propane oxidation activity. Using different methods such as thermal decomposition and hydrothermal methods synthesize  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with different crystals.<sup>21</sup> Kouotou et al.<sup>1</sup> found that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film exhibits good performance toward catalytic combustion of C<sub>3</sub>H<sub>6</sub>. Zheng et al.<sup>8</sup> found that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles that have a uniform quasi-cubic structure with six identical {110} planes exhibit outstanding catalytic performance for CO oxidation because the exposed {110} planes have a high density of Fe atoms.

In this work, three kinds of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with different micromorphologies and exposed facets (i.e., nanosphere-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3</sub>-S), nanocube-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3</sub>-C), and nanorod-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3</sub>-R), respectively, with predominantly exposed (110), (202), and (012) facets) were rationally synthesized, and the synthesized catalysts were extensively characterized by different technologies including electron energy loss spectroscopy (EELS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), high-resolution transmission electron microscopy (HR-TEM), Mössbauer spectroscopy, field-emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), Raman/ in situ Raman, and temperature-programmed reduction by hydrogen (H<sub>2</sub>-TPR). In addition, the formation energy of oxygen vacancy and surface electronic structure on different crystal faces of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were studied by the density functional theory (DFT) calculations. The catalytic performance of obtained materials toward the total oxidation of ethane was studied, and the effect of oxygen vacancy, lattice defect, and crystal facets on catalyst surface chemical composition, reduction property, and catalytic performance was discussed in detail.

## 2. EXPERIMENTAL SECTION

The detailed experimental section is described in Text S1 (Supporting Information).

## 3. RESULTS

**3.1. Structural Property.** As shown in Figure 1, the micromorphologies of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R

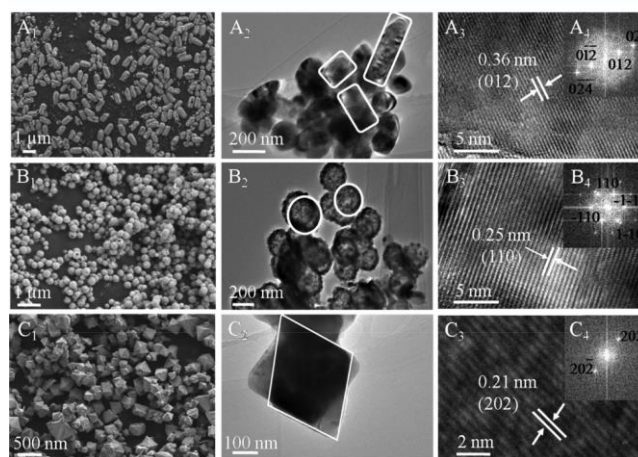


Figure 1. FE-SEM and HR-TEM images of (A, A<sub>1</sub>, A<sub>2</sub>) Fe<sub>2</sub>O<sub>3</sub>-R, (B, B<sub>1</sub>, B<sub>2</sub>) Fe<sub>2</sub>O<sub>3</sub>-S, and (C, C<sub>1</sub>, C<sub>2</sub>) Fe<sub>2</sub>O<sub>3</sub>-C (insets: FFT images of (A<sub>3</sub>) Fe<sub>2</sub>O<sub>3</sub>-R, (B<sub>3</sub>) Fe<sub>2</sub>O<sub>3</sub>-S, and (C<sub>3</sub>) Fe<sub>2</sub>O<sub>3</sub>-C).

catalysts were determined by FE-SEM and HR-TEM. Fe<sub>2</sub>O<sub>3</sub>-R has a uniform diameter of 100–200 nm with a length in the range of 100–1000 nm (Figure 1A<sub>1</sub>,A<sub>2</sub>). A lattice spacing of 0.36 nm attributed to the (012) plane can be observed (Figure 1A<sub>3</sub>), and similar results can be obtained from the fast Fourier transformation (FFT) of Fe<sub>2</sub>O<sub>3</sub>-R (Figure 1A<sub>4</sub>). The Fe<sub>2</sub>O<sub>3</sub>-S sample shows a spherical morphology with a rough surface, and the average diameter of particles is 200 ± 20 nm (Figure 1B<sub>1</sub>,B<sub>2</sub>). Results of HR-TEM (Figure 1B<sub>3</sub>) and FFT transformation (Figure 1B<sub>4</sub>) confirm that Fe<sub>2</sub>O<sub>3</sub>-S is enclosed by the (110) planes mainly with a lattice spacing of 0.25 nm. Figure 1C<sub>1</sub>,C<sub>2</sub> suggests that Fe<sub>2</sub>O<sub>3</sub>-C has an octahedron shape with a side size of 240 ± 10 nm. HR-TEM image (Figure 1C<sub>3</sub>) and corresponding FFT (Figure 1C<sub>4</sub>) reveal that the lattice fringe is 0.21 nm, implying that Fe<sub>2</sub>O<sub>3</sub>-C is mainly enclosed by (202) facets.

XRD patterns of prepared materials are shown in Figure 2. The diffraction peaks of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R samples agree well with the  $\alpha$ -hematite crystallographic phase of Fe<sub>2</sub>O<sub>3</sub> (rhombohedral structure, JCPDS 33-0664, space group R-3c) with lattice constants of  $a = 0.5035$  nm and  $c = 1.3740$  nm. The lattice constants of prepared materials (Fe<sub>2</sub>O<sub>3</sub>-S:  $a = 0.5039$  nm,  $c = 1.3746$  nm; Fe<sub>2</sub>O<sub>3</sub>-C:  $a = 0.5034$  nm,  $c = 1.3750$  nm; Fe<sub>2</sub>O<sub>3</sub>-R:  $a = 0.5038$  nm,  $c = 1.3748$  nm) were calculated by the least-square fitting method, which are in accordance with the above data. The peak width at half height of Fe<sub>2</sub>O<sub>3</sub>-S diffractions is wider than those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R, indicating that Fe<sub>2</sub>O<sub>3</sub>-S has a smaller grain size than Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R materials, in agreement with the data calculated by the Scherrer equation (average grain sizes of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R are 20, 177, and 189 nm, respectively).

The specific surface area and porosity of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R materials were studied by low-temperature N<sub>2</sub> sorption, as displayed in Figure S1 and Table 1. It can be

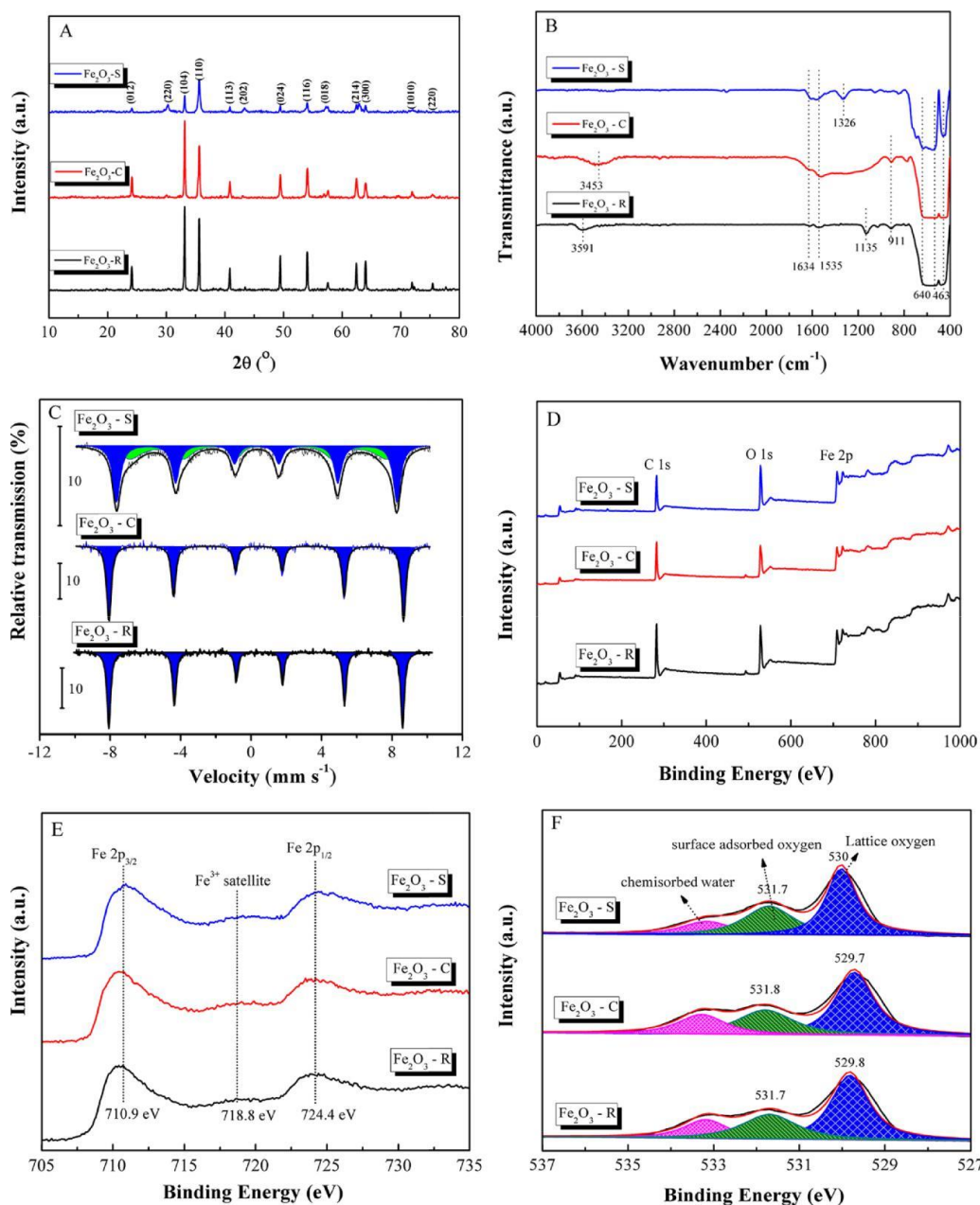


Figure 2. (A) XRD patterns, (B) FT-IR spectra, (C) room-temperature Mössbauer spectra, and (D) XPS survey spectra and corresponding (E) Fe 2p and (F) O 1s XPS spectra of prepared catalysts.

Table 1. Textural Property of Prepared Materials

sample	SBET <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>t</sub> <sup>b</sup> (cm <sup>3</sup> g <sup>-1</sup> )	C <sub>s</sub> <sup>c</sup> (nm)	D <sub>p</sub> <sup>d</sup> (nm)	I <sub>H1</sub> <sup>e</sup> (×10 <sup>-4</sup> mmol g <sup>-1</sup> s <sup>-1</sup> )	I <sub>H2</sub> <sup>e</sup> (×10 <sup>-4</sup> mmol g <sup>-1</sup> s <sup>-1</sup> )
Fe <sub>2</sub> O <sub>3</sub> -S	44.5	0.11	20	7.5	1.41	1.51
Fe <sub>2</sub> O <sub>3</sub> -C	8.5	0.02	177	3.5	0.21	0.23
Fe <sub>2</sub> O <sub>3</sub> -R	8.8	0.04	189	4.7	0.14	0.18

<sup>a</sup>Specific surface area obtained at P/P<sub>0</sub> = 0.05–0.30. <sup>b</sup>Total pore volume estimated at P/P<sub>0</sub> = 0.99. <sup>c</sup>Crystal size obtained from the results of XRD. <sup>d</sup>BJH pore diameter calculated from the desorption branch. <sup>e</sup>Initial H<sub>2</sub> consumption rates of synthesized catalysts at 340 and 350 °C.

observed in Table 1 that the specific surface area, total pore volume, and average pore diameter of Fe<sub>2</sub>O<sub>3</sub>-S (44.5 m<sup>2</sup> g<sup>-1</sup>, 0.11 cm<sup>3</sup> g<sup>-1</sup>, and 7.5 nm, respectively) are much higher than those of Fe<sub>2</sub>O<sub>3</sub>-C (8.5 m<sup>2</sup> g<sup>-1</sup>, 0.02 cm<sup>3</sup> g<sup>-1</sup>, and 3.5 nm, respectively) and Fe<sub>2</sub>O<sub>3</sub>-R (8.8 m<sup>2</sup> g<sup>-1</sup>, 0.04 cm<sup>3</sup> g<sup>-1</sup>, and 4.7 nm, respectively). Figure S1A suggests that the Fe<sub>2</sub>O<sub>3</sub>-S sample possesses a type IV isotherm with a clear H3-type hysteresis

loop, characteristic of a mesoporous material.<sup>22</sup> The pore size distribution (PSD) was obtained by the Barrett-Joyner-Halenda (BJH) method (Figure S1, inset). Fe<sub>2</sub>O<sub>3</sub>-S shows unimodal pore size distribution with a predominant pore radius of around 20 nm, indicating the homogeneous distribution of pores;<sup>22</sup> however, Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R with type III isotherms can be observed (Figure S1B,C),<sup>23</sup> and the

pore size distribution curves of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R show several mesopore peaks in the range of 15–45 nm, indicating the heterogeneity distribution of pores, which is considered to be mainly caused by an interspace between the component nanoparticles.<sup>22</sup>

**3.2. Surface Property.** Figure 2B shows the FTIR spectra of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R materials. All samples show a broad band at 463–640 cm<sup>-1</sup>. This band can be attributed to the Fe–O bond vibration of Fe<sub>2</sub>O<sub>3</sub>.<sup>24</sup> The bands at 1634 and 1535 cm<sup>-1</sup> are assigned to the bending and vibration of H<sub>2</sub>O molecules and C–O bond, respectively.<sup>25</sup> The strong absorption peaks at 3453 cm<sup>-1</sup> (over Fe<sub>2</sub>O<sub>3</sub>-C) and 3591 cm<sup>-1</sup> (over Fe<sub>2</sub>O<sub>3</sub>-R) can be assigned to the O–H stretching vibration of intermolecular hydrogen bonding,<sup>25</sup> and the weak band at 911 cm<sup>-1</sup> over Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R can be attributed to the vibration of Fe–OH.<sup>26</sup> For Fe<sub>2</sub>O<sub>3</sub>-R, the peak at 1135 cm<sup>-1</sup> can be assigned to the asymmetric and symmetric stretching vibrations of sulfonic acid group (–SO<sub>3</sub><sup>-</sup>).<sup>27</sup> The band at around 1326 cm<sup>-1</sup> over Fe<sub>2</sub>O<sub>3</sub>-S corresponds to the typical stretching mode of C–N heterocycles.<sup>28</sup>

Figure 2C shows the room-temperature transmission Mössbauer spectra of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R materials. The fitted hyperfine parameters of subspectra, for example, isomer shifts (IS), quadruple splittings (QS), magnetic hyperfine field (Bhf), and resonance half-height line widths (LW), are listed in Table 2. The Mössbauer spectrum

Table 2. Characterized Results of Synthesized Materials Obtained from the Mössbauer Spectra

sample	IS <sup>a</sup> (mm s <sup>-1</sup> )	QS <sup>b</sup> (mm s <sup>-1</sup> )	LW <sup>c</sup> (mm s <sup>-1</sup> )	Bhf <sup>d</sup> (T)	abundance (%)
Fe <sub>2</sub> O <sub>3</sub> -S	0.32	0.002	0.55	49.5	57.3
	0.41	0	0.49		42.7
Fe <sub>2</sub> O <sub>3</sub> -C	0.37	-0.15	0.31	51.9	100
Fe <sub>2</sub> O <sub>3</sub> -R	0.37	-0.21	0.25	51.8	100

<sup>a</sup>Isomer shift (relative to the source). <sup>b</sup>Quadrupole shift/splitting.

of Fe<sub>2</sub>O<sub>3</sub>-S is well fitted with two sextets, and the spectra of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R materials are well fitted with one sextet. The IS values of all samples listed in Table 2 are lower than 0.5 mm s<sup>-1</sup>, indicating that the valence state of iron in all catalysts is +3.<sup>29</sup> The sextets with Bhf around 51 T can be assigned to the characteristic of high-spin Fe<sup>3+</sup> ions in octahedral coordination of the α-Fe<sub>2</sub>O<sub>3</sub> phase (hematite).<sup>30</sup> The room-temperature existence of a doublet in the Mössbauer spectrum is related to the presence of superparamagnetic nanoparticles, which have critically lower dimension based on the results of XRD (Figure 2A).<sup>31</sup> The first sextet component with an IS value of 0.32 mm s<sup>-1</sup> (about 57.3%) is assigned to the presence of large hematite particles, whereas the second sextet

component with an IS value of 0.41 mm s<sup>-1</sup> (about 42.7%) is ascribed to small particles.<sup>32</sup> In Mössbauer spectroscopy, because of the magnetic field distribution caused by local lattice distortion, the line width  $\Gamma$  of some spectral components is widened, and the presence of vacancies in the nearest neighbor of the Mossbauer probe or a sufficiently large impurity atom can also be observed.<sup>32</sup> Table 2 shows that the line widths  $\Gamma$  of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R are 0.55, 0.31, and 0.25 mm s<sup>-1</sup>, respectively, suggesting that the amount of lattice defects in prepared materials are following the order of Fe<sub>2</sub>O<sub>3</sub>-S > Fe<sub>2</sub>O<sub>3</sub>-C > Fe<sub>2</sub>O<sub>3</sub>-R.

The surface chemical composition and chemical states of prepared materials were investigated by XPS, as displayed in Figure 2D–F and Table 3. The doublet peaks of Fe 2p<sub>1/2</sub> and Fe 2p<sub>3/2</sub> are located at around 724.4 and 710.8 eV, respectively (Figure 2E), in well agreement with typical binding energies of Fe<sup>3+</sup> in Fe<sub>2</sub>O<sub>3</sub>.<sup>33,34</sup> Besides, a satellite peak at around 718.8 eV is also attributed to the characteristic peak of Fe<sub>2</sub>O<sub>3</sub>.<sup>33,34</sup> The binding energy between the satellite and Fe 2p<sub>3/2</sub> peaks is 7.90 eV for all samples, which suggests the presence of α-Fe<sub>2</sub>O<sub>3</sub>,<sup>34</sup> consistent with the results of Mössbauer spectra (Figure 2C). In catalytic oxidation reactions, relative ratios and status of different oxygen species play crucial roles, and O 1s XPS spectra are shown in Figure 2F. The O 1s spectra of all materials can be divided into three peaks. The peaks located at 529.4–530.6, 530.8–532.0, and 532.1–532.2 eV can be assigned to the lattice oxygen for metal oxides (O<sub>α</sub>), adsorbed oxygen (O<sub>β</sub>), and surface oxygen by adsorbed water species (O<sub>λ</sub>), respectively.<sup>35,36</sup> Generally, because of the excellent fluidity of O<sub>β</sub>, the high relative concentration of O<sub>β</sub> on the surface of the catalyst can be correlated with the high activity in the oxidation reaction. It is shown in Table 3 that the ratios of O<sub>β</sub>/O<sub>α</sub> are approximately 0.72, 0.59, and 0.55 for Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R, respectively, suggesting that the largest amount of O<sub>β</sub> species existed over the Fe<sub>2</sub>O<sub>3</sub>-S material. In addition to this, the O<sub>α</sub> peak of Fe<sub>2</sub>O<sub>3</sub>-S (530 eV) shifts toward higher binding energy than those of Fe<sub>2</sub>O<sub>3</sub>-C (529.7 eV) and Fe<sub>2</sub>O<sub>3</sub>-R (529.8 eV), indicating that there are more defective oxygen sites over Fe<sub>2</sub>O<sub>3</sub>-S than the other materials.<sup>37</sup>

We further divided and analyzed the Fe 2p<sub>3/2</sub> XPS peak (Figure 2E) to get some understanding of sample characteristics, as shown in Figure 3. Four multiplet peaks (except the surface peak and pre-peak) in a bind energy range of 708–716 eV can be obtained.<sup>37,38</sup> It is found that peak 1 is more intense (Figure 3D) and its peak area is larger than the second multiplet peak (peak 2) for samples. For hematite particles, the higher integral peak area and intensity of the first multiple peak (peak 1) are expected.<sup>37,38</sup> The splitting indicates that some Fe<sup>3+</sup> cations in hematite samples have tetrahedral coordination, and all cations in this phase should have octahedral coordination.<sup>37,38</sup> It can be seen in the ratios of area between peak 1 and peak 2 (Table S1) in different catalysts; that is, the

Table 3. XPS Results of Prepared Catalysts

sample	binding energy (eV)				
	Fe <sup>3+</sup> 2p <sub>1/2</sub>	Fe <sup>3+</sup> 2p <sub>3/2</sub>	O <sub>α</sub> <sup>a</sup>	O <sub>β</sub> <sup>b</sup>	O <sub>β</sub> /O <sub>α</sub> <sup>c</sup>
Fe <sub>2</sub> O <sub>3</sub> -S	724.4	710.9	530 (39555.3)	531.7 (28550.2)	0.72
Fe <sub>2</sub> O <sub>3</sub> -C	724.4	710.8	529.7 (30264.4)	531.8 (17815.3)	0.59
Fe <sub>2</sub> O <sub>3</sub> -R	724.4	710.8	529.8 (48470.8)	531.7 (27038.9)	0.55

<sup>a</sup>Lattice over prepared catalysts (corresponding peak areas are listed in brackets). <sup>b</sup>Adsorbed oxygen over prepared catalysts (corresponding peak areas are listed in brackets). <sup>c</sup>Peak area ratio.

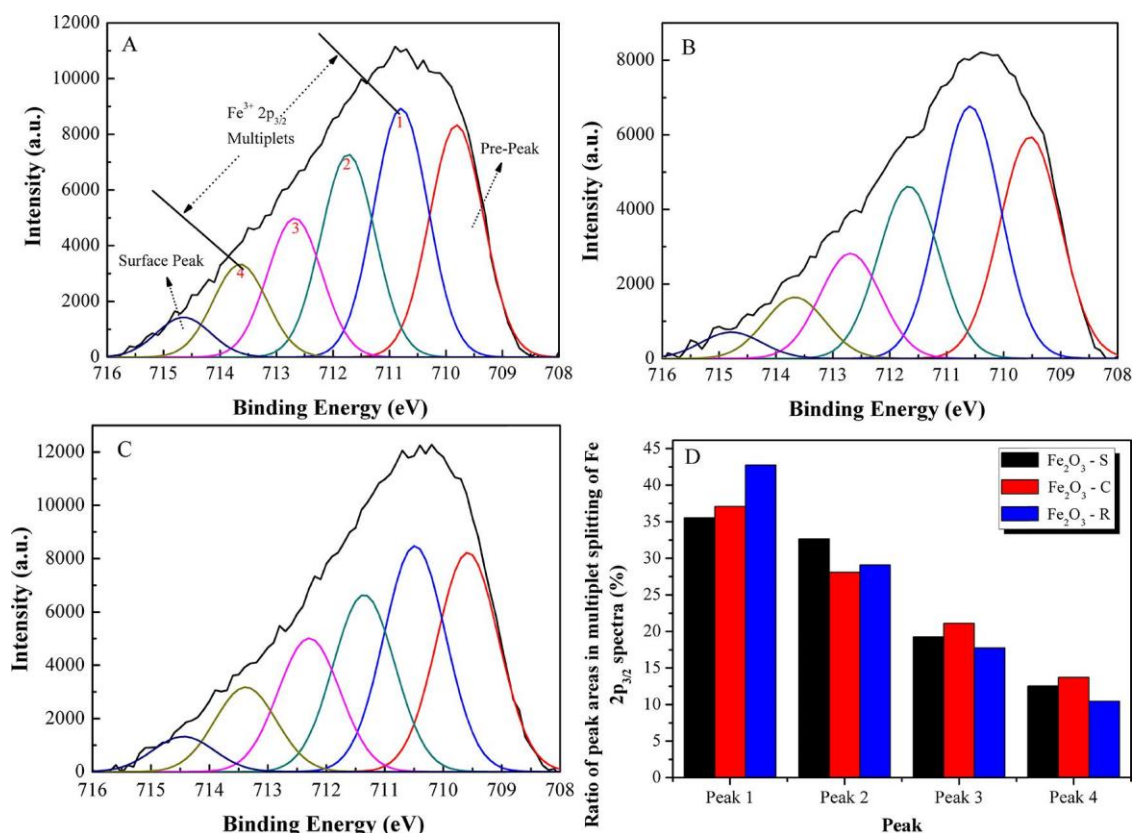


Figure 3. Analysis of the multiplet splitting of the Fe 2p<sub>3/2</sub> peak of each hematite nanomaterial from the XPS results of (A) Fe<sub>2</sub>O<sub>3</sub>-S, (B) Fe<sub>2</sub>O<sub>3</sub>-C, and (C) Fe<sub>2</sub>O<sub>3</sub>-R. (D) Corresponding ratio of peak areas in multiplet splitting of Fe 2p<sub>3/2</sub> for Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R.

ratio closer to 1 indicates that some of the Fe<sup>3+</sup> cations are tetrahedrally coordinated in the catalyst. It is similar to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> where some of the Fe<sup>3+</sup> cations are tetrahedrally coordinated.<sup>37</sup> It can be explained that, with nanoparticles becoming smaller, dimension-dependent structural conversion may occur, resulting in surface hematite defects and leading to the appearance of tetrahedrally coordinated Fe<sup>3+</sup> cations.<sup>39</sup> As such, the Fe<sub>2</sub>O<sub>3</sub>-S sample with the smallest grain size (20 nm, close to the maximum diameter of defect frequency (30 nm)) possesses more defects on the surface than Fe<sub>2</sub>O<sub>3</sub>-C (177 nm) and Fe<sub>2</sub>O<sub>3</sub>-R (189 nm).

To have more details about the phase of the synthesized materials, Raman spectroscopy was utilized as shown in Figure 4. The bands at 219 and 499 cm<sup>-1</sup> are attributed to the A<sub>1g</sub> mode of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and those observed at 286, 405, and 608 cm<sup>-1</sup> correspond to the E<sub>g</sub> mode of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>1</sup> The interactions between two magnons formed on antiparallel spins, typically of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Figure 4A),<sup>40</sup> can lead to the appearance of the broad band between 1200 and 1400 cm<sup>-1</sup>. By comparing those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R, the peaks over the Raman spectrum of Fe<sub>2</sub>O<sub>3</sub>-S are broader and weaker, demonstrating that the hematite nanoparticles with smaller crystalline size and long-range disordered accumulation in the structure can result in many factors such as poor crystallization, lattice defects, and oxygen vacancies.<sup>41</sup> The Raman spectra region between 550 and 750 cm<sup>-1</sup> was extracted and further divided into three peaks (E<sub>g</sub> of 608 cm<sup>-1</sup>, LO of 660 cm<sup>-1</sup>, and T of 690 cm<sup>-1</sup>), as shown in Figure 4B-D. The intensity of LO and T peaks can explain that the degree of disorder in the lattice of hematite and the existence of lattice defects on the surface of nanoparticles are related, respectively.<sup>37</sup> As shown in Table

S2, the intensity of the LO band decreases in the order of Fe<sub>2</sub>O<sub>3</sub>-S (15.77) > Fe<sub>2</sub>O<sub>3</sub>-C (6.68) > Fe<sub>2</sub>O<sub>3</sub>-R (3.59), similar with that the T band (Fe<sub>2</sub>O<sub>3</sub>-S (11.42) > Fe<sub>2</sub>O<sub>3</sub>-C (6.55) > Fe<sub>2</sub>O<sub>3</sub>-R (4.70)). Above results suggest that Fe<sub>2</sub>O<sub>3</sub>-S has the largest amounts of structural defects than Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R materials, in agreement with the result of Mössbauer spectroscopy (Figure 2C).

Figure 5 shows the in situ Raman spectra of prepared Fe<sub>2</sub>O<sub>3</sub> samples. It is found that the intensity of all Raman peaks decrease dramatically (becoming wider) with the increase in temperature. For hematite, the expansion of these bands is a size-dependent phenomenon caused by uneven strain broadening associated with particle size dispersion and phononic construction.<sup>42</sup> Especially, the band at about 608 cm<sup>-1</sup> becomes broader and weaker for all materials due to the increase in oxygen vacancies.<sup>43</sup> Figure S2 displays the related contour map of the in situ Raman spectra of prepared materials. It can be observed that the Raman peaks of Fe<sub>2</sub>O<sub>3</sub>-S reduce to the minimum at only 100 °C, whereas the related temperatures for Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R materials are 250 and 350 °C, respectively, implying that Fe<sub>2</sub>O<sub>3</sub>-S is more likely to form oxygen vacancies than Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R. The data are collected by EELS, and a zero loss peak value on energy scale calibration was performed with a low-loss-area deconvolution to minimize the multiple scattering effect.<sup>44</sup> Figure 6A represents the EELS spectra of oxygen K-edge energy-loss near-edge fine structure (ELNES) for Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R. Four peaks, denoted as a, b, c, and d, can be found in all materials.<sup>44</sup> In general, a derives from the O 1s to 2p core level hybridized with the Fe 3d orbital, and b originates from the O 2p states hybridized with the transition

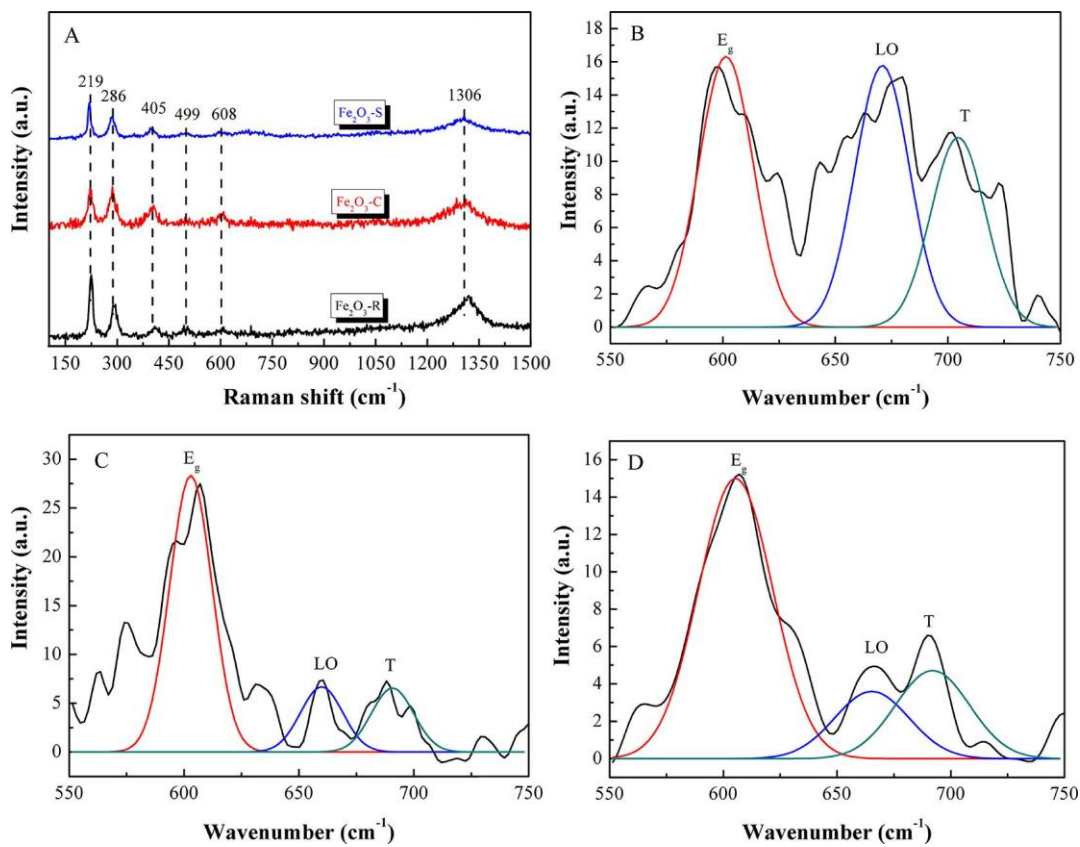


Figure 4. (A) Full Raman spectra of all hematite nanomaterials and corresponding peak deconvolution of the  $E_g$ , LO, and T bands of (B)  $Fe_2O_3$ -S, (C)  $Fe_2O_3$ -C, and (D)  $Fe_2O_3$ -R samples.

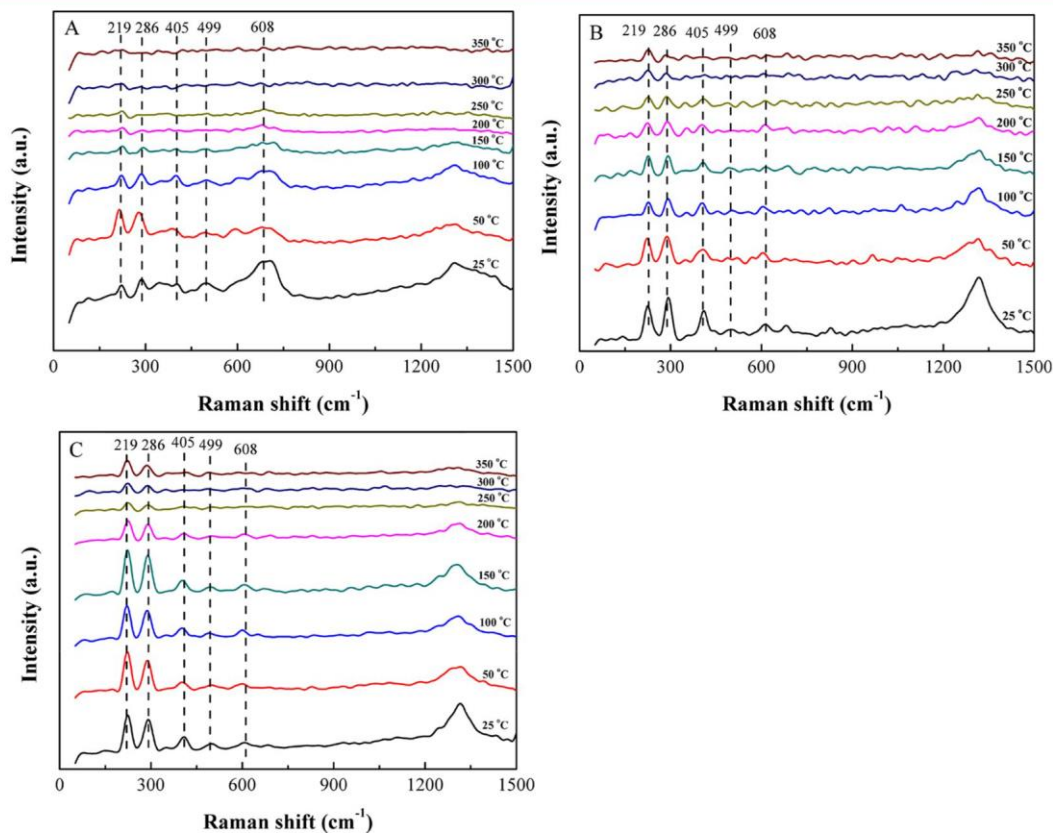


Figure 5. In situ Raman spectra of (A)  $Fe_2O_3$ -S, (B)  $Fe_2O_3$ -C, and (C)  $Fe_2O_3$ -R.

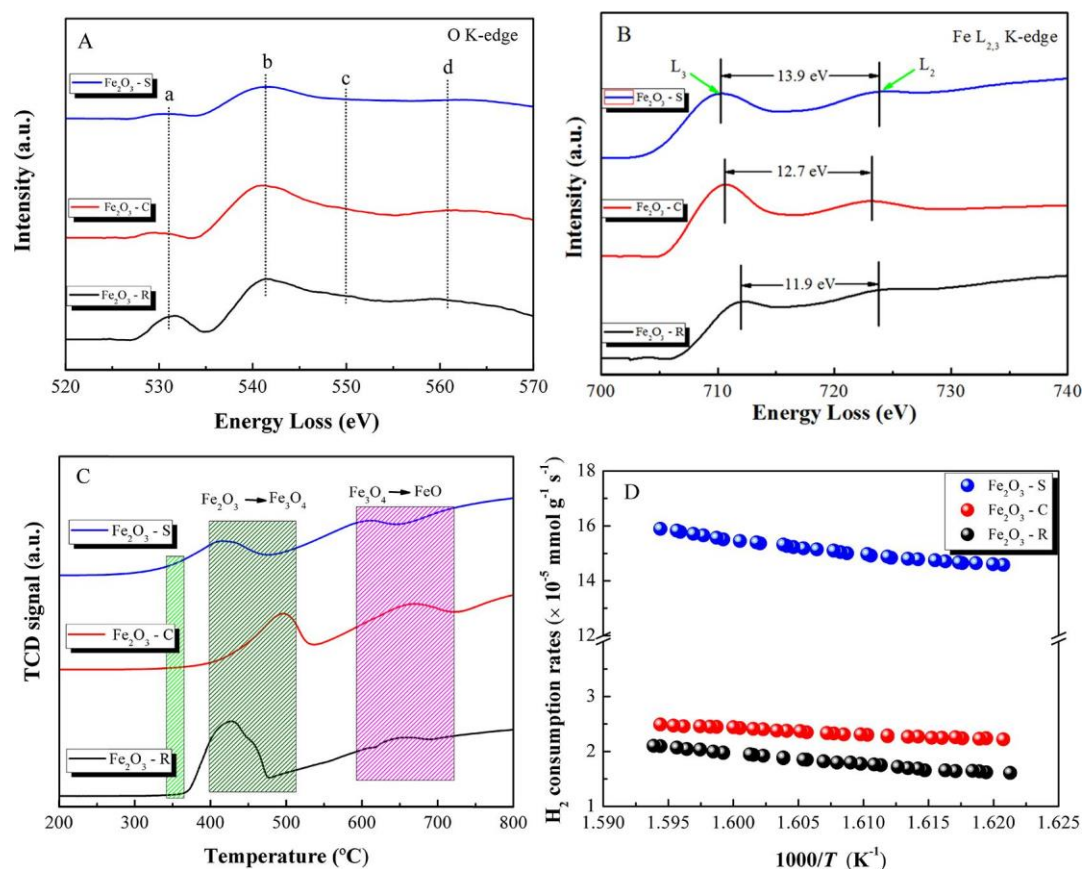


Figure 6. EELS spectra of (A) oxygen K-edge ELNES and (B) Fe L-edge of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (C) H<sub>2</sub>-TPR profiles and (D) initial H<sub>2</sub> consumption rates of synthesized catalysts.

metal 4s and 4p states. The c and d result from the scattering of the third and first oxygen coordination shells by outgoing or backscattering electrons.<sup>44,45</sup> It is obvious that the intensities of a and b of Fe<sub>2</sub>O<sub>3</sub>-S are lower than those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R samples (Fe<sub>2</sub>O<sub>3</sub>-S < Fe<sub>2</sub>O<sub>3</sub>-C < Fe<sub>2</sub>O<sub>3</sub>-R). The intensity decreases of a and b are caused by the oxygen vacancies inside the prepared materials, resulting in diminishing hybridization of metal 3d and O 2p orbitals.<sup>44</sup> As such, it can be demonstrated that the amount of oxygen vacancies in all materials follows the order of Fe<sub>2</sub>O<sub>3</sub>-S > Fe<sub>2</sub>O<sub>3</sub>-C > Fe<sub>2</sub>O<sub>3</sub>-R. The ionization state of the metal cation can be provided by the L edge via the determination of intensity and relative position of individual L<sub>3</sub> and L<sub>2</sub> edges, respectively.<sup>44</sup> Figure 6B represents the Fe L<sub>2,3</sub> K-edge spectra of Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R. It can be noted that the L<sub>3</sub> line is the transition 2p<sub>3/2</sub> → 3d<sub>3/2</sub>3d<sub>5/2</sub>, whereas the L<sub>2</sub> line refers to the transition 2p<sub>1/2</sub> → 3d<sub>3/2</sub>. For Fe<sub>2</sub>O<sub>3</sub>-S, the L<sub>3</sub> line is located at 710.3 eV and is separated by 13.9 eV from the L<sub>2</sub> line; however, the corresponding data are 710.5 and 12.7 eV and 711.9 and 11.9 eV for Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R, respectively. The chemical shift of L<sub>3</sub> lines likely results from oxygen vacancies, which partially decrease the oxidation states of Fe cations from Fe<sup>3+</sup> to Fe<sup>2+</sup>.<sup>44,45</sup> By comparing the degree of chemical shift of L<sub>3</sub> lines, it can be concluded that Fe<sub>2</sub>O<sub>3</sub>-S has the maximum amount of oxygen vacancies, followed by Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R, in accordance with the result of oxygen K-edge energy loss (Figure 6A).

3.3. Reducibility. Figure 6C and Figure S3 represent the H<sub>2</sub>-TPR profiles of prepared materials, and all samples present two H<sub>2</sub> consumption stages due to the reduction of Fe<sub>2</sub>O<sub>3</sub> to

Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> to FeO.<sup>36,46</sup> The theoretical H<sub>2</sub> consumption amount for the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> is 2.09 mmol g<sup>-1</sup>. In the present work, the H<sub>2</sub> consumption amount of the first reduction stage for Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R samples are 2.07, 2.06 and 2.03 mmol g<sup>-1</sup>, respectively, indicating that a substantial fraction of Fe<sup>3+</sup> in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be reduced to Fe<sup>2+</sup> below 550 °C. For the purpose of comparing the reducibility at low temperature for the prepared samples, the initial H<sub>2</sub> consumption of the first reduction band was calculated for each sample before phase transition (the initial H<sub>2</sub> consumption of the first reduction band of the catalyst is less than 25%),<sup>49</sup> and the results are shown in Figure 6D. It can be noted that the initial H<sub>2</sub> consumption rate (IH<sub>2</sub>, Table 1) of Fe<sub>2</sub>O<sub>3</sub>-S is much higher than those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R

with an order of Fe<sub>2</sub>O<sub>3</sub>-S ≫ Fe<sub>2</sub>O<sub>3</sub>-C > Fe<sub>2</sub>O<sub>3</sub>-R. For instance, the IH<sub>2</sub> of Fe<sub>2</sub>O<sub>3</sub>-S at 350 °C is 1.5 × 10<sup>-4</sup> mmol g<sup>-1</sup> s<sup>-1</sup>, over six times higher than those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R. To investigate the nature of oxygen species involved in ethane oxidation, O<sub>2</sub>-TPD experiments were conducted. As shown in Figure S4, all samples display two desorption peaks centered at around 150 and 500 °C. The first peak ( $\alpha$ 1-oxygen) can be attributed to the physically adsorbed oxygen or O<sub>2</sub><sup>-</sup> (ad) species.<sup>48</sup> The second peak ( $\alpha$ 2-oxygen) is associated with the desorption of chemically adsorbed oxygen O<sup>-</sup> species. Generally speaking, O<sup>-</sup> often belongs to the surface active oxygen,<sup>47</sup> and these surface reactive oxygen species are known to promote the catalytic oxidation activity.<sup>47</sup> Compared with the Fe<sub>2</sub>O<sub>3</sub>-S sample, the O<sub>2</sub> desorption peaks of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R materials obviously shift to higher temperatures, and the intensity of these peaks is also much weaker as a result of



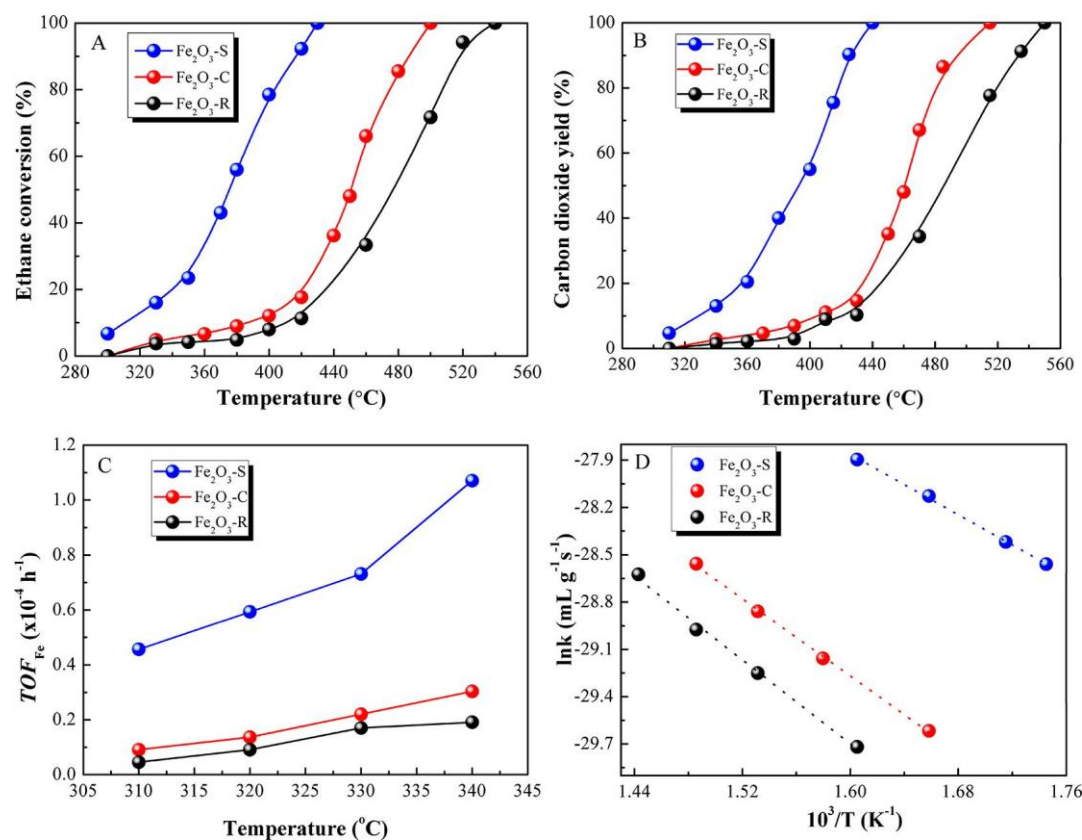


Figure 7. (A) Ignition curve, (B) CO<sub>2</sub> yield, (C) TOF, and (D) apparent activation energy ( $E_a$ ) of different catalysts for ethane oxidation.

Table 4. Catalytic Performance of Prepared Materials for Ethane Oxidation

sample	$T_{50}^a$ (°C)	$T_{90}^a$ (°C)	$r_1^b$ ( $\times 10^{-3}$ mmol mL <sup>-1</sup> h <sup>-1</sup> )	$r_2^b$ ( $\times 10^{-3}$ mmol mL <sup>-1</sup> h <sup>-1</sup> )	$TOF_{Fe1}^c$ ( $\times 10^{-4}$ h <sup>-1</sup> )	$TOF_{Fe2}^c$ ( $\times 10^{-4}$ h <sup>-1</sup> )	$E_a^d$ (kJ mol <sup>-1</sup> )
Fe <sub>2</sub> O <sub>3</sub> -S	380	415	0.46	0.67	0.73	1.07	39.7
Fe <sub>2</sub> O <sub>3</sub> -C	450	485	0.14	0.19	0.22	0.30	50.9
Fe <sub>2</sub> O <sub>3</sub> -R	480	515	0.11	0.12	0.17	0.19	55.3

<sup>a</sup>Temperatures at 50 and 90% conversion of ethane. <sup>b</sup>Reaction rate of ethane converted over various catalysts at 330 and 340 °C. <sup>c</sup>Turnover frequency based on Fe at 330 and 340 °C. <sup>d</sup>Apparent activation energy obtained from Arrhenius plots.

the surface oxygen vacancies. Compared with the area of desorption peaks, it can be found that the amount of oxygen released from Fe<sub>2</sub>O<sub>3</sub>-S is much higher than those from Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R samples.

**3.4. Catalytic Activity.** Figure 7A,B reveals that the catalytic activity of prepared materials for ethane destruction follows the sequence of Fe<sub>2</sub>O<sub>3</sub>-S > Fe<sub>2</sub>O<sub>3</sub>-C > Fe<sub>2</sub>O<sub>3</sub>-R. Under a GHSV of 12000 h<sup>-1</sup>, the Fe<sub>2</sub>O<sub>3</sub>-S sample can completely decompose 2500 ppm of ethane into CO<sub>2</sub> at 430 °C, which is significantly lower than that of Fe<sub>2</sub>O<sub>3</sub>-C (500 °C) and Fe<sub>2</sub>O<sub>3</sub>-R (540 °C). Figure 7C demonstrates that the TOF<sub>Fe</sub> values of Fe<sub>2</sub>O<sub>3</sub>-S for ethane oxidation are much higher than those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R materials. For example, in Table 4, the calculated TOF<sub>Fe</sub> values at 330 °C ( $0.73 \times 10^{-4}$  h<sup>-1</sup>) and 340 °C ( $1.07 \times 10^{-4}$  h<sup>-1</sup>) of Fe<sub>2</sub>O<sub>3</sub>-S are over three ( $0.22 \times 10^{-4}$  h<sup>-1</sup> at 330 °C;  $0.30 \times 10^{-4}$  h<sup>-1</sup> at 340 °C) and five ( $0.17 \times 10^{-4}$  h<sup>-1</sup> at 330 °C;  $0.19 \times 10^{-4}$  h<sup>-1</sup> at 340 °C) times higher than those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R, respectively, demonstrating the excellent low-temperature activity of Fe<sub>2</sub>O<sub>3</sub>-S for ethane destruction. In addition to this, further introduction of apparent activation energy ( $E_a$ ) to compare the catalytic activity of synthetic materials as catalysts and lower  $E_a$  value can make ethane more easily oxidized. According to the

catalyst map of Arrhenius for ethane oxidation (Figure 7D), the  $E_a$  values for ethane oxidation increase in the order Fe<sub>2</sub>O<sub>3</sub>-S (39.7 kJ mol<sup>-1</sup>) < Fe<sub>2</sub>O<sub>3</sub>-C (50.9 kJ mol<sup>-1</sup>) < Fe<sub>2</sub>O<sub>3</sub>-R (55.3 kJ mol<sup>-1</sup>) (Table 4), suggesting that ethane is more easily oxidized over Fe<sub>2</sub>O<sub>3</sub>-S. Table S4 documented some typical catalysts reported in the literature for ethane oxidation. It is shown that 0.98% Co/1.27% Cu-ZSM-5 had a T<sub>50</sub> value of 420 °C for ethane combustion,<sup>50</sup> and TiO<sub>2</sub> had a T<sub>50</sub> value greater °C for ethane combustion.<sup>51</sup> Catalysts of than480 La<sub>0.7</sub>Sr<sub>0.3</sub>Mn<sub>0.75</sub>Co<sub>0.25</sub>O (T<sub>50</sub> of 476 °C and T<sub>90</sub> of 485 °C)<sup>52</sup> and La<sub>0.7</sub>Bi<sub>0.3</sub>Mn<sub>0.75</sub>Co<sub>0.25</sub>O<sub>3</sub> (T<sub>50</sub> of 427 °C and T<sub>90</sub> of 542 °C)<sup>53</sup> were also less active than the Fe<sub>2</sub>O<sub>3</sub>-S catalyst. Ethane conversion over the Fe<sub>2</sub>O<sub>3</sub>-S catalyst was even higher than some noble metal loaded catalysts (e.g., T<sub>50</sub> and T<sub>90</sub> of 425 and 475 °C, respectively, over a reported Pt/Al<sub>2</sub>O<sub>3</sub> material).<sup>55</sup>

**3.5. Catalytic Stability.** Reaction stability is a key criterion for industrial applications. Figure 8A shows that Fe<sub>2</sub>O<sub>3</sub>-S has excellent ethane combustion stability, and only a slight decrease in ethane conversion from 91 to 88% can be observed in the first 30 h. In addition, the stability of Fe<sub>2</sub>O<sub>3</sub>-S for ethane destruction at a lower temperature of 360 °C was also studied, as displayed in Figure 8B. We found that Fe<sub>2</sub>O<sub>3</sub>-S possesses satisfied reaction stability at different temperatures,

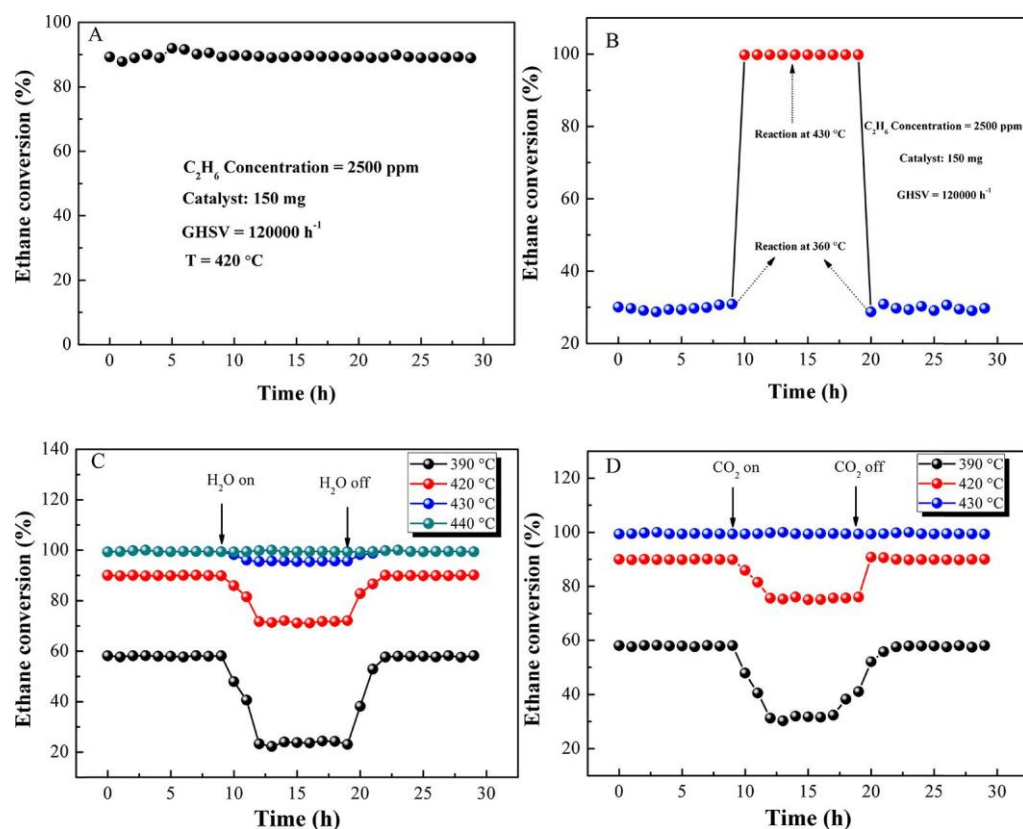


Figure 8. (A, B) Catalytic stability and effect of (C) H<sub>2</sub>O and (D) CO<sub>2</sub> on the conversion of ethane over the Fe<sub>2</sub>O<sub>3</sub>-S catalyst.

and the heating and cooling processes have an insignificant effect on the activity of Fe<sub>2</sub>O<sub>3</sub>-S. The good stability provides the possibility for the practical elimination of ethane. As shown in Figure S5, the Fe<sub>2</sub>O<sub>3</sub>-S sample has almost no weight loss in a temperature range of 20–700 °C. The desorption of oxygen and water leading to the weight losses of Fe<sub>2</sub>O<sub>3</sub>-C (0.2 wt %) and Fe<sub>2</sub>O<sub>3</sub>-R (0.5 wt %) in a temperature range of 20–100 °C can be attributed to the desorption of H<sub>2</sub>O and oxygen,<sup>54</sup> and no weight loss can be found when the temperature is further increased. Above results indicate the good thermal stability of prepared catalysts. Coke deposition on Fe<sub>2</sub>O<sub>3</sub>-S after the stability test was further analyzed, as shown in Figure S6. The used sample displays two stages of small weight losses in a temperature range of 20–700 °C. The first one at 20–200 °C (0.3 wt %) can be attributed to the combustion/desorption of adsorbed C<sub>2</sub>H<sub>6</sub> and the desorption of O<sub>2</sub> and H<sub>2</sub>O, and the second one at 200–700 °C (0.9 wt %) corresponds to the combustion of coke deposited on the catalyst,<sup>54</sup> which demonstrates that Fe<sub>2</sub>O<sub>3</sub>-S is an effective catalyst for catalytic oxidation of C<sub>2</sub>H<sub>6</sub>. The crystal structure of the Fe<sub>2</sub>O<sub>3</sub>-S catalyst after reaction was determined by XRD, as shown in Figure S7. The diffraction peaks of the used Fe<sub>2</sub>O<sub>3</sub>-S sample are almost unchanged compared with the fresh sample, indicating that Fe<sub>2</sub>O<sub>3</sub>-S has a good chemical stability in catalytic reaction.

The influences of H<sub>2</sub>O and CO<sub>2</sub> on catalytic activity of prepared materials for ethane destruction were further investigated. Results show that the addition of H<sub>2</sub>O (10 vol %) has negative effects on the conversion of ethane (especially at low temperatures (<420 °C)) due to the competition between water and oxygen adsorption on the catalyst surface; however, this negative effect becomes smaller when the reaction temperature is increased, and the influence of H<sub>2</sub>O

can be ignored at 440 °C. It is indicated that the deactivation of the catalyst was reversible, and a complete conversion of ethane can be restored when H<sub>2</sub>O was no longer added, although recovery took longer at low temperatures.<sup>56</sup> Similarly, the introduction of CO<sub>2</sub> (10 vol %) also has obvious inhibition effects on ethane conversion, and increase in the reaction temperature can obviously reduce this effect (can be ignored at 430 °C). Moreover, when the addition of CO<sub>2</sub> was stopped, the catalytic activity recovered immediately, whereas a longer time was taken to recover the activity of the catalyst after stopping the addition of water vapor, suggesting that H<sub>2</sub>O was adsorbed more strongly than CO<sub>2</sub> to active sites.

## 4. DISCUSSION

4.1. Adsorption of Ethane. Figure S8 shows the in situ DRIFTS spectra of O<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> adsorption on prepared samples at room temperature. The IR bands in the region of 3100–2800 cm<sup>-1</sup> can be assigned to the C–H stretching (ν<sub>CH</sub>) of alkanes or adsorbed C–H bond containing species, and the peaks at 3000–2850 cm<sup>-1</sup> can be attributed to the ν<sub>CH</sub> of C<sub>2</sub>H<sub>6</sub>.<sup>57</sup> A broad band with a maximum at 3700–3100 cm<sup>-1</sup> belongs to the sorbed water or acidic OH groups that are hydrogen-bonded to the basic oxygen atoms of the catalysts.<sup>58</sup> It is well known that stretching bands for gaseous ethane were at 2954 and 2994 cm<sup>-1</sup>.<sup>59</sup> Table S3 reveals that the position of C–H stretching bands for adsorbed ethane over Fe<sub>2</sub>O<sub>3</sub>-S, Fe<sub>2</sub>O<sub>3</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-R samples is similar, while all the bands are red-shifted to some extent in comparison with those of gaseous ethane due to a combination of ligand-to-metal electron donation from the C–H σ-bond to vacant Fe<sup>3+</sup> s-orbit combined with the metal-to-ligand back donation from the iron dπ-orbital to C–H σ\*-orbital because these interactions lead

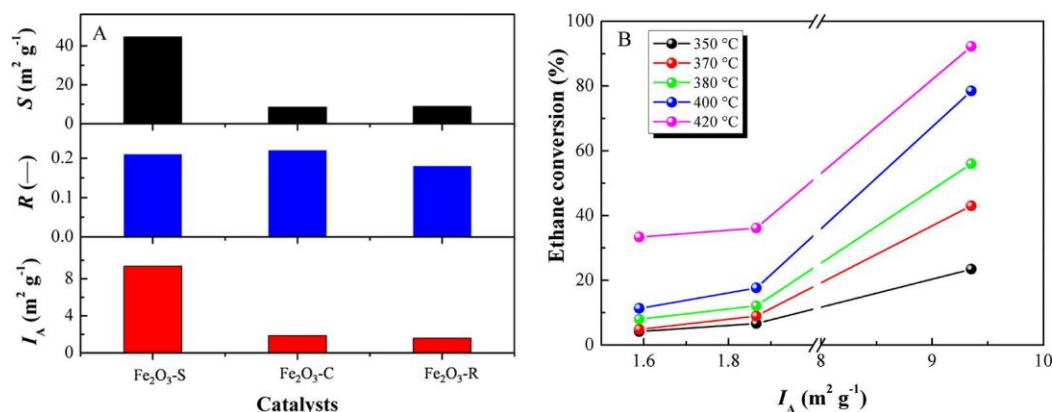


Figure 9. (A) Correlation between S, R, and I<sub>A</sub>. (B) Relation between the conversion of ethane and index I<sub>A</sub> for all catalysts.

to a very marked weakening of the C–H bond.<sup>59,60</sup> It has been proved that the adsorption of light alkanes by metal oxides in the form of cations results in the change of relative intensity distribution of absorption bands, which largely depends on the properties of cations and metallic oxides.<sup>60</sup> According to the adsorption strength of ethane on all samples, it is found that Fe<sub>2</sub>O<sub>3</sub>-C is easier to adsorb water than ethane. However, compared with water, it has stronger adsorption for ethane on Fe<sub>2</sub>O<sub>3</sub>-S and Fe<sub>2</sub>O<sub>3</sub>-R. It is also shown that the strongest perturbation and polarization oscillations are initially fully symmetrical C–H stretching oscillations, which are directly related to the chemical activation of adsorbed molecules.<sup>61</sup> The greatest red shift of the C–H band was observed for C<sub>2</sub>H<sub>6</sub> adsorption on Fe<sub>2</sub>O<sub>3</sub>-S. This means that Fe<sub>2</sub>O<sub>3</sub>-S has stronger chemical activation for ethane molecules.<sup>61</sup>

Figure S9 shows the in situ DRIFT spectra of ethane and air adsorption over synthesized catalysts at different temperatures. The intensity of bands at 3700–3100 cm<sup>-1</sup> shows a continuous reduction (disappeared at 150 °C) when increasing the temperature, indicating the removal of sorbed water from materials.<sup>62</sup> It should be noted that the intensity variation of bands at 3100–2800 cm<sup>-1</sup> assigned to the C–H stretching (ν<sub>CH</sub>) of alkanes or adsorbed C–H bond containing species over Fe<sub>2</sub>O<sub>3</sub>-S (even visible at 200 °C) is much smaller than those over Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R materials, suggesting the strongest ethane adsorption (dissociative adsorption) over the Fe<sub>2</sub>O<sub>3</sub>-S sample. As shown in Figure S9, for Fe<sub>2</sub>O<sub>3</sub>-S, the intensity of the bands in the region of 2800–3100 cm<sup>-1</sup> is the strongest among all samples, indicating that ethane adsorbed on Fe<sub>2</sub>O<sub>3</sub>-S has a lower activation barrier.<sup>63</sup>

**4.2. Correlation of Physicochemical Property and Activity.** Specific surface area, concentration and distribution of reactive oxygen species, surface defects and oxygen vacancies, and catalyst reducibility can affect its catalytic performance in oxidation reaction. Zheng et al.<sup>8</sup> proved that the high density of Fe atoms on the exposure {110} planes of α-Fe<sub>2</sub>O<sub>3</sub> leads to high activity for catalytic combustion of CO. Kameoka et al.<sup>56</sup> stated that surface Fe sites on La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (x = 0.0–1.0) perovskites are an active species for methane combustion.

Kouotou et al.<sup>1</sup> proved that the more iron content in α-Fe<sub>2</sub>O<sub>3</sub> exposed planes, the more active sites for catalytic for catalytic combustion of propene. As it is known, the density of active sites such as the iron atoms is different over various exposed planes in a hematite crystal structure. Table 1 shows that the specific surface area of prepared catalysts and the

surface metal compositions obtained from XPS analysis are included in Figure 9. Fe/(Fe + O), defined as the R ratio, is an important factor representing α-Fe<sub>2</sub>O<sub>3</sub> catalyst activity. Surface area plays a role in catalyst activity, the product of the BET surface area (S) and R, defined as the index I<sub>A</sub>.<sup>56</sup> It is worth noting that the content of iron atoms over all catalysts is smaller than two-thirds because all catalysts adsorbed a large amount of oxygen on their surface. Figure 9 shows the relationships of different parameters (S, R, and I<sub>A</sub>; I<sub>A</sub> and ethane conversion) of different catalysts, and results indicate that the surface Fe content over catalysts is directly proportional to the conversion of ethane. Fe<sub>2</sub>O<sub>3</sub>-S has a maximum I<sub>A</sub> value (9.35 m<sup>2</sup> g<sup>-1</sup>) and has the highest catalytic activity for catalytic oxidation of ethane.

The Mars van Krevelen (MVK) mechanism has been widely used in interpreting the catalytic oxidation process of hydrocarbons, especially for hydrocarbon oxidation over transition metal oxides, which involves a redox cycle (migration of bulk oxygen to the catalyst surface to oxidize hydrocarbon molecules and replace the bulk oxygen by oxygen from the gas phase) and is closely related to the mobility of the lattice oxygen.<sup>1</sup> As such, the oxygen mobility associated with catalyst reducibility is an important factor for the MVK mechanism.<sup>64</sup> Taking into account the TPR results, it can be concluded that the lattice oxygen mobility in the prepared samples is in the order of Fe<sub>2</sub>O<sub>3</sub>-S > Fe<sub>2</sub>O<sub>3</sub>-C > Fe<sub>2</sub>O<sub>3</sub>-R. High lattice oxygen mobility can accelerate the redox cycle in ethane oxidation and guarantee the superior activity of Fe<sub>2</sub>O<sub>3</sub>-S. On the basis of the MVK mechanism and in situ DRIFTS results displayed in Figure S8, a reaction scheme for ethane oxidation was proposed: First, ethane is considered to be adsorbed dissociatively on the surface of the catalyst with extraction of a hydrogen atom and then the release of oxygen atom along with the reduction of the catalyst. Finally, oxygen from the gas phase will reoxidize the reduced iron cations to Fe<sub>2</sub>O<sub>3</sub>.<sup>65</sup>

XPS results reveal that the percentage of O<sub>β</sub> on the Fe<sub>2</sub>O<sub>3</sub>-S catalyst (0.72) is higher than those of Fe<sub>2</sub>O<sub>3</sub>-C (0.59) and Fe<sub>2</sub>O<sub>3</sub>-R (0.55), indicating that Fe<sub>2</sub>O<sub>3</sub>-S possesses higher concentration of chemisorbed oxygen species, which leads to higher proportion of Fe<sup>3+</sup> in Fe<sub>2</sub>O<sub>3</sub>-S and has generated more oxygen vacancies (Figure 9).<sup>66</sup> Results of EELS (Figure 6) and Raman (Figure 4) also suggest that the concentration of oxygen vacancies on Fe<sub>2</sub>O<sub>3</sub>-S is higher than those of Fe<sub>2</sub>O<sub>3</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-R. Above results indicate that the Fe<sub>2</sub>O<sub>3</sub>-S sample can produce more reactive oxygen species participating in the oxidation of ethane. Additionally, Mössbauer spectroscopy and Raman

results reveal that there are more defect sites over F2O3-S than F2O3-C and F2O3-R samples, which enhance the oxygen transfer and reduction efficiency, promoting the ethane oxidation rate.<sup>66</sup>

4.3. Formation Energy of Oxygen Vacancy. Oxygen vacancies are suggested to play an important role in the decomposition of ethane, and its activity much rests with the nature of oxygen vacancy.<sup>67</sup> In the present work, the formation energy of a single O defect at  $\alpha$ -Fe2O3 exposed facets is studied by DFT calculations, as shown in Figure 10. Results

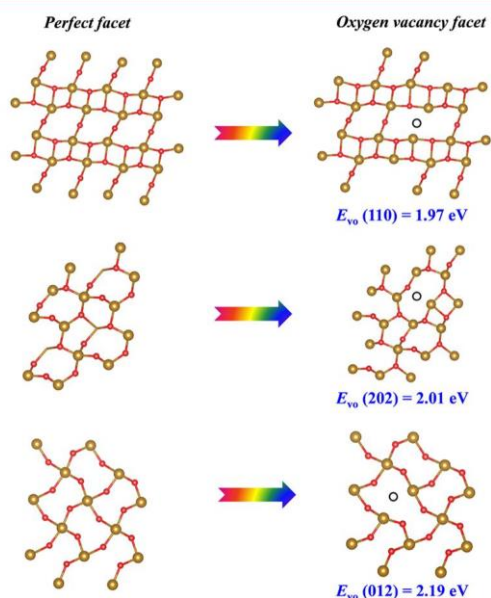


Figure 10. Formation energy of oxygen vacancy over  $\alpha$ -Fe2O3 with different exposed facets.

demonstrate that the formation energy of oxygen vacancy on the (110) facet ( $E_{VO}(110) = 1.97$  eV) is lower than those of (202) facet ( $E_{VO}(202) = 2.01$  eV) and (012) facet ( $E_{VO}(012) = 2.19$  eV), indicating that the oxygen vacancies are more

easier to form on (110) facets of F2O3-S (consistent with the in situ Raman results (Figure S2)), endowing the superior ethane destruction activity of the F2O3-S catalyst.

4.4. Adsorption of O2, C2H6, and H2O on Exposed Facets. The O2 adsorption capability is a very important parameter for VOC oxidation reactions according to the MVK mechanism. As such, the adsorption energy of O2 on different perfect facets and facets with oxygen vacancies was obtained by DFT (Figure 11). The perfect facets of (110), (202), and (12) have an analogous adsorption capacity for oxygen, and the adsorption energy is very small (0.2 eV); it shows that the adsorption of O2 on all perfect facets showed very weak physical adsorption. However, when the oxygen vacancy is introduced to the crystal surface, the adsorption energy of molecular O2 on all facets becomes higher, which indicates that oxygen vacancy is more conducive to catalytic oxidation of ethane. The adsorption energies of O2 on facets with oxygen vacancies of (110), (202), and (012) are 1.58, 1.55 and 1.22 eV, respectively (Figure 11), indicating that O2 is easily adsorbed on the face of (110). In addition, the (110) surface is strongly bonded with O2 with the O-O bond distance, which is 1.405 Å. The longer bond length than this on the (202) (1.394 Å) and (012) (1.371 Å) facets indicates that O2 can be destroyed more and activated easily. The strong adsorption of O2 on the (110) surface facilitates the quick addition of oxygen consumed by the oxidation reaction and is beneficial to the catalytic oxidation of ethane. The corresponding adsorption energies of ethane on (110), (202), and (012) surfaces were calculated to be -0.26, -0.23, and -0.21 eV, respectively (Figure S10), in good accordance to the order of catalytic performance of prepared materials. In addition, the adsorption energy of water on the (110) surface is calculated. As shown in Figure S11, we found that the adsorption energy of H2O (-1.54 eV) is close to that of O2 (-1.58 eV), suggesting the reason for the competition between water and oxygen adsorption on the surface of the catalyst.

Figure 12 shows the total electronic density of states (DOS) and its projections over the 3d orbitals of iron cations and the 2p orbitals of the O anions for (110), (202), and (012)

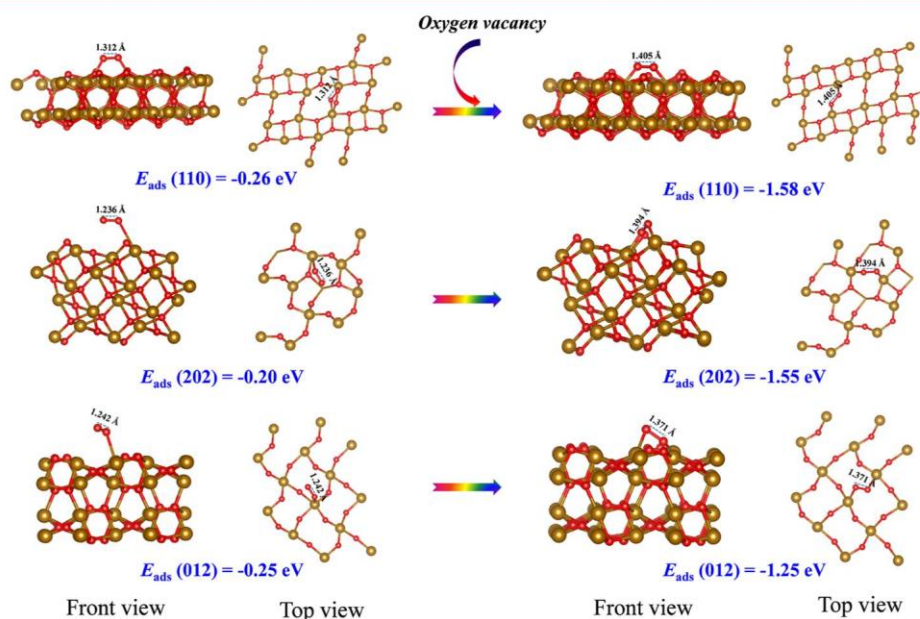


Figure 11. Adsorption energy of O2 over  $\alpha$ -Fe2O3 with different exposed perfect crystal surfaces and crystal surfaces with oxygen vacancies.

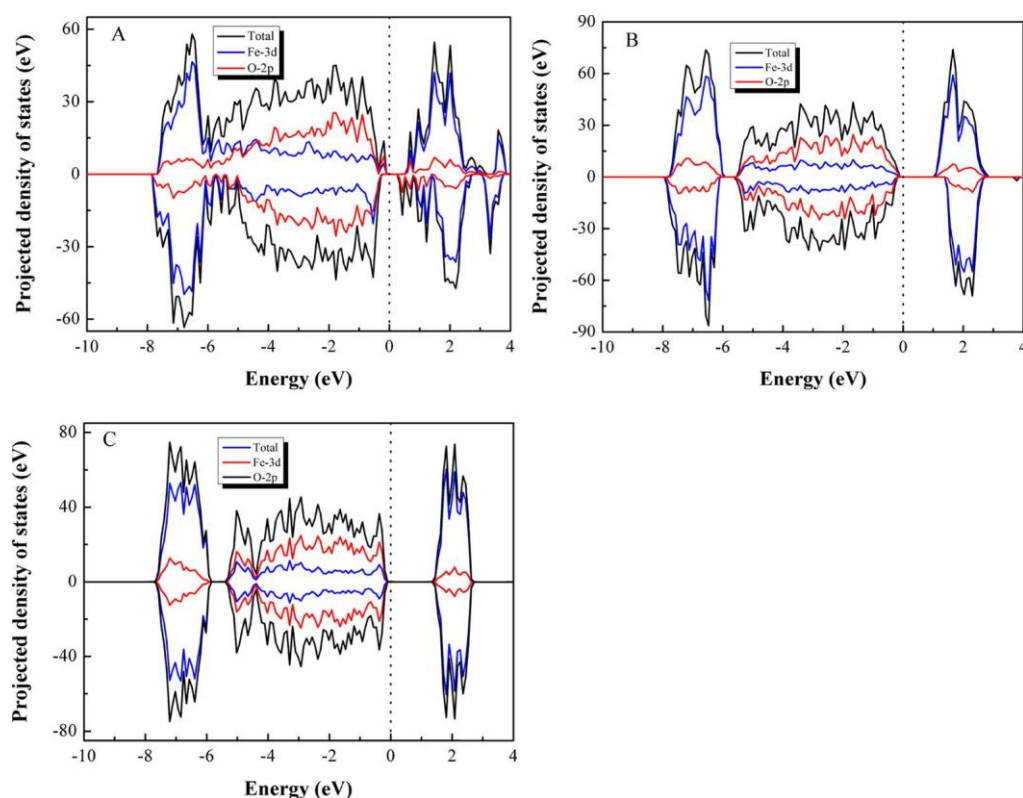


Figure 12. Projected density of states (PDOS) of different catalysts: (A) Fe<sub>2</sub>O<sub>3</sub>-S, (B) Fe<sub>2</sub>O<sub>3</sub>-C, and (C) Fe<sub>2</sub>O<sub>3</sub>-R (Fe 3d and O 2p states are plotted as solid and dotted lines, respectively). The Fermi energy is set to be 0, highlighted by a black vertical dashed line.

surfaces of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>68</sup> For all samples, the top of the valence band is mainly of O 2p character, while the occupied 3d levels of Fe lie around 6–8 eV below the Fermi level. The unoccupied 3d levels of Fe, which have an octahedral coordination, mainly populate the bottom of the conduction band.<sup>68</sup> As such, maghemite is a charge transfer-type insulator, and the first excitation term should correspond to the transfer of electrons from O<sup>2-</sup> anions to octahedral Fe<sup>3+</sup> cations.<sup>68</sup> Furthermore, the existence of some of these surface states in the bulk band gap indicates the variation of metal characteristics in all of these models.<sup>68</sup> By gathering the DOSs of surface ions, the (110) surface shows the highest metallic behavior with a narrow band gap of 0.26 eV compared to the (202) and

(12) surfaces with band gaps of about 1.11 and 1.46 eV, respectively. These results highlight the promising role of the (110) surface of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in surface redox reactions.

For the (110) surface, the electronic state covers most of the bulk band gap regions and shows higher polarity on the surface than other regions because the stabilization of the polarized surface can be achieved by the depolarization field, which causes some changes in the electronic surface state so that some states appear in the bulk band gap region.<sup>68</sup> Subsequently, neutralization of the polarized surfaces can be obtained by the flow of free charge within the surface layer.<sup>68</sup> The (110) surface shows the highest metal features with a very narrow band gap. Furthermore, these states can provide a depolarizing field, which has a vital role in the stabilization of the polar termination.<sup>68</sup>

Finally, the (100) surfaces are more polar than stoichiometry, which cause a relatively low stability of these models. It is indicated that the (110) surface is more likely to lose electrons, which makes it easier for oxidation–reduction reactions.

## 5. CONCLUSIONS

In summary,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples with different morphologies were successfully synthesized by the simple solvothermal method. Fe<sub>2</sub>O<sub>3</sub>-S exhibits superior catalytic activity in the oxidation of ethane due to its highest low-temperature reducibility and largest number of active surface lattice defects and oxygen vacancies. Theoretical calculations confirm that the exposed (110) facet has the lowest oxygen vacancy formation energy (1.97 eV), which is favorable for the formation of surface active oxygen species. In addition, the exposed (110) facets facilitate the adsorption and activation of O<sub>2</sub> ( $E_{\text{ads}} = -1.58$  eV; bond length of adsorbed O<sub>2</sub> is 1.405 Å, which is far greater than the distances of 1.394 and 1.371 Å for (202) and (12) facets) and an easier redox process, which promotes the ethane oxidation activity. These results can provide a simple and effective strategy for the engineering design of reaction exposed surfaces and deepen the understanding of the small side-related catalytic activity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in hydrocarbon destruction.

## ASSOCIATED CONTENT

N<sub>2</sub> adsorption–desorption isotherms and pore size distribution, intensity of the fitted  $E_g$ , LO, and T bands present in the Raman spectra, in situ Raman spectra, TPR profiles, in situ DRIFTS spectra of ethane adsorption, summary of some active catalysts for ethane oxidation, and adsorption energy of ethane and H<sub>2</sub>O on catalysts (PDF)

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### Notes

The authors declare no competing financial interest.

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