

# Subnano-FeO<sub>x</sub> Clusters Anchored in an Ultrathin Amorphous Al<sub>2</sub>O<sub>3</sub> Nanosheet for Styrene Epoxidation

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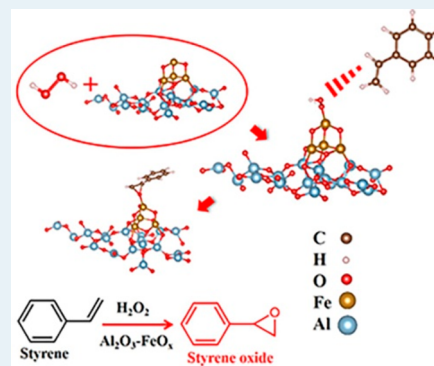
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**ABSTRACT:** The development of low-cost, high-performance catalysts at the atomic level has drawn scientists' attention due to the high atom efficiency, unique structure, and potentially high catalytic selectivity. Among the atomically tailored catalysts, nanoclusters are of particular interest because they represent an underexplored medium state between isolated single atoms and typical nanoparticles. In this study, we report a wet-chemistry approach to synthesize highly dispersed subnano-FeO<sub>x</sub> clusters anchored on an ultrathin amorphous Al<sub>2</sub>O<sub>3</sub> nanosheet (or Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet) and its excellent catalytic performance for selective conversion of styrene to styrene oxide. The reasons for the high catalytic performance of the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet are 2-fold. One is that the unsaturated and amorphous nature of the Fe atoms in the subnano-FeO<sub>x</sub> clusters promotes the adsorption of styrene onto the catalytic sites of FeO<sub>x</sub> clusters for epoxidation. The other is that the amorphous Al<sub>2</sub>O<sub>3</sub> nanosheet prevents the aggregation of catalytic FeO<sub>x</sub> clusters during the epoxidation reaction because its defective structure immobilizes the FeO<sub>x</sub> clusters.

**KEYWORDS:** 2D material, subnanocluster, catalysis, styrene epoxidation, amorphous material



## INTRODUCTION

Nanoclusters are a new class of nanomaterials that typically contain from two to a few hundred atoms. Nanoclusters often show unique catalytic performance relative to their bulk counterparts due to the quantum confinement effect,<sup>1–3</sup> and more impressively, their properties are highly tunable at the atomic level.<sup>4,5</sup> Previous studies have demonstrated that noble metal nanoclusters exhibit significantly enhanced catalytic activities for the oxygen reduction reaction,<sup>6,7</sup> hydrogen evolution reaction,<sup>8</sup> and selective hydrogenation of nitrobenzene,<sup>9</sup> acetophenone,<sup>10</sup> and phenylacetylene.<sup>11</sup> The excellent catalytic activity of the noble metal nanoclusters was attributed to the large number of active sites of the nanoclusters and the strong interactions between the metallic nanoclusters and the support matrix. However, the real-world applications of these noble metal nanocluster catalysts are limited due to their high cost, scarcity, and poor long-term stability.<sup>12,13</sup> There is an unmet need for low-cost alternatives.

The 3d transition metals such as Fe, Co, and Ni are being studied to substitute for these noble metal-based catalysts.<sup>14–16</sup> Among these 3d transition metals, Fe is the most promising one due to its high natural abundance and tunable 3d orbital configuration. However, it remains challenging to anchor Fe species with high loading on a solid support while preventing the aggregation of Fe atoms or clusters into large particles during catalytic reactions, which causes the catalyst degradation. A popular strategy to overcome this challenge is to form coordination bonds between metal species with the functional

groups of the solid support.<sup>17,18</sup> Previous studies have reported the use of ordered mesoporous carbon CMK-3,<sup>19–21</sup> pyrolyzed glucosamine,<sup>22</sup> and mesoporous graphitic carbon nitride<sup>23</sup> to support atomic Fe or Fe clusters.

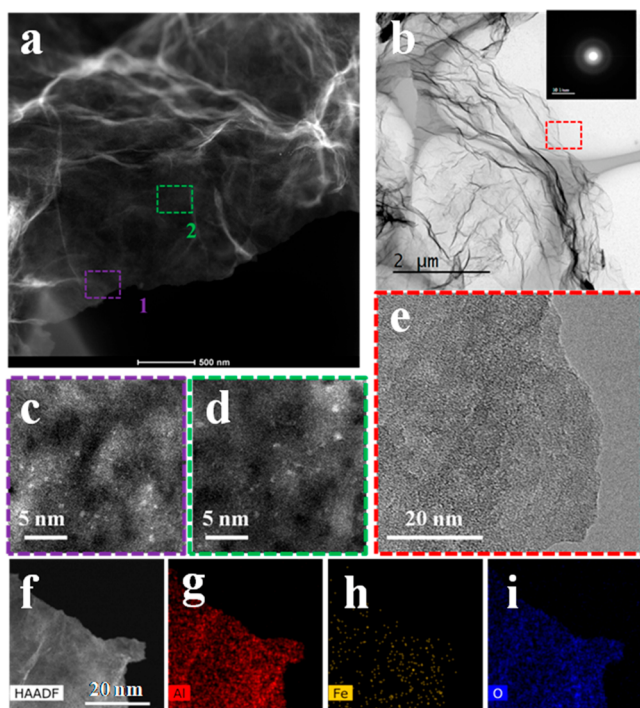
Inspired by these prior studies, we developed a new Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet material which uses ultrathin amorphous Al<sub>2</sub>O<sub>3</sub> nanosheets rich in defects and dangling bonds as the support to disperse FeO<sub>x</sub> nanoclusters with sizes < 1 nm. We tested the catalytic activity of the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet for styrene epoxidation to styrene oxide. The existing catalysts for styrene epoxidation reaction, such as Schiff base complexes,<sup>24</sup> multicomponent metal-organic framework derivatives,<sup>25</sup> and mixed metal oxides,<sup>26</sup> often have a low product selectivity and produce a mixture of styrene oxide and benzaldehyde. Here, we show that the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst addresses the selectivity challenge and achieves a high selectivity of 81% toward styrene oxide in 6 h. Even though the catalytic activity slowly decreased during consecutive runs due to the formation of organic pollutants on the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst, the catalyst can be fully regenerated by calcination, not achievable using commercial Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> catalyst.

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## RESULTS AND DISCUSSION

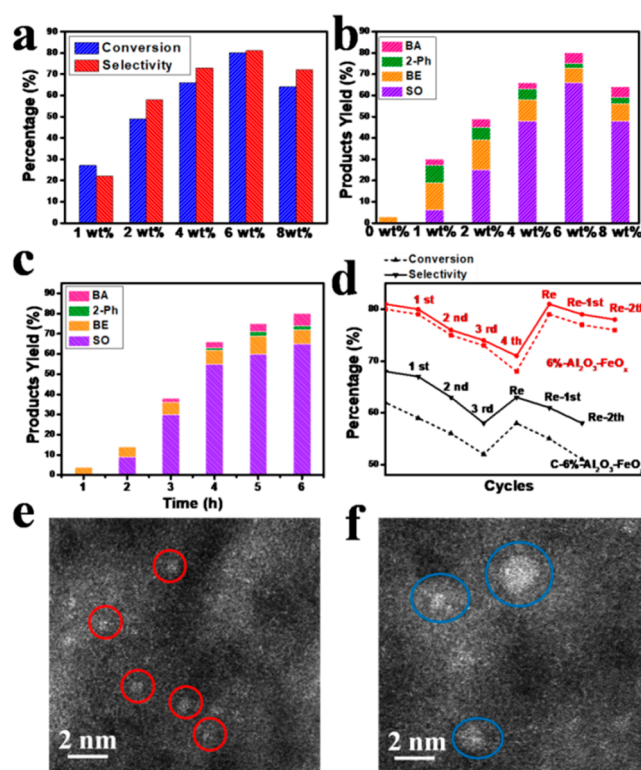
We prepared the  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheets by mixing the  $\text{FeCl}_3$  precursor with ultrathin amorphous  $\text{Al}_2\text{O}_3$  nanosheets in deionized water. The  $\text{Al}_2\text{O}_3$  nanosheets were first synthesized using a previously reported wet-chemical method.<sup>27–30</sup> The mixture of  $\text{FeCl}_3$  and  $\text{Al}_2\text{O}_3$  nanosheets was then freeze dried before being heated to 500 °C under a 5%  $\text{H}_2/\text{Ar}$  atmosphere for 2 h to produce the final  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheets. The Fe loading in  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheets can be adjusted by controlling the amount of  $\text{FeCl}_3$  precursor. We use  $n\%$ - $\text{Al}_2\text{O}_3\text{-FeO}_x$  to name the  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheet samples, where  $n\%$  is the weight ratio of  $\text{FeCl}_3$  and  $\text{Al}_2\text{O}_3$  in the synthesis. Figure 1a–e shows the high-angle annular dark field-



**Figure 1.** Structural characterization of  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheets. (a) HAADF-STEM image of  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheet catalyst with 6 wt % Fe loading, denoted as 6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$ . (b) TEM image with SAED inserted. (c and d) Expanded view of the HAADF images of the purple and green regions labeled in a. (e) HRTEM image captured at the red area in b. (f–i) HAADF-EDS mapping of Al, Fe, and O.

scanning transmission electron microscopy (HAADF-STEM) images (Figure 1a, 1c, and 1d) and the typical transmission electron microscopy (TEM) images (Figure 1b and 1e) of the 6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheets: wrinkled nanosheet uniformly decorated with the subnano- $\text{FeO}_x$  clusters (bright dots in Figure 1c and 1d). The selected area electron diffraction (SAED) pattern in Figure 1b (inset) shows a broad and diffused halo ring, indicating the amorphous state of the  $\text{Al}_2\text{O}_3$  nanosheet. No particle aggregation was found in the TEM image (Figure 1e). The corresponding elemental mapping results in Figure 1f–i reveal that Al, O, and Fe were uniformly distributed across the nanosheet.

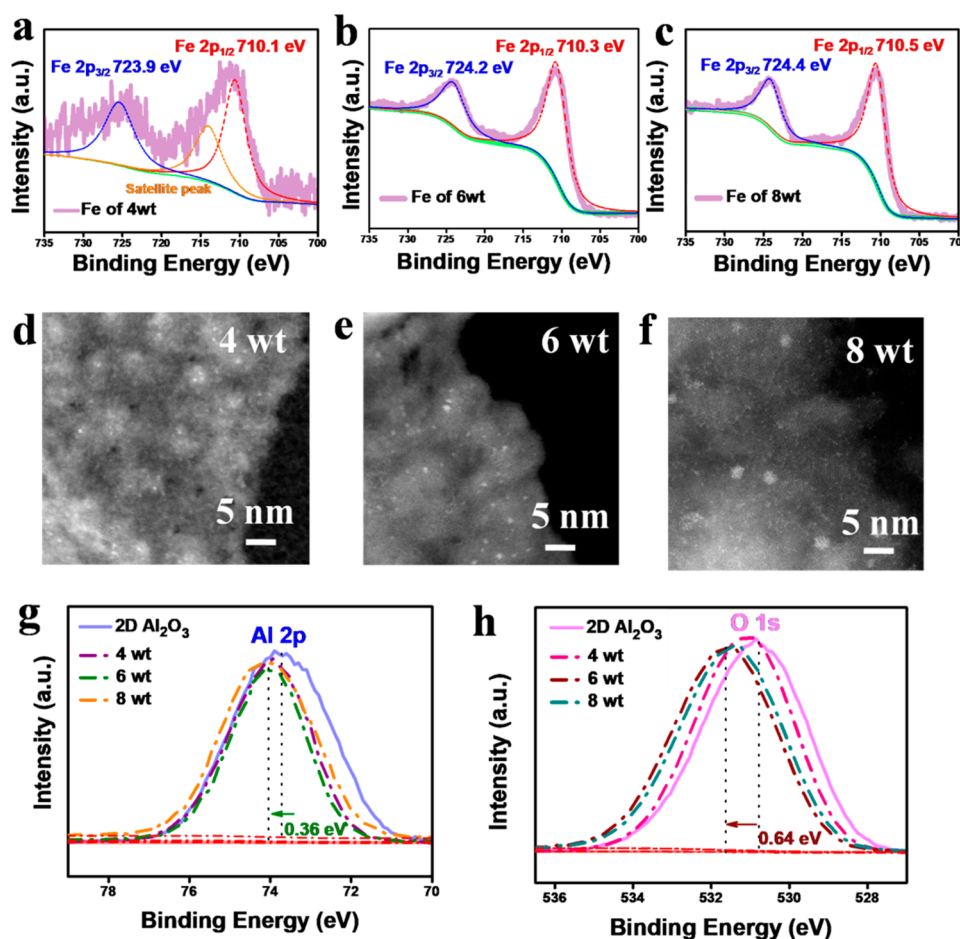
The  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheets with various Fe loadings were tested for catalytic epoxidation of styrene. The catalytic styrene epoxidation reaction could yield several products, including styrene oxide, benzaldehyde, benzoic acid, and 2-phenylacetaldehyde (Figure 2a). Styrene oxide is one of the most



**Figure 2.** Catalytic performance of the  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheets for styrene epoxidation. (a) Molecular structures of styrene and its oxidized products. (b) Conversion and styrene oxide selectivity and (c) product yield distribution after 6 h reaction using  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheet catalysts with different Fe loadings. SO, styrene oxide; BE, benzaldehyde; 2-Ph, 2-phenylacetaldehyde; BA, benzoic acid. (d) Product yield distributions at different reaction times. (e) Comparison of the selectivity for styrene oxide (solid lines) and styrene conversion (dash lines) between 6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheet catalyst (red) and C-6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$  catalyst prepared using commercial  $\text{Al}_2\text{O}_3$  nanoparticles as the support (black) during consecutive catalytic runs and after recalcination (Re). HAADF-STEM images of (f) 6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheet catalyst and (g) C-6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$  control after recalcination. Bright dots marked with circles are  $\text{FeO}_x$  species.

valuable products due to its use in the synthesis of epoxy resin, UV (ultraviolet) absorbents, and pharmaceutical intermediates and the perfume industry. Figure 2b shows the 6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$  catalyst gives the highest styrene conversion of 80% and the highest selectivity of 81% for styrene oxide. A closer look at the product distribution in Figure 2c shows that the formation of 2-phenylacetaldehyde and benzaldehyde was suppressed with increasing Fe loading. The production of benzoic acid was always under 5%.

To understand the superior selectivity of the 6%- $\text{Al}_2\text{O}_3\text{-FeO}_x$  catalyst, we performed the time-dependent product composition analysis to gain insights into the reaction pathways to different products. We sampled and analyzed the reaction mixture every hour (Figure 2d). In the first hour, benzaldehyde was observed, and no styrene oxide was produced. The conversion of styrene oxide began in the second hour and continued growing thereafter, whereas the conversion of benzaldehyde remained constant. The initial formation of benzaldehyde is possibly caused by the random and fast release of superoxide species ( $\text{O}_2^{\bullet-}$ ) from  $\text{H}_2\text{O}_2$ ,<sup>31,32</sup> where styrene would first transfer into styrene diol by direct



**Figure 3.** Electronic interactions between the FeO<sub>x</sub> nanoclusters and the Al<sub>2</sub>O<sub>3</sub> nanosheet. (a–c) XPS Fe 2p spectra and (d–f) corresponding HAADF-STEM images of Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheets with different Fe loadings. From left to right: 4%, 6%, and 8%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub>. (g and h) XPS spectra of Al 2p and O 1s for pure Al<sub>2</sub>O<sub>3</sub> nanosheet (2D Al<sub>2</sub>O<sub>3</sub>) and Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheets with different Fe loadings.

dihydroxylation, followed by oxidative cleavage via an unobserved  $\alpha$ -hydroxy-carboxylic acid.<sup>33</sup> Unlike benzaldehyde, styrene oxide is produced by peroxidic species (HOO<sup>•</sup>) from H<sub>2</sub>O<sub>2</sub> attacking the C=C bond of styrene.<sup>26</sup> To verify the role of peroxidic species in styrene epoxidation, we introduced isopropyl alcohol, a radical scavenger. After the first hour of reaction, the selectivity for styrene oxide decreased to less than 5% (Figure S1). The possible reason for the suppressed formation of benzaldehyde after the first hour is that the Fe active sites of the Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheets could intercept the free peroxidic species (HOO<sup>•</sup>) released from H<sub>2</sub>O<sub>2</sub>, forcing the styrene oxidation to proceed through the styrene oxide pathway. This explanation is partially supported by the observation that no styrene oxide was detected when using pure Al<sub>2</sub>O<sub>3</sub> nanosheets without the Fe catalyst, while the yield of benzaldehyde was not affected. Besides styrene oxide and benzaldehyde, we also observed two minor products, benzoic acid and 2-phenylacetaldehyde. Benzoic acid is an oxidation product of benzaldehyde, and 2-phenylacetaldehyde is produced by the rearrangement of styrene oxide over Lewis acid sites.<sup>34</sup> The yield of 2-phenylacetaldehyde was also suppressed by the increasing Fe loading, suggesting that FeO<sub>x</sub> clusters can suppress the ring-opening reaction.

After running styrene epoxidation tests consecutively 4 times, we observed a decrease in the catalytic activity for the 6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheet catalyst in terms of styrene conversion and product selectivity (Figure 2e). Similar catalyst

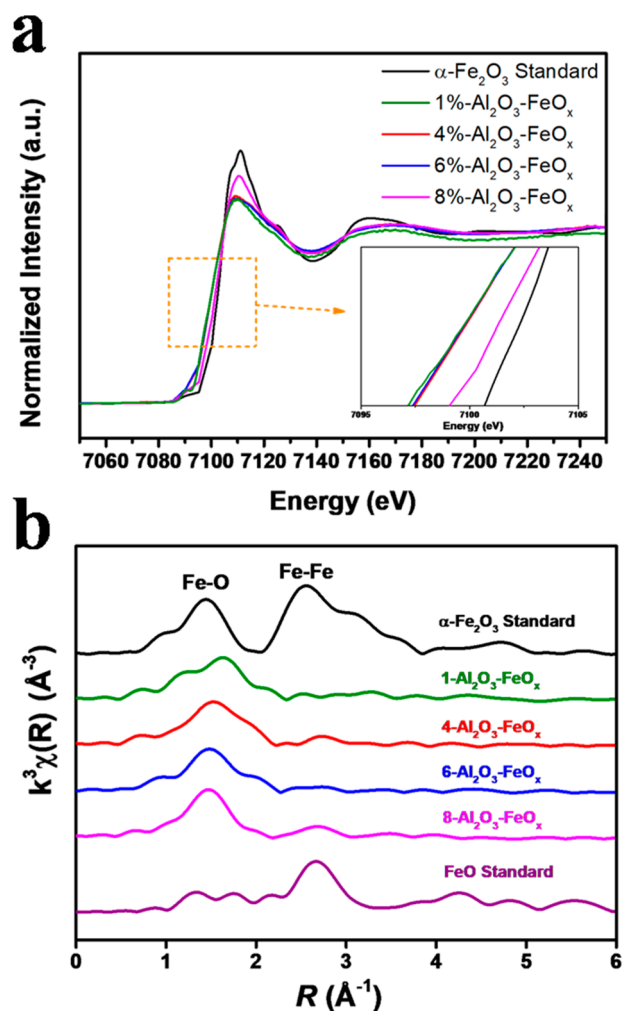
deactivation was observed in the control experiment using the C-6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> catalyst prepared following the same synthetic method except with commercial Al<sub>2</sub>O<sub>3</sub> power rather than the synthesized Al<sub>2</sub>O<sub>3</sub> nanosheets. The catalyst deactivation is possibly caused by the accumulation of organic pollutants blocking the catalyst's active sites. The difference between the 6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheet catalyst and the C-6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> catalyst, however, is the ability to be regenerated by recalcination of the deactivated catalyst in air to remove the organic pollutants. After recalcination, styrene conversion using the 6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheet catalyst was nearly fully recovered to 79%. In comparison, the recalcinated C-6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> catalyst only shows a partial recovery of catalytic activity (Figure 2e). The difference in catalytic regeneration is caused by the higher thermal stability of the 6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheet catalyst (the SEM (scanning electron microscopy) image is shown in Figure S2) than the C-6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> catalyst (the SEM image is shown in Figure S3). The SEM images of the 6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheet catalyst before and after recalcination show no noticeable change in the catalyst's morphology during recalcination (Figure S2). The X-ray diffraction patterns (Figure S4) of the 6%–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> nanosheet catalyst before and after recalcination show that our nanosheet retains its amorphous feature, whereas the X-ray diffraction patterns of C–Al<sub>2</sub>O<sub>3</sub>–FeO<sub>x</sub> can be indexed as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Under HAADF-STEM, we did not observe any noticeable size change of the

FeO<sub>x</sub> nanoclusters for the 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst (Figure 2f and Figure S5) either, indicating the high thermal stability of the 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst. In contrast, the C-6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> catalyst shows the aggregation of FeO<sub>x</sub> clusters on the commercial Al<sub>2</sub>O<sub>3</sub> support (Figure 2g and Figure S5), forming FeO<sub>x</sub> particles with sizes over 2 nm. The size increase of the FeO<sub>x</sub> clusters reduces the active sites, resulting in the permanent partial loss of catalytic activity after recalcination. The higher thermal stability of the 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst than its commercial counterpart can be attributed to the large number of defect sites and cavities of Al<sub>2</sub>O<sub>3</sub> nanosheets. These defective structures with dangling bonds were highly active for efficiently binding foreign elements, thus resulting in larger diffusion barriers to prevent the sintering of metal species via particle migration or Ostwald ripening.<sup>35–38</sup> Moreover, electron paramagnetic resonance (EPR) measurement was carried out to compare our Al<sub>2</sub>O<sub>3</sub> amorphous nanosheet (2D Al<sub>2</sub>O<sub>3</sub>) and commercial Al<sub>2</sub>O<sub>3</sub> nanoparticle (C-Al<sub>2</sub>O<sub>3</sub>), as shown in Figure S6. A clear signal in electron paramagnetic resonance results at  $g = 2.004$  can be found with a 2D Al<sub>2</sub>O<sub>3</sub> nanosheet, while the signal for C-Al<sub>2</sub>O<sub>3</sub> was weaker, indicating a highly crystalline feature. The signal at  $g = 2.004$  can be attributed to the presence of oxygen vacancies.<sup>39,40</sup> The difference in the EPR signal between the two Al<sub>2</sub>O<sub>3</sub> supports suggested that our synthesized Al<sub>2</sub>O<sub>3</sub> is rich in defects.

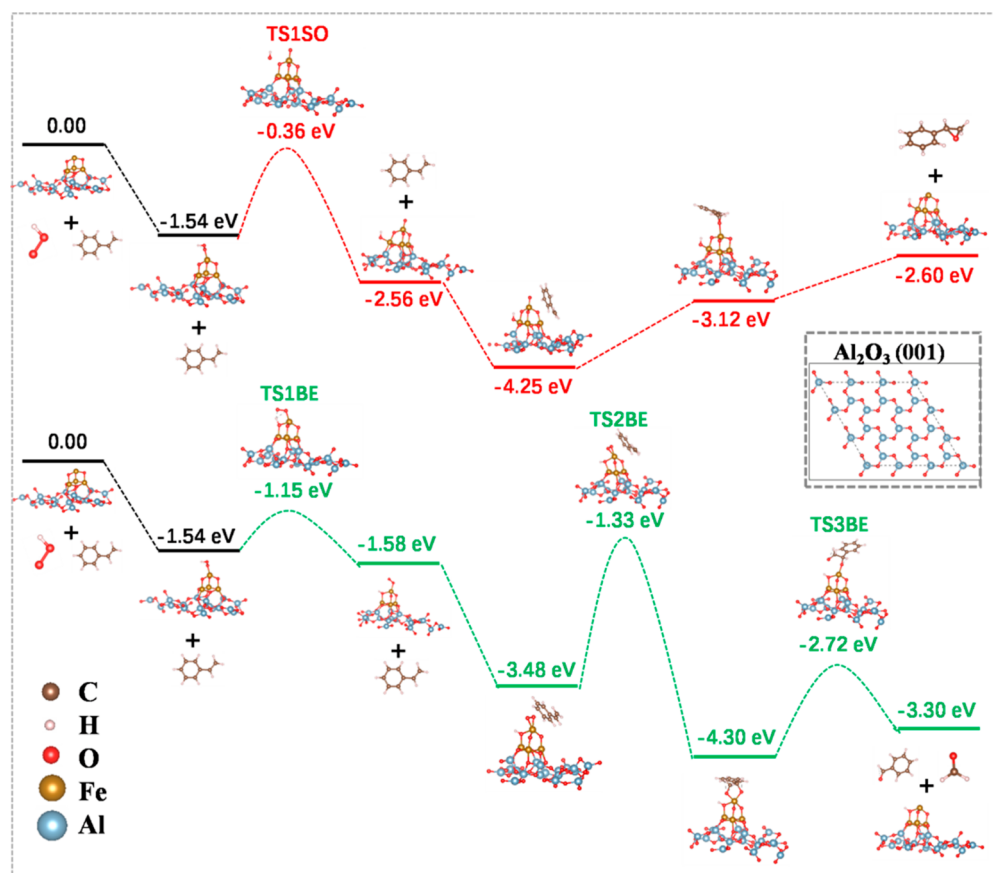
Thus far, we have shown that the FeO<sub>x</sub> nanocluster sites of the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst are responsible for the high selectivity toward styrene oxide and that the Al<sub>2</sub>O<sub>3</sub> nanosheet support is critical to the high thermal stability by immobilizing the active Fe species on its surface. Next, we investigated the role of the electronic interactions between the FeO<sub>x</sub> nanoclusters and the Al<sub>2</sub>O<sub>3</sub> nanosheet using X-ray photoelectron spectroscopy (XPS) to understand the catalytic activity trend for the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalysts with different Fe loadings. Figure 3a–c shows the XPS spectra of different Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalysts in the Fe 2p region. Two characteristic peaks at around 710 eV for Fe 2p<sub>3/2</sub> and 724 eV for Fe 2p<sub>1/2</sub> indicate an approximately +3 valence state of Fe,<sup>41,42</sup> suggesting the Fe clusters can be referred to as “FeO<sub>x</sub>”. Moreover, we noticed a positive shift of the binding energy of Fe 2p with increasing Fe loading; thus, Fe 2p of 8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> shows the highest binding energy among those Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> catalysts (1%-, 4%-, and 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>) (Figure 3a–c and Figure S7). The HAADF images in Figure 3d–f confirm that 4%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> has a smaller FeO<sub>x</sub> cluster size than 6%- and 8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>. Moreover, the HAADF image of 1%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> is shown in Figure S8; those HAADF images show the change from subnanoclusters of FeO<sub>x</sub> to nanoparticles on increasing the Fe loading in the precursors. After running the styrene epoxidation test 4 times, there was no noticeable change in the Fe 2p region of the XPS spectra (Figure S9), suggesting the unchanged valence state of Fe after interacting with the oxidant. For the Al<sub>2</sub>O<sub>3</sub> nanosheets, the binding energies of Al 2p and O 1s shift to lower values compared with that of bulk Al<sub>2</sub>O<sub>3</sub><sup>43</sup> due to the lattice distortion of the amorphous Al<sub>2</sub>O<sub>3</sub> nanosheet and extra chemical bond formation, shortening the interatomic distance and making electrons easier to hop over for both the Al and the O elements.<sup>44,45</sup> With Fe loadings, a constant positive shift of ~0.36 eV for the Al 2p peaks was observed compared to the unloaded Al<sub>2</sub>O<sub>3</sub> nanosheets (Figure 3g). In comparison, the shift of the O 1s peak in Figure 3h is more complex: 0.30, 0.64,

and 0.58 eV for 4%-, 6%-, and 8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>, respectively. The highest O 1s binding energy for 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> among the three Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> samples suggests more electrons transfer from Fe to O in 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> than in the other two Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> samples, which could favor the adsorption of styrene for catalytic epoxidation, leading to the highest catalytic activity of 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>. Besides the electron transfer effect, the FeO<sub>x</sub> cluster size and density can also contribute to the highest catalytic activity of 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> as the STEM images in Figure 3d–f show that 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> has more FeO<sub>x</sub> nanoclusters than 4%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> and a smaller nanocluster size than 8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>.

We further measured the coordination environment of the Fe atoms in the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalysts using X-ray absorption spectroscopy. The X-ray absorption near-edge structure (XANES) spectra at the Fe K-edge are shown in Figure 4a. The valence state of Fe in 8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> is close to that in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, indicating a valence state of ~+3, while the Fe K-edges of 1%-, 4%-, and 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> fall between FeO and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, indicating a valence state between +2 and +3. This observation confirmed that nanoparticles (8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>) have a higher oxidation state than subnanoclusters (1%-,



**Figure 4.** Measurements of the coordination environment of the Fe atoms in the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheets using X-ray absorption spectroscopy. (a) Fe K-edge XANES spectra. (b)  $k^3$ -weighted Fourier transforms of Fe K-edge EXAFS spectra for FeO standard,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> standard, and 1%-, 4%-, 6%-, and 8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>.



**Figure 5.** DFT-calculated energy diagrams for styrene oxidation to benzaldehyde and styrene oxide on a  $\text{FeO}_x$  cluster on the  $\text{Al}_2\text{O}_3$  (001) facet.

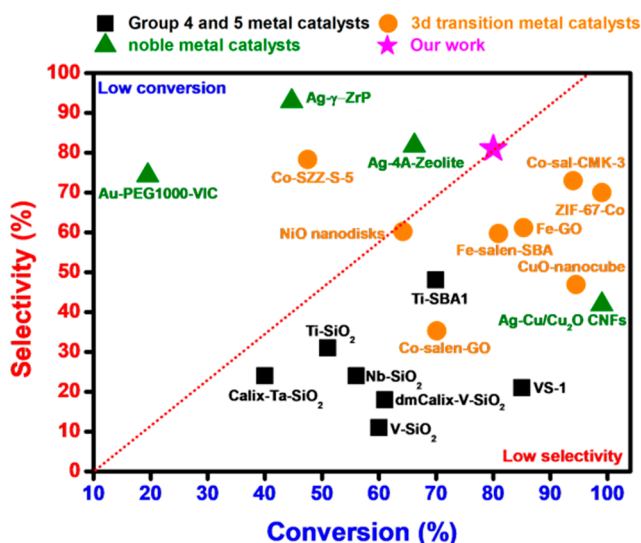
4%, and 6%  $\text{Al}_2\text{O}_3\text{-FeO}_x$ ). The XANES result was consistent with the XPS spectra. We performed Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) analysis (Figure 4b). The fitting result in Figure S10 and Table S1 shows that the  $\text{Al}_2\text{O}_3\text{-FeO}_x$  nanosheet catalysts show nearly 4-fold coordination, significantly lower than the 6-fold Fe–O coordination environment in  $\alpha\text{-Fe}_2\text{O}_3$ . The significantly reduced coordination number is consistent with the sub-1 nm size of the  $\text{FeO}_x$  clusters in the HAADF-STEM images (Figures 1c, 1d, and 3d–f). The weak Fe–Fe scattering peak is also attributed to the ultrasmall size.<sup>46</sup> The X-ray absorption spectroscopy data reveals the unsaturated and amorphous nature of the Fe atoms in our catalyst, which should facilitate the adsorption of styrene for epoxidation. Meanwhile,  $\text{H}_2$ -temperature-programmed reduction ( $\text{H}_2$ -TPR) measurement was carried out to compare the reduction properties of subnanoclusters (1%, 6%  $\text{Al}_2\text{O}_3\text{-FeO}_x$ ) and nanoparticles (8%  $\text{Al}_2\text{O}_3\text{-FeO}_x$ ), as shown in Figure S11. The reduction peak of 8%  $\text{Al}_2\text{O}_3\text{-FeO}_x$  at around 400 °C is related to the transition of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , while the other peak at higher temperature can be attributed to the transition of  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$ .<sup>47</sup> We also noticed that the reduction peak of 6%  $\text{Al}_2\text{O}_3\text{-FeO}_x$  shifted to lower temperature compared with the other two catalysts. This indicated that 6%  $\text{Al}_2\text{O}_3\text{-FeO}_x$  contributed the best catalytic performance at low temperature.<sup>48</sup> The  $\text{H}_2$ -TPR result is consistent with the styrene epoxidation experimental result.

Next, we performed density functional theory (DFT) calculations to gain an understanding of how the  $\text{FeO}_x$  nanocluster dictates the product selectivity. Figure 5 shows the calculated energy diagrams for the styrene oxidation

pathways to styrene oxide and benzaldehyde (with the initial state set as 0.00). The red route represents the formation of styrene oxide: this reaction pathway starts from the peroxidic species ( $\text{HOO}^{\bullet-}$ ) first adsorbing onto the  $\text{FeO}_x$  cluster supported on the  $\text{Al}_2\text{O}_3$  (001) facet. Then cleavage of the O–OH bond occurs, which needs to overcome an energy barrier of 1.18 eV via a transition state (TS1SO),<sup>49</sup> followed by reacting with styrene via a Fe active center, yielding styrene oxide. Meanwhile, the reaction pathway to form benzaldehyde (the green route) indicates the decomposition of styrene to benzaldehyde and formic acid by interacting with superoxide species ( $\text{O}_2^{\bullet-}$ ). The kinetics features of the green route revealed energy barriers of 0.39, 2.15, and 1.58 eV via transition states: formation of superoxide species (TS1BE), attack of superoxide species to styrene (TS2BE), and desorption of benzaldehyde from the catalyst (TS3BE). Apparently, styrene oxide is the more favorable product than benzaldehyde in the presence of  $\text{Al}_2\text{O}_3\text{-FeO}_x$  catalyst because the formation of styrene oxide has smaller energy barriers to overcome compared to that of benzaldehyde. The difference in free energy profiles for the two styrene oxidation pathways was confirmed by a temperature-dependence study. Figure S12a shows that when the reaction temperature increased to 85 °C, even though the conversion reached 93%, the selectivity toward styrene oxide decreased to 75% because a high reaction temperature helps overcome the energy barrier in the production of benzaldehyde. When the reaction temperature was decreased to 55 °C, the formation of benzaldehyde was further suppressed and the selectivity toward styrene oxide increased to 84%. A small quantity of styrene diol was also detected in this experiment, possibly because the oxidation of

styrene to styrene diol in the absence of catalyst is thermodynamically spontaneous (Figure S12b; potential energies of reactants, intermediates; and final products are shown in Figure S13). Furthermore, the catalytic data of 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> at various temperatures (from 55 to 85 °C) were fitted in a pseudo-first-order model to study the kinetics. An Arrhenius plot of  $-\ln k$  against  $1/T$  was then plotted (Figure S14) to obtain the activation energy. By substituting the value of the slope in Figure S14, the activation energy of the reaction was determined to be 61.34 kJ/mol. This value is comparable to the previously reported value that was from catalytic systems that used acetonitrile, the same solvent as our catalytic experiment.<sup>50–53</sup>

Finally, we compared our Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst with the state-of-the-art catalysts for styrene epoxidation in the literature. We categorized the existing catalysts into two groups based on the size of the active component in the catalyst. The first group is nano- or microsized catalysts. These catalysts used 3d transition metals (Co, Ni, Fe, Cu), group 4 and 5 metals (Ti, Si, Nb, V), or noble metals (Au and Ag) as the active components and graphene and carbon nanotube as the solid support.<sup>25,54–67</sup> As shown in Figure 6, some noble metal



**Figure 6.** Comparison between the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst in this work (purple star) and the state-of-the-art catalysts for selective styrene oxidation to styrene oxide in terms of conversion and product selectivity.

catalysts such as Ag- $\gamma$ -ZrP exhibited better selectivity for styrene oxide than our catalyst but suffered from low styrene conversion,<sup>63</sup> whereas 3d transition metal catalysts such as ZIF-67-Co achieved a higher styrene conversion than our catalyst but are limited by the low selectivity.<sup>25</sup> In comparison, our Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst achieved the best combination of selectivity and conversion, both higher than 80%. The turnover frequency value (TOF) of those metal catalysts is shown in Table S2. The second group of catalysts is the recently reported nanocluster or single-atom catalysts. For example, Xiong et al. reported a pyrolyzing coordinated polymer strategy to obtain a single atomic site (SAS) Fe catalyst with a high yield of 64% and an excellent selectivity of 89% toward styrene oxide.<sup>68</sup> Compared with this SAS-Fe, our catalyst exhibits a comparable styrene oxide yield (64% at 70 °C and 70% at 85 °C). Another example is ligand-free Au

nanoclusters confined in mesoporous silica,<sup>69</sup> which also produced a high styrene oxide yield of 64%. However, this Au nanocluster catalyst used an organic oxidant, *tert*-butyl hydroperoxide, which is less environmentally friendly than our catalyst that uses H<sub>2</sub>O<sub>2</sub> as the oxidant. In addition, our nanosheet catalyst achieved a turnover frequency value of >280 h<sup>-1</sup> that rivals the recently reported isolated single-atom Ru catalyst supported on the Lewis acid site of Beta zeolite.<sup>70</sup> Meanwhile, a TOF value comparison of our Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> catalysts with different Fe loading in Table S3 suggested that 4%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> exhibited the highest TOF value (476 h<sup>-1</sup>) at 70 °C among those catalysts. Even though 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> contributed the best performance in terms of conversion and selectivity toward styrene oxide, the loss of its atomic efficiency is unavoidable as the size of the FeO<sub>x</sub> clusters increase, giving a TOF value of 280 h<sup>-1</sup>. When further increasing Fe loading, those Fe species would aggregate to nanoparticles (8%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>), resulting in a decrease of the TOF value (214 h<sup>-1</sup>), as shown in Table S3.

## CONCLUSION

In summary, we reported a simple wet-chemical route to prepare unsaturated FeO<sub>x</sub> subnanoclusters supported on ultrathin amorphous Al<sub>2</sub>O<sub>3</sub> nanosheets. As a catalyst for styrene epoxidation, this new material has achieved the combination of high selectivity and high conversion, selectively generating styrene oxide while suppressing the formation of overoxidized products such as 2-phenylacetaldehyde. The high catalytic performance originates from the stabilization of peroxidic species (HOO<sup>•</sup>) by the Fe active sites of undercoordinated FeO<sub>x</sub> subnanoclusters, promoting the styrene epoxidation pathway. The amorphous Al<sub>2</sub>O<sub>3</sub> nanosheet stabilizes the catalytic FeO<sub>x</sub> clusters and prevents them from sintering at high temperatures owing to its defective structure. The high thermal stability of the Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> nanosheet catalyst enables the regeneration of catalytic activity by heat treatment to effectively remove the organic adsorbates that block the catalytic sites without destructing the catalyst structure. Our work showcases the importance of choosing the right combination of nanocluster catalyst, support, and catalyst-support interaction in achieving the desired catalytic performance.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c01366>.

Comparison between product yields with or without the addition of isopropyl using 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> as the catalyst; SEM images, XRD patterns, and HAADF-STEM images of 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> and C-6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub>; comparison of Fe 2p XPS spectra before and after running catalytic test 4 times; EXAFS spectra fitting results; product yield using 6%-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> as catalyst under different reaction conditions; catalytic properties of various Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> samples for styrene epoxidation with H<sub>2</sub>O<sub>2</sub> as the oxidant; EXAFS fitting parameters at the Fe K-edge for various samples ( $S_0^2 = 0.79$ ) (PDF)

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### Author Contributions

Z.Y., H.Z., and L.G. designed and directed the study. Z.Y. conceived and performed the fabrication work. S.Z. performed XAFS and analyzed the results. A.L. performed the first-principles calculations and analyzed the results. Z.Y. performed the spherical aberration-corrected transmission electron microscopy. L.L., H.Z., and L.G. participated with characterization and data analysis. All authors contributed to the discussion. Z.Y., L.L., and L.G. wrote the manuscript. All authors reviewed the paper.

### Notes

The authors declare no competing financial interest.

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