A tailored multi-functional catalyst for ultra-efficient styrene production under a cyclic redox scheme

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Styrene is an important commodity chemical that is highly energy and CO2 intensive to produce. We report a redox oxidative dehydrogenation (redox-ODH) strategy to efficiently produce styrene. Facilitated by a multifunctional (Ca/Mn)\textsubscript{1−x}O@KFeO\textsubscript{2} core-shell redox catalyst which acts as (i) a heterogeneous catalyst, (ii) an oxygen separation agent, and (iii) a selective hydrogen combustion material, redox-ODH auto-thermally converts ethylbenzene to styrene with up to 97% single-pass conversion and >94% selectivity. This represents a 72% yield increase compared to commercial dehydrogenation on a relative basis, leading to 82% energy savings and 79% CO2 emission reduction. The redox catalyst is composed of a catalytically active KFeO\textsubscript{2} shell and a (Ca/Mn)\textsubscript{1−x}O core for reversible lattice oxygen storage and donation. The lattice oxygen donation from (Ca/Mn)\textsubscript{1−x}O sacrificially stabilizes Fe\textsuperscript{3+} in the shell to maintain high catalytic activity and coke resistance. From a practical standpoint, the redox catalyst exhibits excellent long-term performance under industrially compatible conditions.
As an important chemical feedstock for rubber and plastics production, the global styrene production exceeded 31 million tons in 2018 and results in an annual CO$_2$ emission of over 27 million tons.$^{1,2}$ At present, catalytic dehydrogenation (DH) of ethylbenzene accounts for ~90% of the styrene produced worldwide. This well-established approach suffers from high energy consumption, equilibrium-limited ethylbenzene conversion, and complex product separation, leading to significant CO$_2$ emissions.$^{13,14}$ To compensate the heat required by the highly endothermic DH reaction, the industrial DH process uses significant amount of superheated steam as a heat source. At a typical dilution rate of ~22:1 (steam:ethylbenzene by mole), co-injection of steam increases the equilibrium conversion while inhibiting coke formation and over-reduction of the potassium-promoted iron oxide DH catalyst.$^{15,16}$ Despite the large steam consumption that is highly energy-intensive, commercial DH process needs two reactors in series with interstage heating in order to achieve 64% ethylbenzene conversion.$^{17,18}$ The limited ethylbenzene conversion, coupled with by-products such as benzene and toluene, in turn complicates the product separation scheme. As such, transformative approaches to convert ethylbenzene to styrene with lowered energy conversion, higher single-pass yield, and simpler process scheme is highly desirable.

Oxidative DH (ODH) is a promising alternative to DH, since simultaneous oxidation of hydrogen to water eliminates equilibrium limitations and leads to an exothermic overall reaction.$^{19,20}$ However, co-feeding gaseous oxygen in ODH often leads to undesirable carbon dioxide formation, lowering the selectivity to styrene. State-of-the-art ethylbenzene O$_2$–ODH catalysts include high-surface-area activated carbon materials, carbon-doped boron nitride, and supported vanadium-based oxide. Styrene yields from these catalysts are typically limited to 60%, with ethylbenzene feed partial pressure <0.1 atm.$^{9-12}$ Moreover, the consumption of gaseous oxygen also increases the energy consumption, cost, and complexity of the process. Besides gaseous oxygen, carbon dioxide was also investigated as a soft oxidant for ethylbenzene ODH, typical mechanisms include a modified Mars-van Krevelen-type redox mechanism, and a reverse water-gas-shift reaction, which converts the H$_2$ coproduct into water and CO.$^{13,14}$ Reported catalysts include CeO$_2$,$^{13}$ activated carbon-supported FeO$_x$,$^{15}$ and other mixed transition metal oxides.$^{16-19}$ Although CO$_2$–ODH can facilitate CO$_2$ utilization and enhance the equilibrium styrene yield, high carbon dioxide to ethylbenzene molar ratios (~10:1) are necessary given the equilibrium-limited reverse water-gas-shift reaction.$^{16}$ The limited CO$_2$ conversion would in turn increase the complexity and energy demand for the product separation steps. Moreover, CO$_2$–ODH is more endothermic than conventional DH. As such, CO$_2$–ODH processes are likely to be more energy-intensive than the conventional DH route.

To address these challenges, we propose a redox-ODH scheme to efficiently convert ethylbenzene to styrene using a tailored multifunctional redox catalyst, which acts as a heterogeneous catalyst, an oxygen separation agent, and a selective oxidation material (Fig. 1a). Facilitated by the redox catalyst, redox-ODH follows a chemical-looping-based approach, which has been previously reported for CO$_2$ capture from fossil fuel combustion$^{20-22}$, methane-selective oxidation$^{23-29}$, thermochemical water/CO$_2$ splitting$^{30-37}$, air separation$^{38-40}$, and ODH of light alkanes$^{41-43}$. To our knowledge, previous chemical-looping studies have yet to investigate catalytic conversion to hydrocarbon molecules containing more than four carbon atoms, mainly due to the high operating temperature required by conventional redox catalysts and/or lack of product selectivity$^{44,45}$. In comparison, redox-ODH converts ethylbenzene at relatively low temperatures in two steps, with integrated air separation: in the ODH step, ethylbenzene is catalytically converted into styrene and water, where the active lattice oxygen in the redox catalyst assists ethylbenzene activation and selective hydrogen combustion (SHC). In the subsequent oxidation step, the lattice oxygen in the redox catalyst is replenished via reactive air separation. Resulted from effective SHC by the redox catalyst, the conversion of ethylbenzene to styrene becomes autothermal and is no longer limited by the thermodynamic equilibrium, achieving high single-pass styrene yield while simplifying the downstream product separation. Moreover, the in situ air separation facilitated by the redox catalyst renders a much safer and more efficient ODH scheme.$^{44}$ Figure 1b compares redox-ODH with conventional and emerging styrene production approaches. As can be seen, significant advantages can be anticipated resulting from the multifunctional redox catalyst and the unique redox-ODH scheme. In the following sections, the performance of the multifunctional redox catalyst is first presented. This is followed with detailed characterization and density functional theory (DFT) calculations to reveal the underlying reaction mechanism and redox catalyst design and optimization strategy. Finally, the performance of the redox-ODH scheme is simulated with detailed ASPEN Plus simulations. Specifically, the redox catalyst reported in this study demonstrated 72% increase in single-pass styrene yield on a relative basis. The significantly intensified redox-ODH scheme has the potential to reduce energy consumption by >80% when compared to the commercial DH process.

**Results**

**Redox-ODH performance of ethylbenzene to styrene.** This section reports the performance of the (Ca/Mn)$_x$O$_y$KFeO$_2$ redox catalyst for redox-ODH of ethylbenzene. Details related to catalyst preparation and experimental setup are provided in the “Methods” section in the supplementary document (see Supplementary Fig. 1). As shown in Fig. 2a, redox-ODH on fully oxidized (Ca/Mn)$_x$O$_y$KFeO$_2$ can be divided into two regions. Region 1 exhibited high CO$_2$ selectivity (29.1%), whereas region 2 exhibited 94.6% styrene selectivity with merely 0.1% selectivity towards CO$_2$. A partial reoxidation with air can tune the degree of oxidation for the (Ca/Mn)$_x$O$_y$KFeO$_2$ redox catalyst to take the advantage of the highly selective region 2. As can be seen in Fig. 2b, the nonselective region 1 was near completely eliminated and (Ca/Mn)$_x$O$_y$KFeO$_2$ exhibited excellent ethylbenzene conversion (97%) and styrene selectivity (94.2%) throughout the ODH step. Figure 2c summarizes the redox-ODH performance of (Ca/Mn)$_x$O$_y$KFeO$_2$ as a function of ethylbenzene partial pressure. We note that commercial ethylbenzene DH (DH) process typically operates in a two-stage reactor with interstage reheating and at steam to ethylbenzene molar ratio of ~22:1.$^{18}$ The ethylbenzene partial pressure entering the secondary stage of the commercial reactor is around 0.1 atm. At this partial pressure, the single-pass ethylbenzene conversion is thermodynamically limited to 73% at 600 °C, whereas the actual plant performance gives rise to 64% ethylbenzene conversion with 83% selectivity towards styrene (53.1% single-pass yield). In comparison, redox-ODH is not subjected to this equilibrium limitation since in situ combustion of the H$_2$ by-product with (Ca/Mn)$_x$O$_y$KFeO$_2$ leads to a thermodynamically favored, exothermic process. As can be seen in Fig. 2c, near 100% conversion of ethylbenzene can be achieved throughout the partial pressure ranges we investigated (up to 0.1 atm). More importantly, styrene selectivity maintained at a high level (94%) with 0.1 atm (industrially comparable) ethylbenzene feed (balance Ar). The experimentally demonstrated redox-ODH yield at 0.1 atm ethylbenzene was 18% higher.
than the maximum equilibrium yields for the conventional DH route. Compared to the practical yield in the commercial DH process, redox-ODH demonstrated 38% yield increase (absolute basis) or 72% on a relative basis. In all cases, close to 100% H2 were combusted to steam, ensuring autothermal operation while providing a protective atmosphere to maintain oxidation state of the catalytic surface without the needs for externally injected steam (Supplementary Fig. 2). Practically speaking, redox-ODH has the potential to operate at 1 atm ethylbenzene feed without steam dilution. The long-term stability of the redox catalyst was verified, as summarized in Fig. 2d. Aside from a gradual increase in styrene selectivity over the first 50 cycles, stable and satisfactory redox catalyst performances were observed over the 100 cycle continuous testing with complete reoxidation of the redox catalyst. Coke formation was <5% and was completely removed during the reoxidation step. It is noted that the redox-ODH performance relies on the participation of lattice oxygen species and deeply reduced (lattice oxygen-deprived) \((\text{Ca/Mn})_1-x\text{O} @ \text{KFeO}_2\) exhibits much lower ethylbenzene conversion and H2 by-product conversion (Supplementary Fig. 3). Further characterization of the redox catalyst and the reaction mechanism is discussed next.

**Fig. 1 Schematic and the advantages of redox-ODH.** a Schematic illustration of redox-ODH of ethylbenzene. MeMe’O represents a generic redox catalyst. b A comparison between ethylbenzene DH, O2-ODH, CO2-ODH, and redox-ODH. Green background stands for desirable features. a Steam dilution is necessary to avoid combustion limit. b CO2-ODH is still equilibrium limited compared to O2- and redox-ODH due to the equilibrium limitation in R-WGS (reverse water-gas-shift).

**Fig. 2 Redox-ODH performance.** Performance comparison of redox-ODH of ethylbenzene (EB) with a fully reoxidized and b partially reoxidized redox catalyst, EB partial pressure = 0.01 atm, temperature = 600 °C. c ODH performance comparing to DH equilibrium conversions in the range of 0.01-0.1 atm ethylbenzene feed partial pressure (balance Ar) using partially reoxidized redox catalyst. d Long-term cycle and product distributions in redox-ODH using fully reoxidized redox catalyst.
Redox catalyst characterizations. Figure 2a indicates that the degree of reoxidation of \((\text{Ca/Mn})_{1-x}\text{O@KFeO}_2\) has a significant impact on the styrene selectivity. Since the redox catalyst’s phases, surface elemental compositions, and surface structures undergo dynamic changes in the redox-ODH scheme, detailed understanding of such changes can reveal important mechanistic insights. Figure 3a shows the dynamic phase change observed with in situ X-ray diffraction (XRD) under cyclic ethylbenzene ODH and air reoxidation steps at 600 °C. Under the styrene-selective region (region 2), the primary phases observed include a \(\text{CaO–MnO solid solution phase and a potassium ferrite (KFeO}_2\) phase. The \(\text{CaO–MnO solid solution, with cation defects, continues to release lattice oxygen during the ODH step, as indicated by the continuous peak shift (from 40.5 to 39.9° and from 34.9 to 34.4°). Over-reduction of } \((\text{Ca/Mn})_{1-x}\text{O@KFeO}_2\) formed metallic Fe, which can be reversibly incorporated back into the redox catalyst. On the other hand, complete oxidation of \((\text{Ca/Mn})_{1-x}\text{O@KFeO}_2\) led to the dynamic exchange of cations between the \(\text{CaO–MnO solid solution and KFeO}_2\), forming two new phases, that is, \(\text{Ca}_2\text{Fe}_2\text{O}_5\) and \(\text{K}_{0.296}\text{Mn}_{0.926}\text{O}_2\). KFeO2 is still observed in the fully oxidized redox catalyst. Detailed XRD peak assignment for (a) fully oxidized redox catalyst and (b) redox catalyst under redox-ODH operating regime are shown in Supplementary Fig. 4a, b. Transmission electron microscopy with energy-dispersive X-ray spectroscopy (TEM-EDS) further confirmed that Ca and Mn were segregated in separate phases for the fully oxidized redox catalyst (Supplementary Fig. 5). Partial reoxidation, however, prevents the formation of \(\text{K}_{0.296}\text{Mn}_{0.926}\text{O}_2\) (Supplementary Fig. 4c). The dynamic phase change observed with in situ XRD is consistent with the Mn and Fe oxidation state measurements obtained from X-ray photoelectron spectroscopy (XPS) for the redox catalyst at different reaction stages. Based on stoichiometry and literature\(^46,47\), Mn oxidation state in \(\text{K}_{0.296}\text{Mn}_{0.926}\text{O}_2\) is +4, whereas in \(\text{CaO–MnO}\) it is between +2 and +3. As shown in Fig. 3b, it is observed in Mn 2p XPS that peaks shift to lower binding energy (BE) by 1 eV during the reaction stage. This corresponds to the phase transformation from \(\text{K}_{0.296}\text{Mn}_{0.926}\text{O}_2\) (Mn\(^{4+}\)) to \(\text{CaO–MnO}\) (Mn\(^{3+}/2^+\)). The XPS peak fittings on Mn 2p\(_{3/2}\) peaks further agreed with this oxidation change, as shown in Supplementary Fig. 6. In comparison, Fe 2p peaks stayed at the same BE for the oxidized and reduced samples (Fig. 3c) and the oxidation state remained at Fe\(^{3+}\) (see Supplementary Fig. 6 for detailed peak fitting on Fe 2p\(_{3/2}\)). These results indicate that, within the operating regime, Fe oxidation state stayed constant at +3 resulting from the “sacrificial” reduction of Mn\(^{3+}/4^+\). Given that KFeO2 with Fe oxidation state being +3 is known to be the active phase for DH of ethylbenzene\(^48\), the presence of Mn in the redox catalyst not only helps to maintain Fe at a desirable oxidation state but also provides the lattice oxygen donation/storage capabilities. These
results are further confirmed by Mössbauer spectroscopy measurements (Supplementary Fig. 7), where fully oxidized and reduced (Ca/Mn)\(_{1-x}\)O@KFeO\(_2\) under operating scheme exhibited consistent Fe oxidation states. It is also noted that deep reduction of (Ca/Mn)\(_{1-x}\)O@KFeO\(_2\), which is outside our typical operating regime, reduces Fe oxidation state as seen by the downward shift in BE by 0.4 eV. This is consistent with the observation of metallic iron under XRD and is accompanied with a decrease in catalytic activity due to the lack of active lattice oxygen for redox-ODH (Supplementary Fig. 3). The majority of the iron cations, however, remain at +3 state.

Besides the dynamic phase/oxidation state changes, (Ca/Mn)\(_{1-x}\)O@KFeO\(_2\) also undergoes dynamic surface composition and structure changes during redox-ODH of ethylbenzene. The surface elemental composition change, determined by XPS, is illustrated in Fig. 4a. XPS shows that the surface of fully oxidized (Ca/Mn)\(_{1-x}\)O@KFeO\(_2\) contains a significant amount of Mn (23%) and Fe (20%). On the other hand, reduced redox catalyst is highly K-enriched and the presence of surface Mn was reduced by ~5-folds. The surface enrichment of K on reduced samples was further confirmed with LEIS spectroscopy, which can detect the composition of topmost surface layers of a redox catalyst\(^{49}\). LEIS confirmed that the reduced samples are enriched with K and surface Mn/Fe are significantly suppressed (Fig. 4b). These were also confirmed with TEM-EDS in Fig. 4c, d. Consistent with in situ XRD results, EDS on fully oxidized sample showed a segregation between Ca and Mn, with no surface enrichment feature clearly observed (Supplementary Fig. 5). In comparison, the reduced sample, within the operating range of redox-ODH, showed a surface enrichment of K and a bulk enrichment of Mn as shown by the EDS line scan (Fig. 4c). High-resolution TEM showed that the surface structure of the partially oxidized sample belongs to (101) plane of crystalline KFeO\(_2\) phase, according to the \(d\)-spacing (Fig. 4d). This shows that a core-shell structure is formed on redox catalyst under its operating condition, where the core is MnO\(_x\)-enriched ((Ca/Mn)\(_{1-x}\)O) and the shell is a layer of KFeO\(_2\).

**Reaction mechanism study.** Ethylbenzene Fourier transform infrared spectroscopy (FTIR) with both temperature-programmed surface reaction (TPSR) and isothermal mode were further conducted to determine the surface properties of the core-shell structured redox catalyst. As can be seen in Fig. 5a for TPSR experiment on the operating range (Ca/Mn)\(_{1-x}\)O@KFeO\(_2\), chemisorption of ethylbenzene on the catalyst surface leads to the formation of bicarbonate and a notable amount of polystyrene species at 100 °C, which subsequently disappeared at 200 °C. As reported by Wu and coworkers\(^{13}\) on a high-surface-area CeO\(_2\) catalyst\(^{13}\), the polystyrene species are precursors for coke formation. The absence of the polystyrene peak at operating temperatures for (Ca/Mn)\(_{1-x}\)O@KFeO\(_2\) indicates a lower tendency for coke formation. The absence of the polystyrene peak at operating temperatures for (Ca/Mn)\(_{1-x}\)O@KFeO\(_2\) indicates a lower tendency for coke formation. The peak around 1600 cm\(^{-1}\) was characterized to be bicarbonate instead of deposited carbon based on fitting of other peaks and this bicarbonate was converted to carbonate at elevated temperatures\(^{50}\). In addition, a vinyl overtone peak appeared at 1800 cm\(^{-1}\), which corresponds to the formation of surface styrene species\(^{13}\). Isothermal FTIR was
conducted in Fig. 5b, with continuous ethylbenzene feed on fully oxidized (Ca/Mn)$_1$...O@KFeO$_2$. Both polystyrene and coke peaks were absent, whereas styrene was formed based on the presence of the vinyl peak. The trend for CO$_2$ peaks matched well with the reactivity performance shown in Fig. 2a, where CO$_2$ selectivity is high during the oxidized stage (region 1), whereas styrene selectivity dominates within the operating regime (region 2). A stable carbonate species was still observed but it does not appear to affect the catalyst activity. The formation of carbonate species on the ethylbenzene-contacted redox catalyst was also confirmed by XPS peak fittings of the O 1s peak, as shown in Supplementary Fig. 8. The FTIR results indicate that surface polystyrene species formed on (Ca/Mn)$_1$...O@KFeO$_2$ were further decomposed into styrene rather than coke and the redox catalyst was largely immune to coke formation. This is consistent with the product distribution results in Fig. 2a. Raman was further conducted on used redox catalyst after ethylbenzene ODH and confirmed the minimal amount of carbon deposition (Supplementary Fig. 9).

Based on the structural information obtained, it can be concluded that a layer of KFeO$_2$ predominantly covers the redox catalyst surface, whereas lattice oxygen from the (Ca/Mn)$_1$...O@KFeO$_2$ solid solution reversibly donates its lattice oxygen for the redox-ODH reaction. DFT simulations were hence conducted on KFeO$_2$ (124) surface, which is one of its most stable crystal surfaces. The Cartesian coordinates of each important transition state were attached in the Vienna ab initio simulation package POSCAR format in the Supplementary material. Various orientations of ethylbenzene adsorption on KFeO$_2$ were considered and the most stable adsorbed configuration was determined (Supplementary Fig. 10), shown as configuration I in Fig. 6a. C–H dissociation from α–C is considered as the first hydrogen dissociation step due to its much lower (thermodynamic) reaction energy (0.08 eV) than the H abstraction from β–C (0.91 eV) (Supplementary Fig. 11). β–H dissociation is considered as the second reaction step. Compared with direct H transfer, slightly shifting of the C$_6$H$_{12}$ toward the target lattice oxygen (from configuration II to II’ in Fig. 6a) can reduce the distance between the β–H and the target oxygen from 3.55 to 2.41 Å. This largely reduces the steric hindrance and thereby lowering the barrier for β–H abstraction from 1.76 to 0.37 eV with a transition state of ethyl branch attached in parallel to the KFeO$_2$ surface (configuration TS-[II-III] in Fig. 6a). Electron density shifts in the transition state structures of α and β hydrogen abstraction are depicted in Supplementary Fig. S12a, b, showing that electrons tend to transfer from the C–H bonds to O–H bonds, which correspond to the trends of C–H bonds cleavage and O–H bonds formation. DFT calculation also indicated that a transition state via C–H dissociation from the benzene ring is not likely (Supplementary Fig. 13). The computed activation energies of α and β hydrogen abstraction (0.70 and 0.37 eV) are much lower than those reported over other catalyst surfaces, such as V$_2$O$_5$ (001) (1.96 and 2.23 eV)$^{52}$, CeO$_2$ (111) (1.70 and 0.84 eV)$^{53}$, and zirconium vanadate (2.48 and 1.23 eV)$^{54}$, showing the advantages of our proposed catalyst. Following the α and β hydrogen abstraction, the formed styrene readily desorbs from the catalyst surface with highly favorable energetics. The low tendency for styrene adsorption on the surface also explains the excellent selectivity observed experimentally. This finding is consistent with literatures, where KFeO$_2$ was identified as the active phase for ethylbenzene DH in styrene $^{5,48,55,56}$.

Meanwhile, DH of ethylbenzene to styrene leaves two hydroxyls (-OH) on the KFeO$_2$ surface. To complete the ODH reaction, a proton from one -OH needs to migrate to an adjacent -OH site to form water, which then desorbs from the surface. However, this process is highly endothermic with a prohibitively high barrier of 2.33 eV. Further investigation indicated that the formation of water from unselective combustion of hydrocarbons and/or in situ selective combustion of hydrogen further facilitates ODH activity, as indicated in Fig. 6a–2. As can be seen, the energy barrier for water formation decreased to 0.47 eV under a water-assisted proton transfer mechanism. Here, a hydrogen bond formed between a hydroxyl and water molecule. The hydrogen bond, formed in situ redox-ODH, facilitates proton transfer on the KFeO$_2$ surface, leading to more than 4-folds decrease in the energy barrier for water formation. A similar water-assisted proton transfer phenomena were reported by Merte et al.$^{57}$ as determined by DFT and scanning tunneling microscopy on a FeO thin film. We also explored the effect of water on α and β hydrogen abstraction and did not observe any enhancement effect, indicating that water does not participate in these steps. As such, the overall reaction pathway is summarized in Fig. 6a. The key findings include: (i) α-hydrogen abstraction is the rate-limiting step for ethylbenzene ODH; (ii) water molecules formed from in situ combustion of hydrogen plays an important role in facilitating the ODH reaction, highlighting the importance of the (Ca/Mn)$_1$...O solid solution in terms of providing active lattice oxygen for hydrogen combustion; (iii) styrene molecules readily desorbs from the KFeO$_2$ surface, supporting the high catalytic activity/selectivity of (Ca/Mn)$_1$...O@KFeO$_2$ and the importance of maintaining a KFeO$_2$ terminated surface.
The DFT calculation results are further supported by experimental data. For instance, isotope exchange between H-hydroxylated (Ca/Mn)$_1$O@KFeO$_2$ and deuterated ethylbenzene in FTIR-TPSR experiments indicated that only the Ds from the ethyl branch of ethylbenzene were activated/exchanged <200 °C (Supplementary Fig. 14). This confirms that α and β hydrogen abstraction being the critical first steps for ethylbenzene ODH. To further determine the rate-limiting step, kinetic isotope effect (KIE) for the ODH reaction rates of ethylbenzene (C$_8$H$_{10}$) and deuterated ethylbenzene (C$_8$D$_{10}$) were measured (Fig. 6b). The KIE values were determined to be between 2.12 and 2.62. This confirms that the C–H bond activation on the ethyl branch of ethylbenzene being the rate-limiting step and is consistent with the DFT results. Another interesting experimental finding via co-feeding of C$_8$H$_{10}$ and C$_8$D$_{10}$ (Fig. 6c) is that the resulting styrene isotopes with different amount of D-substitution almost follows a Gaussian distribution. This is only possible in the case of a perfect isotope scrambling, where all H in C$_8$H$_{10}$ have the same chance of being exchanged into D. This confirms that (a) as-formed styrene molecules are absorbed parallel to the KFeO$_2$ surface in a conjugated electronic structure (consistent with DFT calculated configuration III in Fig. 6a-1); (b) water molecules are likely to facilitate proton exchange. The effect of water on proton exchange (and hence ethylbenzene conversion and water formation/desorption) was further confirmed with KFeO$_2$ without (Ca/Mn)$_1$O. Without co-injection of water, stand-alone KFeO$_2$ cannot donate its lattice oxygen for in situ water formation, showed low ethylbenzene conversion (44.3%) and the H$_2$ by-product was not effectively oxidized to water (Supplementary Fig. 15). Overall, these mechanistic findings, supported by both experiment and DFT calculations, provide important insights for redox catalyst design and optimizations.

Process performance and impacts. To quantify the practical impacts of the (Ca/Mn)$_1$O@KFeO$_2$ redox catalyst in the context of the redox-ODH scheme, detailed ASPEN Plus simulations were carried out to simulate both the commercial DH and redox-ODH schemes. The process configuration and operating conditions for commercial ethylbenzene DH process were documented in detail by Luyben. As detailed in the Supplementary document, our simulation accurately reproduced the performance of the commercial DH process (Case 1 in the Supplementary document). Two cases for the redox-ODH process were also analyzed: (1) The base case (Case 2) evaluates the redox-ODH process using the experimental performance of the (Ca/Mn)$_1$O@KFeO$_2$ redox catalyst at 0.1 atm ethylbenzene feed pressure, assuming 90% steam dilution; (2) An optimal case (Case 3), also using the experimental performance but assuming no steam dilution, was considered as well. We note that ethylbenzene was injected in dry conditions without steam dilution in all our experimental cases. These results support the potential feasibility of Case 3, that is, complete avoidance of steam usage in redox-ODH of ethylbenzene.
Dynamic bulk and surface structural changes. Under the working conditions, \((\text{Ca/Mn})_{1-x} \text{O} @ \text{KFeO}_2\) is terminated with a \(\text{KFeO}_2\) rich surface, which is responsible for catalyzing ethylbenzene conversion. Meanwhile, its bulk phase is composed of a cation defected CaO–MnO solid solution that is responsible for reversible lattice oxygen donation (in the ODH step) and uptake (in the reoxidation step). The lattice oxygen donation was facilitated by Mn +3 to +2 transition and the "sacrificial" reduction of Mn cations helps to stabilize the oxidation state of Fe, which remains at its most catalytically active +3 state. Moreover, the facile donation of lattice oxygen also retards coke formation. Through DFT calculations along with experimental validations, a detailed reaction pathway for the redox-ODH reaction on the \(\text{KFeO}_2\) surface was established. It was determined that a hydrogen abstraction is the rate-limiting step for ethylbenzene ODH and water molecules formed in situ significantly lowers the energy barrier for hydrogen combustion via a water-assisted proton transfer mechanism. Moreover, styrene molecules readily desorb from the \(\text{KFeO}_2\) surface, ensuring high product selectivity. Thus, the findings unveil the roles of the \(\text{KFeO}_2\) surface, \((\text{Ca/Mn})_{1-x} \text{O}\) bulk phase, and their synergistic effects, provide important mechanistic insights for designing effective redox catalysts for alkylbenzene conversions. Finally, detailed process simulations based on experimental data indicate up to 82% reduction in energy consumption and 79% decrease in CO\(_2\) emissions. This potentially translates into ~14 million tonnes of CO\(_2\) emission reductions each year for this important yet carbon-intensive industrial process.

**Methods**

**Redox catalyst synthesis.** The \((\text{Ca/Mn})_{1-x} \text{O} @ \text{KFeO}_2\) redox catalyst was prepared in two steps. The \((\text{Ca/Mn})_{1-x} \text{O}\) substrate was synthesized by a modified Pechini method. \(\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} (8.26 \text{ g}, 97.0\%, \text{Sigma-Aldrich})\) and \(\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} (8.77 \text{ g}, 99.0\%, \text{Sigma-Aldrich})\) were dissolved in deionized water with stirring at 30°C. Citric acid (26.87 g, 99.5%, Sigma-Aldrich) was then added into the solution. Next, 11.7 ml ethylene glycol (99.8%, Sigma-Aldrich) was added to the solution. The obtained solution was kept at 80°C with stirring until a gel formation. The gel was then transferred to an oven for drying at 130°C for 24 h. The precursor was finally calcined in a furnace at 950°C for 12 h (5°C/min ramping rate) under continuous airflow. The sample obtained after calcination was crushed into 20–40 mesh. \((\text{Ca/Mn})_{1-x} \text{O} @ \text{KFeO}_2\) was synthesized via wet impregnation by using \((\text{Ca/Mn})_{1-x} \text{O}\) as the substrate. Weight 4 g of the \((\text{Ca/Mn})_{1-x} \text{O}\) substrate was synthesized and put into a glass beaker. Weight 0.91 g of \(\text{KNO}_3\) (99.9%, Sigma-Aldrich) and 18.10 g of \(\text{Fe(NO}_3\text{)}_2\cdot9\text{H}_2\text{O} (98\%, \text{Sigma-Aldrich})\) was added into the beaker. The sample obtained after calcination was into another glass beaker and deionized water to dissolve these. The obtained solution was then added into the \((\text{Ca/Mn})_{1-x} \text{O}\) -containing beaker and stirred until dried. The obtained mixture was crushed under air continuous flow at 650°C for 3 h, and then crushed into 20–40 mesh as final \((\text{Ca/Mn})_{1-x} \text{O} @ \text{KFeO}_2\) redox catalyst. Stand-alone \(\text{KFeO}_2\) was synthesized by adding equal molar amounts of \(\text{KNO}_3\) and \(\text{Fe(NO}_3\text{)}_2\cdot9\text{H}_2\text{O}\) into a glass beaker. Specifically, 3.18 g \(\text{KNO}_3\) and 12.73 g \(\text{Fe(NO}_3\text{)}_2\cdot9\text{H}_2\text{O}\) were added into a glass beaker, and water was then added into the beaker. The solution was stirred at 80°C until dried. The resulting solids were calcined in a furnace for air continuous flow at 650°C for 3 h to obtain stand-alone \(\text{KFeO}_2\).

**Ethylbenzene redox-ODH reactivity test.** Ethylbenzene redox-ODH was conducted via a cyclic experiment. Ethylbenzene ODH step was conducted first. In this step, 0.5 g of redox catalyst was loaded into a fixed bed quartz U-tube reactor with ID of 1/8 in. The U-tube reactor was heated via a furnace equipped with a K-type thermocouple. Typical ethylbenzene ODH reaction was conducted at 600°C. Ethylbenzene vapor was introduced into the U-tube reactor via a bubbler setup in Supplementary Fig. 1. The bubbler was heated in an oil bath. Ar gas (25 ml/min) was introduced into the bubbler, and the exit gas was Ar/ethylene mixture. The ethylbenzene partial pressure was adjusted by changing the temperature of the oil bath. For example, the oil bath was set at 25°C to obtain an ethylbenzene partial pressure of 0.01 atm. The ethylbenzene ODH step lasted for 30 min. The products were detected and quantified via a downstream quadruple mass spectrometry (QMS, MKS Cirrus II) or gas chromatography (Agilent 7890A). After the ethylbenzene ODH step, the U-tube reactor was purged for 20 min. Then, simulated air (25 ml/min, 20% O\(_2\), balanced in Ar) was introduced into the heated U-tube reactor at 600°C for the air reoxidation step. The air reoxidation step lasted for 5 min for a redox catalyst full reoxidation, and for 2 min for a redox catalyst partial reoxidation.
Catalyst characterization. The exothermicity and the weight change of $\text{H}_2\text{O}_2$ redox cycles with (Ca/Mn)$_{0.5}$ $\alpha$-$\text{O@KFeO}_2$ redox catalyst were measured on a thermoderivatograph (TGDA equipment). Approximately 50 micrograms of redox catalysts were loaded into the crucible cell of the TGA (TA instrument). Then, the TGA cell was heated to 600 °C with 10 °C/min under Ar. $\text{H}_2\text{O}_2$ redox cycles were conducted under 600 °C. First, 10% $\text{H}_2$ (balanced in Ar) was introduced for 5 min as the redox catalyst reduction step. Then, the system was flushed with pure Ar for 30 min. After induction period, 10% $\text{O}_2$ (balanced in Ar) was introduced for 5 min as the redox catalyst reoxidation step. Another 5 min Ar-purging step was followed after that to finish one redox cycle. The redox cycle was repeated for ten times and a stabilized exothermicity/weight change curve was achieved.

In situ XRD experiments were conducted on an Empyrean X-ray diffractometer equipped with an Anton-Parr XKR-900 reactor chamber. A scanning range of 10 – 50° (2θ) was used to obtain XRD patterns by using Cu Kα ($\lambda = 0.1542$ nm) radiation operating at 45 kV and 40 mA. To determine the phase behavior and the stability of the catalyst, a ethylbenzene temperature-programmed reduction (TPR) experiment was conducted in the reactor chamber. A scanning range of 100 to 600 °C and FTIR scans were taken at 100 °C/min. Afterwards, the temperature decreased to 600 °C at a rate of 10 °C/min. The ethylbenzene temperature-programmed reduction (TPR) steps were purged with Ar through an ethylbenzene bubbler located at room temperature. FTIR scans were taken at 100 °C/min. The ethylbenzene ODH experiments were conducted by using deuterium ethylbenzene (ODH) mixtures. The products were detected and quantified via either a downstream or an upstream QMS (MKS Circus II).

Isotopic exchange experiment over the redox catalyst was conducted in an isothermal ODH using co-feed of ethylbenzene and deuterium ethylbenzene to explore the styrene isotope. The experimental setup in Fig. 1 was used. To achieve an ethylbenzene conversion close to 100%, a 2 g-ml of the redox catalyst was loaded into a fixed bed reactor. The catalyst was packed by the volume of ethylbenzene by deuterium ethylbenzene to obtain an equal partial pressure. The ODH reaction was conducted at 600 °C with the continuous normal-deuterium ethylbenzene/Ar flow (25 ml/min) for 20 min. The styrene products were detected and quantified by a downstream quadruple mass spectrometer (QMS, MKS Circus II). Styrene and deuterated styrene were the main products with $m/z$ in the range 104–112, corresponding to C$_8$H$_{8}$D$_n^-$. The yields were calculated on the basis of the relative proportion of the signals of C$_8$H$_{8}$D$_n^-$ from mass spectrometry since both the styrene and deuterium styrenes have very similar mass spectrometry response factors.

DFT simulation. First-principles simulations were performed at the DFT level implemented by the Vienna ab initio simulation package. All-electron projector augmented wave model and Perdew–Burke–Ernzerhof functionals were employed. A kinetic energy cutoff of 450 eV was used for the plane-wave expansion of the electronic wave function. The plane-wave basis set was used. The $\alpha$-Fe(001) surface was considered. A $\Gamma$-centered 4 × 4 × 1 Monkhorst-Pack $k$-point grid with a 4 × 4 × 2 Gamma-centered mesh for pure $\text{KFeO}_2$ unit cell and only Gamma mesh for all the surface slab models were chosen for sampling the first Brillouin zone. Due to the complexity of the $\text{KFeO}_2$ surface structure, it is very difficult to accurately try each magnetic ordering. To make the calculations tractable, we apply the ferromagnetic state for all the structures given that the tiny energy differences due to different magnetic ordering are negligible compared with ionic migration. The strong on-site Coulomb interaction on the $d$-orbital electrons on the Fe sites was treated with the GGA + $U$ approach. We adopted $U_{\text{Fe}} = 4$ eV for $\text{Hund’s exchange interaction}$, which has been proved to give reasonable predictions of both geometric and electronic structures in previous works. The computed lattice constants of $\text{KFeO}_2$ ($a = 5.68$ Å, $b = 11.38$ Å, $c = 16.07$ Å) match well with the experimental values ($a = 5.61$ Å, $b = 11.21$ Å, $c = 15.26$ Å), showing the reliability of the present DFT calculations. For the band structure, the $\text{KFeO}_2$ surface structure is computed with $E_{\text{surf}} = E_{\text{bulk}} + E_{\text{surf}} - E_{\text{bulk-surf}}$, where $E_{\text{surf}}$, $E_{\text{bulk}}$, and $E_{\text{surf-surf}}$ are the energies of $\text{KFeO}_2$ surface model, $\text{KFeO}_2$ molecule, and the adsorbed configuration.

Data availability. The data that support the findings of this study are available from the corresponding author on reasonable request.
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**Author contributions**

X.Z. and Y.G. had an equal contribution in designing and conducting the redox-ODH experiments, interpreting experimental results, and writing the manuscript. V.H. conducted the DFT simulation and compiled the corresponding write-up. V.H. conducted the ASPEN Plus simulation and compiled the corresponding write-up. J.L. conducted redox-ODH experiments at high ethylbenzene vapor pressures. Z.B. and Z.W. conducted the Raman experiments for this work. L.M.N. and H.W. provided suggestions to the experiments. F.L. supervised this work and wrote the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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