Active sites for tandem reactions of CO₂ reduction and ethane dehydrogenation

Binhang Yan^{a,b}, Siyu Yao^a, Shyam Kattel^a, Qiyuan Wu^c, Zhenhua Xie^d, Elaine Gomez^d, Ping Liu^a, Dong Su^e, and Jingguang G. Chen^{a,d,1}

^aChemistry Department, Brookhaven National Laboratory, Upton, NY 11973; ^bDepartment of Chemical Engineering, Tsinghua University, 100084 Beijing, China; ^cDepartment of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794; ^dDepartment of Chemical Engineering, Columbia University, New York, NY 10027; and ^eCenter for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

Edited by Alexis T. Bell, University of California, Berkeley, CA, and approved July 9, 2018 (received for review April 24, 2018)

Ethylene (C₂H₄) is one of the most important raw materials for chemical industry. The tandem reactions of CO₂-assisted dehydrogenation of ethane (C₂H₆) to ethylene creates an opportunity to effectively use the underutilized ethane from shale gas while mitigating anthropogenic CO₂ emissions. Here we identify the most likely active sites over CeO₂-supported NiFe catalysts by using combined in situ characterization with density-functional theory (DFT) calculations. The experimental and theoretical results reveal that the Ni-FeO_x interfacial sites can selectively break the C-H bonds and preserve the C-C bond of C₂H₆ to produce ethylene, while the Ni-CeO_x interfacial sites efficiently cleave all of the C-H and C-C bonds to produce synthesis gas. Controlled synthesis of the two distinct active sites enables rational enhancement of the ethylene selectivity for the CO₂-assisted dehydrogenation of ethane.

CO₂ reduction | ethane dehydrogenation | metal-oxide interfaces | selectivity | heterogeneous catalysis

Shale gas has the potential to revolutionize the energy and chemical industry as its verified reserves have continually increased recently. Ethylene, one of the most important intermediates for chemical industry, can be produced from the underutilized ethane (~10% depending on the particular source) in shale gas (1, 2). The traditional routes for ethylene production from thermal steam cracking (3, 4) and direct dehydrogenation (5) of ethane are energy-intensive and inevitably accompanied with serious coking problems (1, 6). Alternatively, the tandem CO₂-assisted dehydrogenation of ethane to ethylene (overall reaction of C₂H₆ + CO₂ → C₂H₄ + CO + H₂O) over bifunctional catalysts (e.g., reducible oxide-supported metal catalysts) has received significant attention (1, 7–10). In this case, CO₂ can dissociate on the reducible oxide to produce CO and reactive oxygen species (*O). Then, the corresponding *O would assist the dehydrogenation of ethane that adsorbs on the metal-oxide interfaces to ethylene and H₂O. According to the thermodynamic study (*SI Appendix*, Fig. S1), the compatible reaction temperatures should be over 823 K, at which these two tandem reactions can operate on different sites simultaneously. In addition, in this temperature range the stability of catalysts is improved as coke can be removed via the reverse Boudouard reaction (CO₂ + C → 2CO). Furthermore, the equilibrium yield of ethylene can be increased as hydrogen is consumed via the reverse water gas shift reaction (CO₂ + H₂ → CO + H₂O). However, the competing dry-reforming pathway (C₂H₆ + 2CO₂ → 4CO + 3H₂) can also occur simultaneously through the C-C bond scission to produce synthesis gas (CO and H₂). Since the scission of the C-C bond (377 kJ/mol) is thermodynamically more favorable than the cleavage of the C-H bond (423 kJ/mol) of ethane (11), it is critical to identify catalysts that do not promote the C-C bond scission to improve the selectivity to ethylene.

Previous work shows that typical catalysts used for CO₂-assisted dehydrogenation of ethane are Ga-based oxides (6, 8), Cr-based oxides (9, 12–16), Co-based oxides (17, 18), metal carbides (1, 19), and other catalysts (7, 20, 21). However, details are lacking on the nature of the active sites for the activation of CO₂ and ethane and

how to selectively control the C-H and C-C bond scission to increase the ethylene selectivity. Here we demonstrate that the selectivity of CO₂-assisted dehydrogenation of ethane to ethylene can be controlled by using CeO₂-supported NiFe catalysts with different Ni/Fe ratios. A small amount of Fe introduction promotes the C-C bond scission activity (e.g., Ni₃Fe₁/CeO₂ with 99% CO selectivity), while an optimal amount of Fe greatly increases the selective C-H bond cleavage activity (e.g., Ni₁Fe₃/CeO₂ with 78% C₂H₄ selectivity). The Ni-FeO_x interfaces and Ni-CeO_x interfaces are identified as the most likely active sites for CO₂-assisted dehydrogenation of ethane (i.e., selectively cleave the C-H bonds while preserving the C-C bond to produce ethylene) and dry reforming of ethane (efficiently break all of the C-H and C-C bonds to produce synthesis gas), respectively. This work shows that the active sites on CeO₂-supported NiFe catalysts can be fine-tuned to rationally manipulate the catalytic selectivity in parallel reaction pathways for the tandem reactions of CO₂ reduction and ethane dehydrogenation.

Results

Effect of Ni/Fe Ratio on Product Selectivity. A series of CeO₂-supported NiFe catalysts with different Ni/Fe ratios (*SI Appendix*, Table S1) were synthesized and tested (873 K, 10 mL/min C₂H₆ + 10 mL/min CO₂ + 20 mL/min Ar, *SI Appendix*, Figs. S2 and S3 and Table S2), to explore the optimal Ni/Fe ratio for CO₂-assisted dehydrogenation of ethane. As shown in Fig. 1A, the selectivity of C₂H₄ can be tuned from 1 to 78% by changing the Ni/Fe ratio, with the Ni₁Fe₃/CeO₂ catalyst showing the highest C₂H₄ selectivity. As a comparison, Ni₃Fe₁/CeO₂ shows the highest CO selectivity (99%)

Significance

Catalytic activity or selectivity of a supported metal catalyst is predominantly determined by its active site structure. Rational optimization of supported metal catalysts requires fundamental insights into active sites and structure-function relationships. Here, we convincingly identify two types of metal-oxide active sites and successfully correlate them with the corresponding catalytic performance for CO₂-assisted dehydrogenation of ethane. Controlled synthesis of the two distinct active sites enables rational manipulation of the activity and selectivity, offering an opportunity to efficiently convert the underutilized ethane from shale gas to value-added products while mitigating anthropogenic CO₂ emissions.

Author contributions: B.Y. and J.G.C. designed research; B.Y., S.Y., Q.W., Z.X., and E.G. performed research; B.Y., S.Y., Q.W., P.L., and D.S. analyzed data; S.K. and P.L. performed DFT calculations; and B.Y., S.K., and J.G.C. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Published under the PNAS license.

¹To whom correspondence should be addressed. Email: jgchen@columbia.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1806950115/-DCSupplemental.

Published online July 30, 2018.

Fig. 1. Flow reactor results for C₂H₆ + CO₂ reactions over CeO₂-supported NiFe catalysts. (A) C₂H₆ conversion and C₂H₄ selectivity for Ni₃/CeO₂, Ni₃Fe₁/CeO₂, Ni₃Fe₃/CeO₂, Ni₁Fe₃/CeO₂, and Fe₃/CeO₂ at 873 K; data were calculated by averaging data points between 11 and 13 h on stream; reduction conditions: 20 mL/min H₂ + 20 mL/min Ar at 723 K for 1 h; reaction conditions: 10 mL/min C₂H₆ + 10 mL/min CO₂ + 20 mL/min Ar, 100-mg catalyst. (B) C₂H₄ selectivity, CO selectivity, and CO₂ conversion for Ni₃Fe₁/CeO₂ and Ni₁Fe₃/CeO₂ under similar C₂H₆ conversions at 873 K; reaction conditions for Ni₃Fe₁/CeO₂: 10 mL/min C₂H₆ + 10 mL/min CO₂ + 20 mL/min Ar, 16-mg catalyst; reaction conditions for Ni₁Fe₃/CeO₂: 4 mL/min C₂H₆ + 4 mL/min CO₂ + 8 mL/min Ar, 100-mg catalyst.

through the dry-reforming pathway. To examine the selectivity at comparable reactant conversion under reaction-limited conditions, two controlled experiments were performed at 873 K. The product selectivity was almost unchanged for both catalysts (70% dehydrogenation selectivity for Ni₁Fe₃/CeO₂ and 97% reforming selectivity for Ni₃Fe₁/CeO₂) at comparable C₂H₆ conversion (Fig. 1B), suggesting that the difference came from the intrinsic kinetics without the effect of the heat/mass transport. Further analysis for the Ni₁Fe₃/CeO₂ and Ni₃Fe₁/CeO₂ catalysts, including the selectivity vs. conversion plots (*SI Appendix*, Fig. S4) and the conversion/selectivity vs. gas hourly space velocity plots (*SI Appendix*, Fig. S5), can be found in *SI Appendix*. Since Ni/CeO₂ showed an excellent reforming activity while Fe/CeO₂ exhibited a poor activity for both reactions, the distinct performance of Ni₁Fe₃/CeO₂ was inferred to

be due to the formation of active sites that originated from interactions between Fe and Ni. To verify this, control experiments using Ni₁Fe₃/CeO₂ and the physically mixed sample (Ni/CeO₂ + Fe/CeO₂) were performed (*SI Appendix*, Fig. S6). Significant differences were observed: Ni₁Fe₃/CeO₂ still showed a dominant dehydrogenation selectivity while the mixed sample produced complete reforming products. This confirmed that the interaction between Fe and Ni resulted in a structural variation of active sites, leading to significant differences in the reaction mechanism and product selectivity.

Structures of CeO₂ Support and Active Metals. In situ X-ray diffraction (XRD) experiments were performed to reveal the structural information of Ni₁Fe₃/CeO₂ and Ni₃Fe₁/CeO₂ under reaction conditions. Abrupt expansions of CeO₂ lattice were observed for both samples (more clearly shown in *SI Appendix*, Fig. S7 for Ni₃Fe₁/CeO₂), indicating an increase of the average Ce–O bond length due to the partial reduction of Ce⁴⁺ to Ce³⁺. The reduced CeO₂ could effectively promote the activation of CO₂, causing direct C–O bond cleavage at 873 K. Under reaction conditions, metallic Ni (or NiFe alloy) with face-centered cubic (fcc) structure was observed on both Ni₁Fe₃/CeO₂ and Ni₃Fe₁/CeO₂ (Fig. 2 and *SI Appendix*, Fig. S8). The main difference between the two catalysts was the appearance of crystalline Fe₃O₄ or Fe₂O₃ on Ni₁Fe₃/CeO₂ while they were barely found on Ni₃Fe₁/CeO₂. To confirm whether the metal on both catalysts was metallic Ni or NiFe alloy, in situ XRD analysis for Fe₃/CeO₂ and Ni₃/CeO₂ was also performed as comparisons (*SI Appendix*, Figs. S9 and S10). For Ni₃/CeO₂, the fcc structural metallic Ni with a lattice constant of 3.558 Å was observed. The lattice constant of the active metal on Ni₁Fe₃/CeO₂ and Ni₃Fe₁/CeO₂ was calculated to be 3.575 and 3.570 Å, respectively, which is slightly larger than that of metallic Ni, indicating the formation of Ni-rich NiFe alloy with fcc structure (22). This conclusion was verified by the corresponding peak shift for both catalysts under various treatment conditions (Fig. 2 and *SI Appendix*, Fig. S11). The Fe in NiFe alloy could be oxidized in a CO₂/He flow to form amorphous FeO_x (23), resulting in a slight right shift of the diffraction peaks (more close to metallic Ni). When Ni₁Fe₃/CeO₂ was treated in a reductive atmosphere, FeO_x could be reduced to form Fe-rich NiFe alloy with fcc structure, leading to a significantly increased lattice parameter (3.621 Å). Therefore, the formation of Ni-rich NiFe alloy on both catalysts under reaction conditions was confirmed.

Valence State of Ni and Fe. To further determine the valence state of Ni and Fe on Ni₁Fe₃/CeO₂ and Ni₃Fe₁/CeO₂, in situ X-ray absorption near-edge structure (XANES) spectra were collected using a home-designed microchannel reactor (*SI Appendix*, Fig. S12).

Fig. 2. Evolution of in situ XRD profiles under various conditions. (A) Ni₁Fe₃/CeO₂ in the 2θ range of 5.3° to 6.9°. (B) Ni₃Fe₁/CeO₂ in the 2θ range of 5.3° to 6.9°. (C) Ni₁Fe₃/CeO₂ in the 2θ range of 6.4° to 6.9°. (D) Ni₃Fe₁/CeO₂ in the 2θ range of 6.4° to 6.9°. Magenta line, temperature ramping stage: from 300 to 873 K, 2.5 mL/min C₂H₆ + 2.5 mL/min CO₂ + 5.0 mL/min He, 10-mg catalyst; blue line, reaction conditions: 873 K, 2.5 mL/min C₂H₆ + 2.5 mL/min CO₂ + 5.0 mL/min He; green line, CO₂ treatment conditions: 873 K, 2.5 mL/min CO₂ + 7.5 mL/min He; red line, H₂ treatment conditions: 873 K, 5.0 mL/min H₂ + 5.0 mL/min He.

Fig. 3. In situ XANES spectra of Ni K edge and Fe K edge. (A) Ni K edge of $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$, $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$, and Ni_3/CeO_2 with Ni foil and NiO as references under reaction conditions. (B) Fe K edge of $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$, $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$, and Fe_3/CeO_2 with Fe foil, FeO, Fe_3O_4 , and Fe_2O_3 as references under reaction conditions. Reaction conditions: 873 K, 5 mL/min C_2H_6 + 5 mL/min CO_2 + 10 mL/min He, 100 mg catalyst.

Under reaction conditions (Fig. 3), the oxidation state of Ni in both catalysts (and Ni_3/CeO_2 as well) was metallic Ni, while the Fe species in both catalysts (and Fe_3/CeO_2 as well) exhibited similar near-edge features between FeO and Fe_3O_4 (more close to Fe_3O_4 , see the linear combination fitting results shown in *SI Appendix, Fig. S13* and *Table S3* for more details). The detailed extended X-ray absorption fine structure (EXAFS) fitting results (*Table 1* and *SI Appendix, Figs. S14* and *S15*) reveal that the coordination numbers (C.N.) of Ni–Ni(Fe) on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ and $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ were 10.4 and 11.3, indicating metallic NiFe alloy resided in the form of particles with diameters of 2.5–4.0 nm (based on hemisphere fcc models). Compared with Ni_3/CeO_2 , a slight increase in the Ni–Ni(Fe) bond length for both catalysts was observed, consistent with the formation of Ni-rich NiFe alloy with fcc structure as revealed by XRD results. This conclusion was further confirmed by the Fe K-edge EXAFS fittings results as metallic Fe–Fe(Ni) bonding at 2.47 Å was observed in $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$. The Fe K-edge EXAFS fitting results with and without the contributions from Ce are also shown in *SI Appendix, Fig. S16*, which suggest that Fe is coordinated with an element with higher *Z* value (i.e., Ce). The Fe–Ce bonding at 3.6–3.7 Å was observed on both $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ and $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$, indicating a strong interaction between Fe and the CeO_2 support. Combined with the small coordination numbers for the Fe–O bonding, the existence of Fe–Ce bonding suggested that the oxidized Fe species tended to form thin layers on CeO_2 .

Physical State of Active Species. To confirm the formation of amorphous FeO_x thin layers on CeO_2 , ex situ scanning transmission electron microscopy with electron-energy-loss spectroscopy (STEM-EELS) analysis was conducted on the spent $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ and $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ catalysts. As shown in Fig. 4, Ni species tended to form particles, agreeing with both in situ XRD and x-ray absorption spectroscopy (XAS) results. Fe species were found on those Ni particles, suggesting the formation of NiFe alloy as revealed by the XRD and XAS data or the formation of amorphous FeO_x at the surface of Ni (or NiFe alloy) particles as stated in the literature (23). The presence of FeO_x layer was confirmed by the high-resolution STEM image as shown in Fig. 4E. A layer of 2-nm amorphous FeO_x formed on CeO_2 particles in $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ were clearly seen (Fig. 4E and *SI Appendix, Fig. S17*). To further verify this conclusion, EELS line-scan analysis of Fe species was conducted on the two samples. Fig. 4F shows the typical EELS line-scan profiles of Fe species over CeO_2 particles for both samples. The profiles indicated the presence of a thin layer of FeO_x formed on CeO_2 particles in $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ while such a layer was absent in $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$.

Activation Mechanisms of C_2H_6 . To better understand the C_2H_6 activation mechanisms on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ and $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$, C_2H_6 pulse experiments were performed. The cumulative amounts of major products (C_2H_4 , H_2 , CH_4 , and CO) after each pulse injection are plotted in *SI Appendix, Fig. S18*. The observations were consistent with the flow reactor data: C_2H_4 was the primary product on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ while CH_4 , CO, and H_2 were the main products on $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$. More coke formation, associated with much higher CH_4 and H_2 production, was found on $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ (*SI Appendix, Fig. S19*) as it promotes the C–C bond scission. This phenomenon was confirmed by the thermogravimetric analysis results (*SI Appendix, Fig. S20*): the total amount of carbon deposits on the spent $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ catalyst after 14-h flow reactor operation was 8.7 wt % (7,250 $\mu\text{mol/g}$), while that on the spent $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ sample was barely seen, only 0.2 wt % (170 $\mu\text{mol/g}$).

The competition between the selective C–H bond cleavage and the C–C bond scission of C_2H_6 can be reflected by the comparison of the amount of C_2H_4 production with the total amount of CH_4 , CO, and coke formation (*SI Appendix, Fig. S21*). The selectivities were almost the same with the flow reactor results, i.e., over 75% C_2H_4 selectivity on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ while over 99% CO selectivity on $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$. As shown in *SI Appendix, Fig. S21C*, two reaction pathways of C_2H_6 , i.e., oxidative dehydrogenation (ODH, $\text{C}_2\text{H}_6 + \text{*O} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$) and direct dehydrogenation (DDH, $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$), were observed on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$. The ODH pathway dominated the production of C_2H_4 at the first three injections, indicating that the ODH pathway was more favorable than the DDH pathway for C_2H_6 activation when the reactive oxygen species on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ were sufficient. For $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$, oxygen-assisted activation ($\text{C}_2\text{H}_6 + \text{*O} \rightarrow \text{CO}$) and direct dissociation of C_2H_6 ($\text{C}_2\text{H}_6 \rightarrow \text{CH}_4$, coke) were competitive at the first three injections, suggesting that the two activation pathways were expected to occur in parallel when the amount of reactive oxygen species (or lattice oxygen) was sufficient.

It is noted that the ratio of the oxygen consumption amount on $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ over that on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ is around 20, which is very close to the molar ratio of Fe in $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ to Ce in $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ (22.3). This might suggest that the oxygen species for oxidative dehydrogenation on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ are originated from iron oxides since the CeO_2 support is partially covered by a thin layer of FeO_x , while the oxygen species for assisted activation of C_2H_6 on $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ mainly comes from ceria lattice.

Table 1. EXAFS fitting results of $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ and $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ under reaction conditions (873 K, 5 mL/min C_2H_6 + 5 mL/min CO_2 + 10 mL/min He, 100 mg catalyst)

Sample	Shell	Bond length, Å	C.N.	σ^2 , Å ²	E_0 shift, eV
$\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ -Ni K edge	Ni–Ni(Fe)	2.48 ± 0.01	10.4 ± 1.0	0.017	3.3
$\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ -Ni K edge	Ni–Ni(Fe)	2.48 ± 0.01	11.3 ± 1.1	0.017	3.6
Ni_3/CeO_2 -Ni K edge	Ni–Ni	2.46 ± 0.01	10.5 ± 0.7	0.017	2.7
$\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ -Fe K edge	Fe–O	1.95 ± 0.02	4.4 ± 1.1	0.013	–1.7
	Fe–Fe	3.08 ± 0.02	6.0 ± 2.0	0.019	
	Fe–Ce	3.71 ± 0.01	1.7 ± 0.8	0.006	
$\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ -Fe K edge	Fe–O	2.00 ± 0.02	3.9 ± 0.9	0.012	5.3
	Fe–Fe(Ni)	2.47 ± 0.02	0.8 ± 0.3	0.002	
	Fe–Fe	3.09 ± 0.02	1.9 ± 0.6	0.007	
	Fe–Ce	3.65 ± 0.03	1.9 ± 0.5	0.005	
Fe_3/CeO_2 -Fe K edge	Fe–O	1.95 ± 0.01	5.3 ± 0.6	0.012	–0.2
	Fe–Fe	3.01 ± 0.01	5.0 ± 1.4	0.021	

calculated. As shown in *SI Appendix, Table S8*, *O-assisted first C–H bond scission of ethane is highly activated on all surfaces and is likely the most difficult step in the oxidative C–H and C–C bond cleavage of ethane. On Ni(111), the *O insertion reaction ($^*\text{CH}_3\text{CH}_2 + ^*\text{O} \rightarrow ^*\text{CH}_3\text{CH}_2\text{O} + ^*$) along the C–C bond cleavage pathway ($\Delta E = -0.14$ eV and $E_a = 0.44$ eV) is thermodynamically and kinetically more favorable than the oxidative dehydrogenation reaction ($^*\text{CH}_3\text{CH}_2 + ^*\text{O} \rightarrow ^*\text{CH}_2\text{CH}_2 + ^*\text{OH}$) along the C–H bond cleavage pathway ($\Delta E = 0.09$ eV and $E_a = 0.97$ eV). The formed $^*\text{CH}_3\text{CH}_2\text{O}$ undergoes two facile dehydrogenation reactions: $^*\text{CH}_3\text{CH}_2\text{O} + ^* \rightarrow ^*\text{CH}_3\text{CHO} + ^*\text{H}$ ($\Delta E = 0.29$ eV and $E_a = 0.92$ eV) and $^*\text{CH}_3\text{CHO} + ^* \rightarrow ^*\text{CH}_3\text{CO} + ^*\text{H}$ ($\Delta E = -0.48$ eV and $E_a = 0.35$ eV) to produce $^*\text{CH}_3\text{CO}$, which facilitates the C–C bond cleavage to form $^*\text{CH}_3 + ^*\text{CO}$ ($\Delta E = -0.48$ eV and $E_a = 1.01$ eV). The favorable C–C bond cleavage via $^*\text{CH}_3\text{CH}_2\text{O}$ and $^*\text{CH}_3\text{CO}$ intermediates shows that the oxidative C–C bond cleavage is preferred on Ni(111). On Ni-terminated- Ni_3Fe (111), *SI Appendix, Table S8* shows that the *O insertion reaction to form $^*\text{CH}_3\text{CH}_2\text{O}$ is comparable with the oxidative dehydrogenation reaction to form $^*\text{CH}_2\text{CH}_2$. Hence, Ni-terminated- Ni_3Fe (111) is expected to promote both the C–C and the C–H bond cleavage. On the other hand, on bulk-terminated- Ni_3Fe (111), the activation energy of oxidative dehydrogenation reaction is 0.16 eV lower in barrier than the *O insertion reaction. As a result, bulk-terminated- Ni_3Fe (111) is predicted to promote the C–H bond cleavage slightly more than the C–C bond cleavage, suggesting that the presence of Fe on the surface is essential to selectively facilitate the C–H bond cleavage of ethane to produce CH_2CH_2 . Furthermore, the DFT results on FeO_x/Ni (111) show that the oxidative dehydrogenation reaction ($\Delta E = -0.13$ eV and $E_a = 1.08$ eV) is more favorable than the *O insertion reaction ($\Delta E = -0.04$ eV and $E_a = 1.67$ eV). Due to the formation of FeO_x , the *O on the surface of FeO_x/Ni (111) is more stable than that on Ni(111). As a result, the formation of $^*\text{CH}_3\text{CH}_2\text{O}$ or the oxidative pathway is hindered (Fig. 5D). Instead, a hydrogen bond is formed between O of FeO_x cluster and H of $^*\text{CH}_3\text{CH}_2$ at the interface (*SI Appendix, Fig. S25H*), which promotes the stability of $^*\text{CH}_3\text{CH}_2$ and therefore the dehydrogenation pathway. Consistent with the prediction from energy diagram in Fig. 5D and experiments, the Ni- FeO_x interface is expected as the active site to promote the dehydrogenation of ethane.

Discussion

As shown in *SI Appendix, Table S2*, the switch between two distinguished pathways is observed: $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ can efficiently break all of the C–H and C–C bonds to produce synthesis gas; in contrast, $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ selectively cleaves the C–H bonds while preserving the C–C bond to produce C_2H_4 . Although there are significant differences in activity and selectivity, the formation of Ni-rich NiFe alloy with fcc structure (Fig. 2) is observed on both catalysts according to the in situ XRD results under reaction conditions. However, the metallic Fe–Fe(Ni) bonding is only found on $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ while barely seen on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ (Table 1), suggesting that the ratio of metallic Fe in overall Fe species is quite low, especially on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$. The average valence state of Fe species on the two catalysts is also quite similar under reaction conditions (between FeO and Fe_3O_4 , more close to Fe_3O_4), as shown in Fig. 3. The crystalline Fe_3O_4 or Fe_2O_3 species are only found on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ with relatively weak signals. This means a large proportion of FeO_x (with an average valence state between FeO and Fe_3O_4) is highly dispersed or in an amorphous form taking into account that the ratio of metallic Fe is extremely low. According to the in situ XRD and XAS measurements, the Ni-rich NiFe alloy exists as particles. Combined with the results revealed by the STEM-EELS analysis, it can be concluded that Fe (in the form of amorphous FeO_x) is preferred to exist between metal particles and the CeO_2 support (as the Fe–Ce bonding is found on both catalysts) under reaction conditions.

For irreducible oxides (e.g., SiO_2 , Al_2O_3) supported Ni catalysts, metallic Ni (Ni^0) particles are believed to be the active sites for CO_2 reforming of alkanes, where the dissociation rate of alkane is faster than that of CO_2 (28). In contrast, for CeO_2 -supported Ni catalysts, the reducible oxide, CeO_2 , helps in enabling the facile CO_2 dissociation and producing *O species on the surface, making them bifunctional catalysts (29). The produced *O species on the support reacts with carbon originated from the ethane decomposition on the metallic Ni particles at the metal–support interfaces to produce CO, leading to a much higher reforming activity compared with Ni/SiO_2 under the same conditions (as shown in *SI Appendix, Fig. S26*). Therefore, the Ni- CeO_x interfacial sites are proposed as the most likely active sites for dry reforming of ethane as they are more active than the metallic Ni sites in irreducible SiO_2 .

When a small amount of Fe is added to Ni_3/CeO_2 (i.e., $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$), although FeO_x is preferred to exist underneath the predominantly Ni particles, the Ni- CeO_x interfacial sites still dominate the conversion of ethane with CO_2 , maintaining the CO selectivity at a high level (over 95%). Meanwhile, the formation of FeO_x slightly promotes the removal of the coke deposits, leading to an enhanced reforming activity (23). Therefore, although the metallic Ni particles, Ni-rich NiFe alloy, and Ni- CeO_x interfaces can be the possible active sites for $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$, the Ni- CeO_x interfaces are identified as the most likely active sites for dry reforming of ethane with CO_2 (effective C–H and C–C bonds scission of C_2H_6 to produce synthesis gas) due to the highest activity observed in $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$.

When a large amount of Fe is introduced (i.e., $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$), the amorphous FeO_x spreads far enough to form the Ni- FeO_x interfacial sites on the perimeter of Ni particles, likely replacing the Ni- CeO_x interfacial sites. Since the FeO_x , CeO_x , and FeO_x - CeO_x interfaces (all of the possible active species on Fe_3/CeO_2) show little activity for either oxidative dehydrogenation or dry reforming of ethane, the Ni- FeO_x interfaces are identified as the most likely active sites for CO_2 -assisted dehydrogenation of ethane (selective C–H bond cleavage of C_2H_6 to produce C_2H_4). The DFT calculations also confirm that the FeO_x/Ni (111) interface can promote the stability of $^*\text{CH}_3\text{CH}_2$ and therefore the dehydrogenation pathway, while hindering the formation of $^*\text{CH}_3\text{CH}_2\text{O}$ and its subsequent dehydrogenation and C–C bond cleavage reactions via $^*\text{CH}_3\text{CO}$ (Fig. 5). The DFT-calculated activation energy of oxidative dehydrogenation reaction (oxygen-assisted C–H bond cleavage) is lower than that of dry-reforming reaction (C–C bond scission) on FeO_x/Ni (111), consistent with the experimental results that the Ni- FeO_x interfaces are identified as the most likely active sites to promote the selective C–H bond cleavage of ethane.

Based on the ethane pulse experiments, the oxidative C–H bond cleavage (dehydrogenation) of ethane is proposed to be the primary reaction pathway on Ni- FeO_x interfaces, while oxygen-assisted scission of C–C bond and direct dissociation of the C–C bond in ethane are competitive and occur in parallel on Ni- CeO_x interfaces. The presence of Ni should help the reduction of its neighbor FeO_x to form NiFe alloy with fcc structure. The higher amount of Ni loading, the lower formation temperature of the NiFe alloy. As shown in Fig. 2, the NiFe alloy on $\text{Ni}_1\text{Fe}_3/\text{CeO}_2$ is not formed until 853 K, while the appearance of the NiFe alloy in the XRD patterns on $\text{Ni}_3\text{Fe}_1/\text{CeO}_2$ starts at a temperature as low as 693 K. It can be inferred that when the loading amounts of Fe and Ni are close, e.g., $\text{Ni}_3\text{Fe}_3/\text{CeO}_2$, a large amount of Ni- FeO_x interfaces with moderate activity for oxidative dehydrogenation would coexist with a small amount of Ni- CeO_x interfaces with high activity for dry reforming, leading to almost equal selectivities for both dry reforming and oxidative dehydrogenation pathways, as shown in *SI Appendix, Table S2*.

Conclusion

Combined in situ/ex situ characterization with DFT calculations were employed to convincingly identify the two types of active sites for CO₂-assisted dehydrogenation of ethane over CeO₂-supported NiFe catalysts. The results demonstrated that the Ni-FeO_x and Ni-CeO_x interfaces are the most likely active sites for CO₂-assisted dehydrogenation of ethane (selective C-H bond cleavage to produce ethylene) and dry reforming of ethane with CO₂ (efficient C-C bond scission to produce synthesis gas), respectively. For CeO₂-supported NiFe catalysts, the role of Fe in controlling the ethylene selectivity is mainly due to the formation of Ni-FeO_x interfacial sites replacing the Ni-CeO_x interfacial sites. These results gain better understanding of the structure-function relationships between the active site and catalytic performance, offering strategies for controlling and tuning the activity and selectivity of oxide-supported metal catalysts for the tandem reactions of CO₂ reduction and ethane dehydrogenation.

Methods

All catalysts were synthesized by an incipient wetness impregnation approach over commercial CeO₂ supports with an aqueous solution of the respective metal precursors. CO uptake measurements were performed using an Altamira AMI-300 ip system. The metal loading amount, atomic ratio, and CO uptake value of each catalyst are listed in *SI Appendix, Table S1*. Flow reactor studies of C₂H₆ + CO₂ reactions were performed in a quartz tube reactor at atmospheric pressure in the presence of reactants (10 mL/min C₂H₆, 10 mL/min CO₂, and 20 mL/min Ar, 873 K). Pulse reactor experiments were carried out at 873 K with 15 pulses of 10% C₂H₆/N₂ via a 1-mL gas loop (423 K). The in situ XRD measurement was performed at Beamline 17-BM of Advanced Photon Source (APS) at Argonne National Laboratory (ANL). For each experiment, ~10 mg sample was held at 873 K for 45 min in the presence of reactants (2.5 mL/min C₂H₆, 2.5 mL/min CO₂, and 5.0 mL/min He).

The in situ XAS experiments were performed at Beamline 9-BM of APS at ANL. Two sets of X-ray absorption fine structure (XAFS) spectra were acquired for each sample: reduction in a H₂/He flow at 723 K and reaction in a C₂H₆/CO₂/He flow at 873 K. The STEM-EELS analysis for the spent Ni₃Fe₁/CeO₂ and Ni₁Fe₃/CeO₂ samples was executed on a Hitachi 2700C STEM with a probe aberration corrector operated at 200 kV. EELS data were collected using the Gatan Enfina spectrometer.

Spin-polarized DFT calculations were performed using Vienna Ab Initio Simulation Package (VASP) code. The Ni(111) surface was modeled using a four-layer 3 × 3 surface slab. The bulk-terminated Ni₃Fe(111) surface was modeled using a four-layer 4 × 4 surface slab to represent Ni-rich NiFe alloy in experiments. The bulk-terminated Ni₃Fe(111) surface was cleaved using an L12-Ni₃Fe cubic crystal structure. The Ni-terminated-Ni₃Fe(111) surface obtained by replacing surface layer of bulk-terminated-Ni₃Fe(111) with Ni atoms was modeled to represent a NiFe alloy with dilute Fe content. The FeO_x/Ni(111) interface was modeled by depositing a small Fe₃O₃ cluster on a three-layer 7 × 7 Ni(111) surface. The various possible adsorption sites shown in *SI Appendix, Fig. S23* were considered during the calculations of binding energies. The transition state of a chemical reaction was located using the climbing image nudged elastic band method implemented in VASP.

More details about the experimental and theoretical methods are provided in *SI Appendix*.

ACKNOWLEDGMENTS. The in situ XRD and XANES measurements were performed at the 17-BM beamline of the APS at Argonne National Laboratory and 2-2 beamline at the Stanford Synchrotron Radiation Lightsource at Stanford Linear Accelerator Center (SLAC) National Accelerator Laboratory, respectively. The work was partly carried out at Brookhaven National Laboratory (BNL) supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract DE-SC0012704. The DFT calculations were performed using computational resources at the Center for Functional Nanomaterials at BNL, a DOE Office of Science User Facility, and at the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility, supported by the Office of Science of the DOE under Contract DE-AC02-05CH11231.

- Porosoff MD, et al. (2015) Identifying different types of catalysts for CO₂ reduction by ethane through dry reforming and oxidative dehydrogenation. *Angew Chem Int Ed Engl* 54:15501–15505.
- Yan BH, et al. (2016) Dry reforming of ethane and butane with CO₂ over PtNi/CeO₂ bimetallic catalysts. *ACS Catal* 6:7283–7292.
- Choudhary VR, Mondal KC, Mulla SAR (2006) Non-catalytic pyrolysis of ethane to ethylene in the presence of CO₂ with or without limited O₂. *J Chem Sci* 118:261–267.
- Gärtner CA, Van Veen AC, Lercher JA (2013) Oxidative dehydrogenation of ethane: Common principles and mechanistic aspects. *ChemCatChem* 5:3196–3217.
- Cavani F, Ballarini N, Cericola A (2007) Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catal Today* 127:113–131.
- Shen Z, et al. (2009) Dehydrogenation of ethane to ethylene over a highly efficient Ga₂O₃/HZSM-5 catalyst in the presence of CO₂. *Appl Catal A Gen* 356:148–153.
- Lei J, et al. (2009) Studies on dehydrogenation of ethane in the presence of CO₂ over octahedral molecular sieve (OMS-2) catalysts. *ChemCatChem* 1:441–444.
- Koirala R, Buechel R, Krumeich F, Pratsinis SE, Baiker A (2015) Oxidative dehydrogenation of ethane with CO₂ over flame-made Ga-loaded TiO₂. *ACS Catal* 5:690–702.
- Asghari E, Haghighi M, Rahmani F (2016) CO₂ oxidative dehydrogenation of ethane to ethylene over Cr/MCM-41 nanocatalyst synthesized via hydrothermal/impregnation methods: Influence of chromium content on catalytic properties and performance. *J Mol Catal Chem* 418–419:115–124.
- Myint M, Yan B, Wan J, Zhao S, Chen JG (2016) Reforming and oxidative dehydrogenation of ethane with CO₂ as a soft oxidant over bimetallic catalysts. *J Catal* 343:168–177.
- Blanksby SJ, Ellison GB (2003) Bond dissociation energies of organic molecules. *Acc Chem Res* 36:255–263.
- Mimura N, Takahara I, Inaba M, Okamoto M, Murata K (2002) High-performance Cr/H-ZSM-5 catalysts for oxidative dehydrogenation of ethane to ethylene with CO₂ as an oxidant. *Catal Commun* 3:257–262.
- Mimura N, Okamoto M, Yamashita H, Oyama ST, Murata K (2006) Oxidative dehydrogenation of ethane over Cr/ZSM-5 catalysts using CO₂ as an oxidant. *J Phys Chem B* 110:21764–21770.
- Deng S, Li H, Li S, Zhang Y (2007) Activity and characterization of modified Cr₂O₃/ZrO₂ nano-composite catalysts for oxidative dehydrogenation of ethane to ethylene with CO₂. *J Mol Catal A Chem* 268:169–175.
- Deng S, Li S, Li H, Zhang Y (2009) Oxidative dehydrogenation of ethane to ethylene with CO₂ over Fe–Cr/ZrO₂ catalysts. *Ind Eng Chem Res* 48:7561–7566.
- Talati A, Haghighi M, Rahmani F (2016) Oxidative dehydrogenation of ethane to ethylene by carbon dioxide over Cr/TiO₂–ZrO₂ nanocatalyst: Effect of active phase and support composition on catalytic properties and performance. *Adv Powder Technol* 27:1195–1206.
- Zhang X, Ye Q, Xu B, He D (2007) Oxidative dehydrogenation of ethane over Co–BaCO₃ catalysts using CO₂ as oxidant: Effects of Co promoter. *Catal Lett* 117:140–145.
- Koirala R, Buechel R, Pratsinis SE, Baiker A (2016) Silica is preferred over various single and mixed oxides as support for CO₂-assisted cobalt-catalyzed oxidative dehydrogenation of ethane. *Appl Catal A Gen* 527:96–108.
- Solymosi F, Németh R (1999) The oxidative dehydrogenation of ethane with CO₂ over Mo₂C/SiO₂ catalyst. *Catal Lett* 62:197–200.
- Baidya T, van Vegten N, Baiker A (2011) Selective conversion of ethane to ethene via oxidative dehydrogenation over Ca-doped ThO₂ using CO₂ as oxidant. *Top Catal* 54:881–887.
- Zhu J, et al. (2009) Na₂WO₄/Mn/SiO₂ catalyst for oxidative dehydrogenation of ethane using CO₂ as oxidant. *Catal Today* 148:310–315.
- Moghimi N, Bazargan S, Pradhan D, Leung KT (2013) Phase-induced shape evolution of FeNi nanoalloys and their air stability by in-situ surface passivation. *J Phys Chem C* 117:4852–4858.
- Kim SM, et al. (2017) Cooperativity and dynamics increase the performance of NiFe dry reforming catalysts. *J Am Chem Soc* 139:1937–1949.
- Graciani J, et al. (2014) Catalysis. Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO₂. *Science* 345:546–550.
- Kattel S, Ramirez PJ, Chen JG, Rodriguez JA, Liu P (2017) Active sites for CO₂ hydrogenation to methanol on Cu/ZnO catalysts. *Science* 355:1296–1299.
- Kattel S, Yan B, Yang Y, Chen JG, Liu P (2016) Optimizing binding energies of key intermediates for CO₂ hydrogenation to methanol over oxide-supported copper. *J Am Chem Soc* 138:12440–12450.
- Kattel S, et al. (2016) CO₂ hydrogenation over oxide-supported PtCo catalysts: The role of the oxide support in determining the product selectivity. *Angew Chem Int Ed Engl* 55:7968–7973.
- Tsipourari VA, Vekyios XE (1999) Carbon and oxygen reaction pathways of CO₂ reforming of methane over Ni/La₂O₃ and Ni/Al₂O₃ catalysts studied by isotopic tracing techniques. *J Catal* 187:85–94.
- Sierra Gallego G, Batiot-Dupeyrat C, Barrault J, Mondragón F (2008) Dual active-site mechanism for dry methane reforming over Ni/La₂O₃ produced from LaNiO₃ perovskite. *Ind Eng Chem Res* 47:9272–9278.