Near 100% CO selectivity in nanoscaled iron-based oxygen carriers for chemical looping methane partial oxidation

Yan Liu1,3, Lang Qin1,3, Zhuo Cheng1,3, Josh W. Goetze1, Fanhe Kong1, Jonathan A. Fan2 & Liang-Shih Fan1*

Chemical looping methane partial oxidation provides an energy and cost effective route for methane utilization. However, there is considerable CO2 co-production in current chemical looping systems, rendering a decreased productivity in value-added fuels or chemicals. In this work, we demonstrate that the co-production of CO2 can be dramatically suppressed in methane partial oxidation reactions using iron oxide nanoparticles embedded in mesoporous silica matrix. We experimentally obtain near 100% CO selectivity in a cyclic redox system at 750–935 °C, which is a significantly lower temperature range than in conventional oxygen carrier systems. Density functional theory calculations elucidate the origins for such selectivity and show that low-coordinated lattice oxygen atoms on the surface of nanoparticles significantly promote Fe–O bond cleavage and CO formation. We envision that embedded nanostructured oxygen carriers have the potential to serve as a general materials platform for redox reactions with nanomaterials at high temperatures.
Syngas, i.e., CO and H₂, is an important intermediate for producing fuels and value-added chemicals from methane via Fischer–Tropsch or other synthesis techniques. Syngas has been produced commercially by steam reforming, autothermal reforming, and partial oxidation of methane for many decades. However, an improvement of its energy consumption, environmental impact, and associated production cost has always been of interest. This has prompted the investigation into alternative routes that can avoid the use of air separation units for producing purified oxygen and are more effective in CO₂ emission control. It is also of interest to reduce the operating temperature of these processes, which are generally endothermic and traditionally require temperatures of 900 °C or higher to attain high reactant conversion rates. The use of high temperatures is problematic because the thermodynamic driving force for carbon deposition, and thus materials obliteration, can be accelerated. Current approaches to reducing reaction temperatures while avoiding side product formation require noble metals such as Pt, Pd, or Au, which leads to dramatic increases in cost.

Chemical looping partial oxidation (CLPO) is an emerging approach that overcomes the above-mentioned shortcomings for syngas production. A CLPO process involves redox reactions taking place in two interconnected reactors: a reducer (or fuel reactor) and an oxidizer (also referred to as air reactor), shown in Fig. 1a. In contrast to conventional fossil fuel gasification and reforming processes, CLPO eliminates the need for an air separation unit, water–gas shift reactor, and acid gas removal unit. It has the potential to directly produce high-quality syngas with desirable H₂:CO ratios. The core of CLPO using natural gas as the feedstock involves complex redox reactions in which methane molecules adsorb and dissociate on metal oxide oxygen carrier surfaces. It also involves internal lattice oxygen ion diffusion in which oxygen vacancy creation and annihilation occurs. These reactions can be engineered to withstand thousands of redox cycles.

The recent progress in chemical looping technology for partial oxidation has advanced to the stage where successful pilot operation has been demonstrated and proven to be highly efficient with a minimal energy penalty in the process applications.

In this technology, the highest CO selectivity that the CLPO can reach is thermodynamically limited to 90% with accompanied 10% CO₂ generation. It is recognized that the CO₂ reduction in low purity syngas is extremely challenging and energy consuming, as CO₂ is among the most chemically stable carbon-based molecules. This 10% of CO₂ in syngas can significantly reduce the productivity of value-added fuels or chemicals generated. Breaking away from the 90% CO yield limits to achieve near 100% CO selectivity requires a different consideration from the metal oxide materials design and synthesis perspective.

We report an approach to metal oxide oxygen carrier engineering for CLPO by designing and synthesizing nanoscale iron oxide carriers embedded in mesoporous silica SBA-15. Mesoporous silica is an engineered nanomaterial that has high surface area, ordered pore structures, and high tunability of morphology. Its unique properties have attracted broad attention in a number of applications such as environmental treatment, catalysis, and biomedical engineering. SBA-15 is a common mesoporous silica that has perpendicular nanochannels with a narrow pore size distribution which is suitable for nanoparticle separation and gas penetration. A schematic of our materials platform is outlined in Fig. 1a. We experimentally achieve a high CO selectivity >99%, which is by far the highest in CLPO systems (Fig. 1b). We also find that cyclic methane partial oxidation with nanoscale oxygen carrier materials can be performed with high selectivity at temperatures as low as 750 °C. These findings underscore the strong size-dependent effects of metal oxide oxygen carriers at the nanoscale on syngas selectivity and reactant conversion in redox processes. This work will have broader impacts not only on CLPO, but also on other chemical looping applications such as carbonaceous fuel conversion and utilization.

Results

Characteristics of Fe₂O₃@SBA-15. Figure 2 shows the transmission electron microscope (TEM) images of Fe₂O₃@SBA-15 before and after redox cycles with no obvious morphological distinction. Nanoparticles with a size of 3–5 nm can be identified.
as α-Fe$_2$O$_3$ based on lattice fringes measurement in which $a = b = 5.038$ Å and $c = 13.772$ Å. Element mapping is presented in Supplementary Fig. 1, suggesting that Fe$_2$O$_3$ nanoparticles are embedded in SBA-15 nanochannels. The TEM images also confirm that the nanoparticles remain embedded in SBA-15 nanochannels with identical morphology after 75 redox cycles. The particle size slightly increases to 5–8 nm after 75 redox cycles due to unavoidable morphology evolution. This result indicates that the nanoparticles will evolve to microparticles of 1–10 µm after 75 redox cycles. On the other hand, the morphology of Fe$_2$O$_3$@SBA-15 arrays before and after 75 redox cycles (Supplementary Fig. 3e, f) remain almost unchanged, indicating high recyclability of Fe$_2$O$_3$@SBA-15 at both nanoscale and microscale.

The mesoporous silica SBA-15 (Supplementary Fig. 2) exhibits a surface area of 550 m$^2$ g$^{-1}$, a uniform pore size of 8 nm, and a pore volume of 0.66 cm$^3$ g$^{-1}$ (Supplementary Methods). The pore volume decreases to 0.52 cm$^3$ g$^{-1}$ which is 23% less than SBA-15 after Fe$_2$O$_3$ nanoparticle loading, implying a Fe$_2$O$_3$ nanoparticle volume loading of ~20%. The average pore size remains at 8 nm with a minor decrease in magnitude, indicating that the silica nanochannels are partially filled by Fe$_2$O$_3$ nanoparticles.

In comparison, Supplementary Fig. 3a, c suggests that the unsupported Fe$_2$O$_3$ nanoparticles are agglomerated with a wide size distribution of 50–100 nm. Supplementary Fig. 3b, d reveals that the nanoparticles will evolve to microparticles of 1–10 µm.

**Fig. 2** Morphological characteristics of Fe$_2$O$_3$@SBA-15. a Fresh Fe$_2$O$_3$@SBA-15 and HR-TEM images of two typical Fe$_2$O$_3$ nanoparticles (Scale bar represents 1 nm); b Fe$_2$O$_3$@SBA-15 after 75 redox cycles and HR-TEM images of two typical Fe$_2$O$_3$ nanoparticles (Scale bar represents 5 nm).

**Fig. 3** Reactivity and selectivity comparison between Fe$_2$O$_3$@SBA-15 and bulk Fe$_2$O$_3$. a Temperature programmed reduction results of Fe$_2$O$_3$@SBA-15 and unsupported Fe$_2$O$_3$. b Conversion rate during redox at 800 °C.

**Methane CLPO with Fe$_2$O$_3$@SBA-15.** The reactivity and recyclability test results are shown in Fig. 3. A stable CO$_2$ concentration of <0.7% g$_{O_2}$$^{-1}$ is observed in Fe$_2$O$_3$@SBA-15 throughout methane partial oxidation, indicating a high syngas selectivity higher than 99.3%. In unsupported Fe$_2$O$_3$, CO$_2$ formation is observed to increase with temperature, resulting in an average selectivity less than 87%. In the range of 750–935 °C, CO concentration from Fe$_2$O$_3$@SBA-15 is over 200% higher than unsupported Fe$_2$O$_3$, suggesting a near 100% CO selectivity with significantly higher CO conversion rate.

Over 75 continuous redox cycles were carried out on both Fe$_2$O$_3$ samples with and without SBA-15 support (Supplementary Fig. 4). Five typical TGA redox cycles are shown in Fig. 3b. The high recyclability is consistent with TEM observation. Fe$_2$O$_3$@SBA-15 not only has a high conversion rate, but is stable at high temperatures. This suggests that the separation of nanoparticles is essential in maintaining high CO selectivity, reactivity, and recyclability. At 800 °C, the conversion rate of Fe$_2$O$_3$@SBA-15 is 67% higher than unsupported Fe$_2$O$_3$. The morphology of post redox nanoparticles can be found in Fig. 2b, where Fe$_2$O$_3$@SBA-15 nanochannels remain almost identical to fresh samples. This demonstrates the high stability and anti-sintering effect of dispersed nanostructures at high temperatures. The average pore size of Fe$_2$O$_3$@SBA-15 is 7.6 nm after 75 redox cycles (Supplementary Fig. 5), which confirms high cyclic stability.

The methane conversion and syngas selectivity of both unsupported Fe$_2$O$_3$ and Fe$_2$O$_3$@SBA-15 were also evaluated in a quartz U-tube (1 cm diameter) fixed bed reactor. As illustrated in Supplementary Fig. 6, a high selectivity near 100% in Fe$_2$O$_3$@SBA-15 is confirmed in both TGA and fixed bed reactor and a higher methane conversion is also obtained compared with unsupported Fe$_2$O$_3$ with different weight hourly space velocity (WHSV).

**Size-dependent reaction modeling.** To gain mechanistic insight into the role of the nanostructures in CO selectivity enhancement of Fe$_2$O$_3$@SBA-15, first-principles calculations were performed.
within the framework of density functional theory (DFT) using
the Vienna Ab Initio Simulation Package (VASP)\textsuperscript{18–20}. To take
into consideration realistic experimental conditions (800 °C for CH\textsubscript{4} partial oxidation), the temperature effect is included by
explicitly taking into account adsorbed CH\textsubscript{4} molecules in terms
of ab initio atomistic thermodynamics. The theoretical description
requires the size and geometry of the model to be as realistic
as possible, for direct comparison with experimental samples.
However, modeling (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{n} nanoparticles of realistic size
(>3 nm) by first-principles calculations is very demanding and the
global optimization is hardly feasible. In this work, (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{60}
(~2 nm) is modeled as the largest nanoparticle to examine the size
effect. Figure 4 shows calculated energies of CH\textsubscript{4} adsorption on Fe
atop site and O atop site of (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{n} nanoparticles as a function
of \(n\), and the corresponding adsorption geometries are described in
Supplementary Fig. 7. The data of the previous computational
study on CH\textsubscript{4} adsorption on Fe\textsubscript{2}O\textsubscript{3} (001) surface are given by the
filled circle\textsuperscript{21}. It can be seen that CH\textsubscript{4} adsorption energies dra-
tomically decrease with increasing number, \(n\) when the sizes of
Fe\textsubscript{2}O\textsubscript{3} nanoparticles are at a relatively small scale. However, they
decrease slowly with increasing \(n\) when the sizes are at relatively
large scale. The strongest adsorption on (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{4} is CH\textsubscript{4} binding
at the Fe atop site with an adsorption energy of 66.2 kJ mol\textsuperscript{−1}.
The second stable configuration is CH\textsubscript{4} adsorption at the O atop site of (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{4} with an adsorption energy of 35.1 kJ mol\textsuperscript{−1}.

When \(n\) increases from 4 to 60, the Fe atop adsorption becomes
weaker with 43.9 kJ mol\textsuperscript{−1} lower adsorption energy. However, the
adsorption at the Fe atop site and the O atop site of (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{60}
nanoparticles is still stronger than adsorption on Fe\textsubscript{2}O\textsubscript{3} (001) surface, as shown in Fig. 5. This is because the average coordi-
nation number of surface Fe atoms in (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{n} nanoparticle is smaller than that on Fe\textsubscript{2}O\textsubscript{3} (001) surface. The undercoordination
results in an upward shift of the Fe d-band, yielding high binding
energies.

In chemical looping partial oxidation process, CH\textsubscript{4} is initially
dissociated over oxygen carriers to form hydrogen and CH\textsubscript{2} radicals. Then the CH\textsubscript{2} radicals are oxidized by lattice oxygen to
generate CO or CO\textsubscript{2}\textsuperscript{21,22}. Since the energy and geometry of CH\textsubscript{2} adsorption on (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{20}
is similar with CH\textsubscript{4} adsorption on (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{60}, Fe\textsubscript{40}O\textsubscript{60} (\(n = 20\)) nanoparticles are chosen as the
model to calculate the reaction barriers of CH\textsubscript{2} dissociation and
oxidation. The energy profile was mapped out as shown in Fig. 5.
The energy barrier for the first step of CH\textsubscript{2} dissociation on
Fe\textsubscript{40}O\textsubscript{60} is 135.8 kJ mol\textsuperscript{−1}, which is 55.7 kJ mol\textsuperscript{−1} lower than that
of CH\textsubscript{4} dissociation on the Fe\textsubscript{2}O\textsubscript{3} (001) surface. Fe\textsubscript{40}O\textsubscript{60} also
exhibit higher activity for CH\textsubscript{3}, CH\textsubscript{2}, and CH dissociation due to
the lower barriers, compared with the Fe\textsubscript{2}O\textsubscript{3} (001) surface. It
indicates that nanostructured Fe\textsubscript{2}O\textsubscript{3} facilitates CH\textsubscript{4} conversion
compared with bulk Fe\textsubscript{2}O\textsubscript{3}, which is in good agreement with TGA and fixed bed test. After methane dissociation, all C–H
bonds are cleaved to generate a carbon atom and four hydrogen
atoms. Fe\textsubscript{40}O\textsubscript{60} has three chemically distinguishable types of
lattice oxygen atoms: 2-fold coordinated lattice oxygen O\textsubscript{2C},
3-fold coordinated lattice oxygen O\textsubscript{3C}, and 4-fold coordinated
lattice oxygen O\textsubscript{sub}. As such, there are three reaction pathways for
CO formation as shown in Supplementary Fig. 8. The calculated
barriers for CO\textsubscript{2C}, CO\textsubscript{3C}, and CO\textsubscript{sub} formation are 37.2 kJ mol\textsuperscript{−1},
69.6 kJ mol\textsuperscript{−1}, and 58.5 kJ mol\textsuperscript{−1}, respectively. This result indi-
cates C binding to O\textsubscript{2C} is the most favorable path, compared with
C binding to O\textsubscript{3C} and O\textsubscript{sub} because Fe–O bonds of low-
coordinated lattice oxygen atoms are easier to break than high-
coordinated lattice oxygen atoms. In contrast to Fe\textsubscript{40}O\textsubscript{60}, all
lattice oxygen atoms in the topmost atomic layer of the Fe\textsubscript{2}O\textsubscript{3}
(001) surface are three-coordinated atoms. Thus, the carbon atom
on the Fe\textsubscript{2}O\textsubscript{3} (001) surface converts to CO only via binding to
O\textsubscript{3C}, leading to a relatively high barrier of 61.2 kJ mol\textsuperscript{−1} as shown in Fig. 5.

The formed CO may further react with surface lattice O atoms
to form CO\textsubscript{2}\textsuperscript{21,22}. For the Fe\textsubscript{40}O\textsubscript{60} nanoparticle, the formation of
CO\textsubscript{2} needs to overcome a barrier of 148.9 kJ mol\textsuperscript{−1}, which is
30.4 kJ mol\textsuperscript{−1} higher than that of CO\textsubscript{2} formation on Fe\textsubscript{2}O\textsubscript{3} (001)
surface. The high barrier with respect to CO\textsubscript{2} formation on

![Fig. 4](image-url) Calculated energies of CH\textsubscript{4} adsorption, \(E_{\text{ad}}\) (kJ mol\textsuperscript{−1}), on Fe atop site
and O atop site of (Fe\textsubscript{2}O\textsubscript{3})\textsubscript{n} nanoparticles as a function of \(n\). The adsorption
trends are shown by the blue and red lines.

![Fig. 5](image-url) Energy profile of CH\textsubscript{4} partial oxidation on Fe\textsubscript{40}O\textsubscript{60} nanoparticle and Fe\textsubscript{2}O\textsubscript{3} (001) surface.
Fe$_{40}$O$_{60}$ is attributed to the surface stress of nanoparticles, induced by surface atoms with unsaturated coordination. The surface stress leads to shorter and thus stronger Fe–O$_{3C}$ bonds compared with Fe–O$_{3C}$ bonds of the Fe$_2$O$_3$ (001) surface. The formation of CO$_2$ on Fe$_{40}$O$_{60}$ is endothermic, with the calculated reaction energy of 58.2 kJ mol$^{-1}$. These results indicate that the CO$_2$ formation on Fe$_{40}$O$_{60}$ is both kinetically and thermochemically unfavorable. Therefore, Fe$_{40}$O$_{60}$ nanoparticles significantly promote CO formation while inhibiting CO$_2$ production. Unfortunately, DFT-based calculations of large nanoparticles consisting of a few thousand atoms, required for confirming this conclusion, are intractable to compute even on the most powerful supercomputers. Nevertheless, the experimental evidence for the extraordinary CO selectivity of Fe$_2$O$_3$ nanoparticles with the size of 5 ± 3 nm indicates that nanostructuring makes Fe$_2$O$_3$ a more active oxide for CO production compared with bulk Fe$_2$O$_3$.

**Discussion**

In summary, we demonstrate that Fe$_2$O$_3$@SBA-15 enables near 100% CO selectivity in chemical looping methane partial oxidation, which is so far the highest value in product selectivity observed for chemical looping systems. Moreover, the effective temperature for syngas generation is lowered to 750–935 °C, which is over 100 °C lower than current state-of-the-art processes. Nanoscaled oxygen carriers are presented to exhibit little high-temperature reactivity property deterioration and adaptability to broader temperature operating windows for chemical looping operation conditions. These are important factors that can contribute to significant energy-saving reactor designs. The theoretical model and calculations reveal that the structure of the nanoparticles play a key role in CO selectivity enhancement of Fe$_2$O$_3$@SBA-15. The CH$_4$ adsorption energies and CO formation barriers depend not only on the nanoparticle size, but also on the type of surface site exhibited by the nanoparticles. The small average coordination number of Fe atoms in the nanoparticle facilitates CH$_4$ adsorption and activation due to an upward shift of the Fe d-band, while the low-coordinated O atoms greatly promote Fe–O bond cleavage and CO formation, leading to a significant increase in CO selectivity. These findings contribute to a nanoscale understanding of the underlying metal oxide redox chemistry for chemical looping processes, and provide a systematic strategy toward the design of robust oxygen carrier nanoparticles with superior activity and selectivity.

**Methods**

**Sample preparation.** Surfactant CTAB and Fe(NO$_3$)$_2$·9H$_2$O were dissolved in 120 mL ethanol. 0.4 g SBA-15 was stirred in the solution for overnight at room temperature. This is followed by a powderization at 90 °C, and then calcination at 600 °C for 5 h. The prepared sample is marked as Fe$_2$O$_3$@SBA-15. Fe$_2$O$_3$ particles without SBA-15 support was also prepared by the same method. For Fe$_2$O$_3$@SBA-15, the volume loading was calculated by Eq. (1):

$$\text{Volume loading} = \frac{m_{\text{Fe}_2\text{O}_3}}{m_{\text{SBA}-15}} \times \text{pore volume}$$

where $m_{\text{Fe}_2\text{O}_3}$ is the total weight of Fe$_2$O$_3$, $m_{\text{SBA}-15}$ is total weight of SBA-15, $p_{\text{Fe}_2\text{O}_3}$ is density of Fe$_2$O$_3$.

**Thermogravimetric analysis (TGA).** The selectivity of Fe$_2$O$_3$@SBA-15 was tested in a SETARAM thermogravimetric analysis (TGA) device. A 20 mg sample was mounted in the TGA, and heated from 750 °C to 935 °C with a temperature ramp of 10 °C/min. 20 mL/min of CH$_4$ balanced with 180 mL/min of He was used in the partial oxidation. The outlet gas composition was analyzed by mass spectrometry (MS). 75 redox cycles were also conducted on both samples to test their recyclability. During the methane partial oxidation, 50 mL/min of CH$_4$ balanced with 100 mL/min of N$_2$ and 30 mL/min of He carrier gases was used in a TGA to react with the sample for 5 min. For the regeneration, 100 mL/min of air balanced with 100 mL/min of N$_2$ was used to oxidize the sample for 5 min. Between the reduction and the oxidation, 100 mL/min of N$_2$ was used as the flushing gas to prevent the mixing of air and methane.

**Fixed bed experiment.** The methane conversion and syngas selectivity of both unsupported Fe$_2$O$_3$ and Fe$_2$O$_3$@SBA-15 were also evaluated in a quartz U-tube (1 cm diameter) fixed bed reactor. Four different methane weight hourly space velocity (HWSV) of 17.8, 25, 30, 37.5 mL (mg Fe$_2$O$_3$ h$^{-1}$) were applied to each sample. In the experiment, the solid were amounted in the center of the reactor that is placed in a tube furnace and heated to 800 °C. The outlet gas was analyzed by MS.

**Computational details.** All plane-wave DFT calculations were performed using the projector augmented wave pseudopotentials provided in the VASP. The Perdew–Burke–Ernzerhof exchange-correlation functional was used with a plane-wave expansion cutoff of 400 eV$^{29,30}$. Due to the valence electrons of Fe 3d state, the Hubbard U approach was used to correct self-interaction errors of Fe$_2$O$_3$. The increase of $U$ from 1 to 4 eV results in better agreement with the density of states by experimental inverse photoemission spectra$^{26}$. However, a further increase in $U$ will cause Fe 3d states to shift to unacceptable low energies. Therefore, $U = 4$ eV was chosen to describe the energy required for adding an extra d electron to the Fe atom. Geometry optimization of the nanoparticle was carried out at the DFT level. All atoms were allowed to relax until the forces are smaller than 0.01 eV Å$^{-1}$, with a total energy threshold determining the self-consistency of the electron density of 1.0 × 10$^{-5}$ eV atom$^{-1}$. Dispersion interactions are modeled using the DFT-D3 method developed by Grimme et al.$^{27,28}$ The calculated a-Fe$_2$O$_3$ bulk lattice parameters were $a = b = 5.04$ Å and $c = 13.83$ Å, in good agreement with the experimental values ($a = b = 5.038$ Å and $c = 13.772$ Å). The a-Fe$_2$O$_3$ (001) surface with Fe–O$_{3C}$–Fe termination was chosen to model the iron oxide slab with a thickness of ~15 Å$^{29}$. Fe$_2$O$_3$ nanoparticles were modeled by a three-dimensional periodic arrangement with a large cubic cell of 5 × 5 × 5 nm$^3$ to minimize lateral interactions. The structures of the free nanoparticles (Fe$_2$O$_3$), (n = 4–60) were fully optimized without any symmetry constraints. The climbing-image nudged elastic band method$^{30,31}$ is used to locate transition states of elementary steps and map out reaction pathways for CH$_4$ dissociation and oxidation on the Fe$_2$O$_3$ nanoparticles. The effect of temperature (800 °C) was taken into account for adsorption and reaction barrier comparison.

**Characterization methods.** The scanning electron microscope measurements were performed with EIM Helios Nanolab 600, with the voltage of 10 kV and the current of 0.17 mA. The TEM images were obtained with a FEI Tecnai G2 30 at 200 kV. The surface area of the sample was analyzed by NOVA 4200e. The sample was first degassed at 300 °C for over 10 h. Then isothermal N$_2$ adsorption was performed at −196 °C. The surface area of both SBA-15 and Fe$_2$O$_3$@SBA-15 was determined by Brunauer–Emmett–Teller method, while the pore size distribution was calculated by Brunauer–Joyner–Halenda method with adsorption branch. Small-angle X-ray diffraction was conducted with Rigaku SmartLab equipped with Cu Kα radiant. Data were collected from 0.7° to 3° with a scanning rate of 0.1° per minute.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions

Y.L. performed TEM, SEM, EDX, TGA redox experiments, TPR, and fixed bed experiments. L.Q. designed the experiments. Y.L., L.Q., J.W.G., and F.K. analyzed data. Z.C. performed the DFT calculation and analyzed the mechanism. J.W.G. did the sample synthesis and surface and pore size analysis. F.K. performed SAXRD experiments. J.A.F. discussed the results and commented on the manuscript. L.S.F. supervised the research. All authors participated in manuscript preparation, data interpretation and discussions.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to L.-S.F.

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