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Peer Review File

Effects of surface hydrophobization on the phase evolution behavior of iron-based catalyst during Fischer–Tropsch synthesis

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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

In this manuscript, the authors presented an interesting and efficient method to stabilize the iron carbides active phase during the Fischer-Tropsch synthesis reaction. They found that a hydrophobic surface could reduce the water concentration in the core locality of catalyst during reaction, thereby suppressing the oxidation of iron carbides by the water produced in situ. As a result, more iron carbides were exposed, which facilitated the C-C coupling process and enhanced the production of long-chain olefins. In general, this manuscript is an interesting and impactful work and can attract wide attentions. I recommend publishing this manuscript after the following issues are quite addressed.

1. In the CO+H2O model experiment, the authors found that water could diffuse through the hydrophilic SiO2 shell and oxidize internal iron species, while the phase composition of the hydrophobic Fe@Mn@0.2Si-c catalyst could hardly be influenced. What was the concentration of water vapour and the velocity of gas mixture used in this model experiment? Detailed experimental methodology for the model experiment should be added in the Section of Methods.

2. The hydrophobic shell of the Fe@Mn@0.2Si-c catalyst inhibited water adsorption and hindered the WGS side reaction, leading to much lower selectivity for CO2 and CH4 than the Fe@Mn@0.2Si catalyst. How about the catalytic stability of the Fe@Mn@0.2Si-c catalyst?

3. The authors found that the amount of SiO2 coated on the iron-based Fischer-Tropsch synthesis catalyst had obvious influence on the phase structure and catalytic performance during syngas conversion. So, the specific contents of silicon in these catalysts should be tested and clarified.

4. Supplementary Figure 14: The CO conversion over the Fe@Mn@0.2Si catalyst was about 70%, while that over the Fe@Mn@0.2Si-c catalyst was about 50%. Because the water produced by the Fischer-Tropsch synthesis reaction increases with the rise of CO conversion, and this may cause different CO2 selectivity. The comparison of CO2 selectivity between the Fe@Mn@0.2Si and Fe@Mn@0.2Si-c catalysts should be made at similar CO conversion level.

5. Supplementary Figure 7: The authors reported that the order of the relative spatial size of different iron phases was Fe2O3 > Fe3O4 > Fe5C2 > Fe3C. How was this calculated?

Reviewer #2 (Remarks to the Author):

During the FTS reaction, water is the main oxygen-containing product, which can cause serious side reaction related to CO2 formation. Besides, the iron carbide species as the active phase of iron-based catalyst is easily oxidized by the water produced during the FTS reaction, resulting in the deterioration of catalytic performance. Hydrophobic modification of catalyst is attracting increasing research interest in the syngas chemistry recently.

Understanding the effect of surface hydrophobization on the phase evolution behavior of iron-based catalyst and its impact on the FTS reaction is highly desirable but still absent. In this work, Xu and co-authors revealed the different phase transformation behaviors of the hydrophilic and hydrophobic catalysts, giving new insights on the function of hydrophobic modification on syngas conversion. They disclosed the importance of appropriate thickness of hydrophobic shell on stabilizing the iron carbide active phase without Fe3O4 formation. This work is well conducted with sufficient details and can be accepted for publication. But I have several questions and suggestions before acceptance.
(1) CO-TPR results suggested that the increase in the thickness of SiO2 shell inhibited the accessibility and carburization of internal iron species by CO molecules. H2 is the other component of syngas. Did the thickness of SiO2 shell influence the accessibility of internal iron species by H2?
(2) As shown in Supplementary Fig. 14., with the increase of the thickness of SiO2 shell, the CO2 selectivity presented different trends on the hydrophilic Fe@Mn@xSi and hydrophobic Fe@Mn@xSi-c catalysts. The authors are suggested to add some explanations about this phenomenon.
(3) As shown in Fig. 3e, the spent Fe@Mn@0.05Si-c catalyst presented in the form of Fe3O4 phase without the diffraction peaks related to iron carbide. Did any iron carbide exist on the surface layer of catalyst? The XPS characterization on the spent Fe@Mn@0.05Si-c catalyst should be added and discussed.
(4) The authors found the contact of chlorotrimethylsilane with the iron-based catalyst during the hydrophobic modification procedure led to catalyst deactivation, and the increase of SiO2 shell thickness could protect catalyst from chlorine poisoning. To better illustrate this point, it is suggested to hydrophobic modify the Fe@Mn catalyst without SiO2 coating and add relevant reaction performance data.
(5) It was well demonstrated that chlorine could inhibit the adsorption of CO on catalyst and hinder the carbonization of iron species. Did chlorine influence the reduction process of iron species by H2?

Reviewer #3 (Remarks to the Author):

The authors investigated the effect surface hydrophobization on the phase evolution of iron catalyst during Fischer–Tropsch synthesis. The main conclusion is the reduced water concentration inhibits the oxidation of iron species, resulting the enhanced C-C coupling. The influence of hydrophobic properties of the Fe catalysts in FTS have been investigated a lot recently. And it is well known that the byproduct H2O as an oxidant usually results in transformation of Fe carbides to oxides. So, I think the novelty of this work is limited. And the characterization is regular and some important information is missing. In addition, the authors used in-situ XRD and DRIFTS to discuss the poisoning effect of chlorine on the phase evolution. However, this is not common for Fe-based catalysts, only exits on the Fe@Mn@xSi-c because of the special surface modification process. It looks like the authors created a problem, and then tried to explain it.
Some of the comments:
Since the Fe carbides are very sensitive, it is better to characterize the Fe species by in-situ technologies (e.g. XRD, Mössbauer).
The authors didn’t present the catalytic performance with time. What time for the spent catalysts? Is there any induction or deactivation period?
The authors supposed several diffusion behaviors in different catalysts, such as Fig. 2f and 2g, but lacked solid evidence.

The authors proposed that the core of the Fe catalyst would shrink because of the density difference between Fe oxides and carbides. However, it is hard to get this conclusion from Fig. 1.

Point-by-point response to the reviewer comments

We sincerely thank the three reviewers for their high evaluations and insightful suggestions on our manuscript. With the help of these comments, the revised manuscript was improved greatly. We have carefully considered all the comments raised by the reviewers, and the detailed responses and revisions are listed below.

Reviewer #1

Overall comment: In this manuscript, the authors presented an interesting and efficient method to stabilize the iron carbides active phase during the Fischer-Tropsch synthesis reaction. They found that a hydrophobic surface could reduce the water concentration in the core locality of catalyst during reaction, thereby suppressing the oxidation of iron carbides by the water produced in situ. As a result, more iron carbides were exposed, which facilitated the C-C coupling process and enhanced the production of long-chain olefins. In general, this manuscript is an interesting and impactful work and can attract wide attentions. I recommend publishing this manuscript after the following issues are quite addressed.

Response: We appreciate the high opinions and instructive advices from the reviewer. With the help of these advices, the revised manuscript was improved greatly. We are pleased that the reviewer has clearly recognized the novelty and merits of this manuscript and hope that our revision work is satisfactory to the reviewer.

Detailed revisions made according to the comments of reviewer #1

Q1. In the CO+H_2O model experiment, the authors found that water could diffuse through the hydrophilic SiO_2 shell and oxidize internal iron species, while the phase composition of the hydrophobic Fe@Mn@0.2Si-c catalyst could hardly be influenced. What was the concentration of water vapour and the velocity of gas mixture used in this model experiment? Detailed experimental methodology for the model experiment should be added in the Section of Methods.

Response: Following the reviewer's suggestion, we have added the detailed experimental methodology for the $CO+H_2O$ model experiment in the methods section of the revised manuscript, as follows.

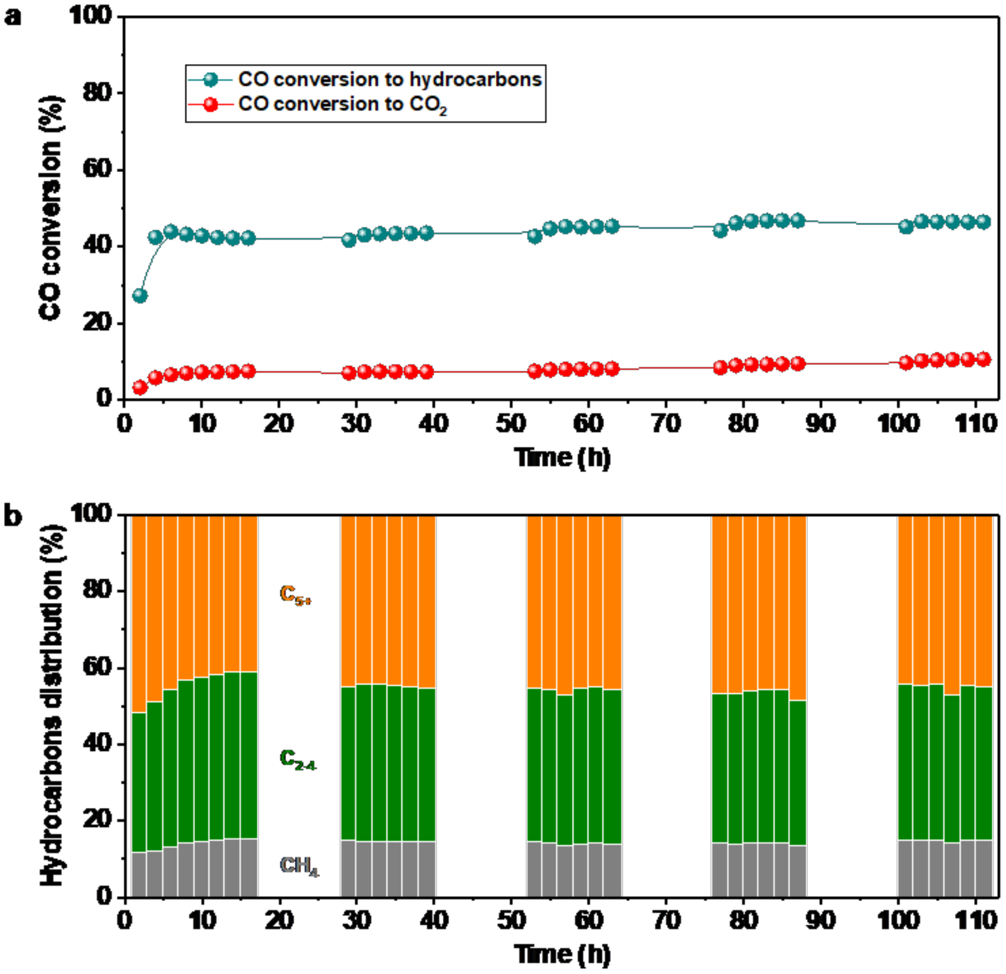
"The $CO+H_2O$ model experiment was performed in the same stainless fixed-bed reactor. Typically, 0.2 g of catalyst was packed into the reactor and firstly reduced in pure H_2 at 350 °C, 0.1 MPa for 20 h. Then, the catalyst was exposed to the CO or $CO+H_2O$ atmosphere at 320 °C, 2.0 MPa for 20 h. When co-feeding CO and H_2O in the reactor, liquid water with a flow rate of 0.002 mL/min was injected in the 31.6%CO/68.4%N_2 gas (16.7 mL/min) via a high pressure constant current pump (eliteHPLC, EPP010S). The mixtures containing liquid water were vaporized in a gasifier at 300 °C before entering the reactor."

Q2. The hydrophobic shell of the Fe@Mn@0.2Si-c catalyst inhibited water adsorption and hindered the WGS side reaction, leading to much lower selectivity for CO_2 and CH_4 than the Fe@Mn@0.2Si catalyst. How about the catalytic stability of the Fe@Mn@0.2Si-c catalyst?

Response: Thanks a lot for your question. We have further performed a stability test on the Fe@Mn@0.2Si-c catalyst. As shown in Supplementary Fig. 10, this catalyst rapidly reached a relatively stable state within 4 hours. Besides, during 110 hours of continuous reaction, the CO conversion to hydrocarbons and CO_2 on the Fe@Mn@0.2Si-c catalyst remained at about 45% and 8%, respectively. Meanwhile, the selectivity for CH_4 in hydrocarbons was stable at around 14%.

These results suggested that the hydrophobic Fe@Mn@0.2Si-c catalyst possessed a good catalytic stability for syngas conversion.

The stability test and relevant discussions have been added at Supplementary Fig. 10 in the revised Supplementary Information.



Supplementary Fig. 10. (a) CO conversion and (b) hydrocarbons distribution during the stability test of the Fe@Mn@0.2Si-c catalyst. The reaction data corresponding to the blank space in the figure was not collected, because the gas chromatograph was switched to another reactor at this time.

Q3. The authors found that the amount of SiO_2 coated on the iron-based Fischer-Tropsch synthesis catalyst had obvious influence on the phase structure and catalytic performance during syngas conversion. So, the specific contents of silicon in these catalysts should be tested and clarified.

Response: Following the reviewer's suggestion, we have tested the specific contents of silicon in these catalysts by inductively coupled plasma (ICP). As shown in Supplementary Table 1, with the dosage of TEOS increased from 0.05 mL to 2.8 mL during catalyst preparation, the content of SiO_2 in these catalysts ranged from 2.7 wt.% to 34.0 wt.%, suggesting that the amount of SiO_2 in catalyst was effectively adjusted by altering the dosage of TEOS.

The elemental analysis results have been added at Supplementary Table 1 in the revised Supplementary Information.

Supplementary Table 1. Elemental analysis of the Fe@Mn@*x*Si catalysts.

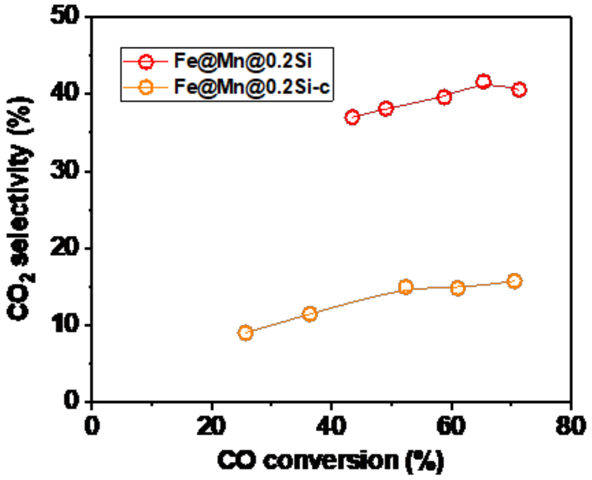
Catalyst	Parameters of catalyst preparation		Content in catalyst (wt.%)[a]		
	Dosage of Fe@Mn	Dosage of TEOS	Mn	Si	SiO_2
Fe@Mn	0.5 g	0 mL	6.1	0.2	0.3
Fe@Mn@0.05Si	0.5 g	0.05 mL	6.5	1.3	2.7
Fe@Mn@0.2Si	0.5 g	0.2 mL	5.9	4.1	8.8
Fe@Mn@0.5Si	0.5 g	0.5 mL	5.8	5.7	12.1
Fe@Mn@1.0Si	0.5 g	1.0 mL	4.2	11.6	24.9
Fe@Mn@2.8Si	0.5 g	2.8 mL	4.4	15.8	34.0

[a] The contents of Mn and Si in the Fe@Mn@*x*Si catalysts were determined by ICP.

Q4. Supplementary Figure 14: The CO conversion over the Fe@Mn@0.2Si catalyst was about 70%, while that over the Fe@Mn@0.2Si-c catalyst was about 50%. Because the water produced by the Fischer-Tropsch synthesis reaction increases with the rise of CO conversion, and this may cause different CO_2 selectivity. The comparison of CO_2 selectivity between the Fe@Mn@0.2Si and Fe@Mn@0.2Si-c catalysts should be made at similar CO conversion level.

Response: Thanks to reviewer #1 for pointing this out. We have tested the CO_2 selectivity on the Fe@Mn@0.2Si and Fe@Mn@0.2Si-c catalysts at a series of CO conversion levels. As shown in Supplementary Fig. 16, at CO conversion of 43~71%, the CO_2 selectivity on the Fe@Mn@0.2Si catalyst was as high as 37~42%, suggesting that water adsorbed easily on the hydrophilic Fe@Mn@0.2Si catalyst and caused serious WGS side reaction. By contrast, at CO conversion of 25~71%, the CO_2 selectivity on the Fe@Mn@0.2Si-c catalyst was suppressed to 9~16%, implying that the hydrophobic SiO_2 shell could inhibit effectively the WGS side reaction and reduce the production of undesired CO_2 by-product.

The relevant catalytic data and discussions have been added at Supplementary Fig. 16 in the revised Supplementary Information.



Supplementary Fig. 16. The CO_2 selectivity on the Fe@Mn@0.2Si and Fe@Mn@0.2Si-c catalysts at different CO conversion levels obtained by adjusting the space velocity. Reaction conditions: 320 °C, 2.0 MPa, $H_2/CO = 2$.

Q5. Supplementary Figure 7: The authors reported that the order of the relative spatial size of different iron phases was $Fe_2O_3 > Fe_3O_4 > Fe_5C_2 > Fe_3C$. How was this calculated?

Response: Thanks a lot for your question. We have added more descriptions and detailed data about the calculation of the relative spatial size of different iron phases at Page S8 and Supplementary Table 2 of the revised Supplementary Information, as follows.

“The relative spatial size of different iron phases was calculated based on the volume of unit cell. First, the volume of each iron phase with 120 Fe atoms was calculated. Then, the volume ratios of different iron phases to Fe_2O_3 *phase with the same number of Fe atoms were calculated. Detailed data were shown in Supplementary Table 2. The order of the relative spatial size of different iron phases is* $Fe_2O_3 > Fe_3O_4 > Fe_5C_2 > Fe_3C$*, implying that the reduction of* Fe_2O_3 *to* Fe_3O_4 *and carbonization of* Fe_3O_4 *to iron carbides (*Fe_5C_2 *and* Fe_3C*) are volume-decreasing processes.”*

Supplementary Table 2. Calculation of the relative spatial size of different iron phases.

Iron phase	V_0 (Å^3) [a]	n_{Fe} [b]	V (Å^3) [c]	Relative spatial size [d]
Fe_2O_3	301.3	12	3012.8	100.0%
Fe_3O_4	575.9	24	2879.7	95.6%
Fe_5C_2	266.0	20	1595.9	53.0%
Fe_3C	154.6	12	1546.2	51.3%

[a] Volume of unit cell.

[b] Number of Fe atom in unit cell.

[c] Volumes of different iron phases with 120 Fe atoms.

[d] The volume ratios of different iron phases to Fe_2O_3 phase with the same number of Fe atoms.

Reviewer #2

Overall comment: During the FTS reaction, water is the main oxygen-containing product, which can cause serious side reaction related to CO_2 formation. Besides, the iron carbide species as the active phase of iron-based catalyst is easily oxidized by the water produced during the FTS reaction, resulting in the deterioration of catalytic performance. Hydrophobic modification of catalyst is attracting increasing research interest in the syngas chemistry recently. Understanding the effect of surface hydrophobization on the phase evolution behavior of iron-based catalyst and its impact on the FTS reaction is highly desirable but still absent. In this work, Xu and co-authors revealed the different phase transformation behaviors of the hydrophilic and hydrophobic catalysts, giving new insights on the function of hydrophobic modification on syngas conversion. They disclosed the importance of appropriate thickness of hydrophobic shell on stabilizing the iron carbide active phase without Fe_3O_4 formation. This work is well conducted with sufficient details and can be accepted for publication. But I have several questions and suggestions before acceptance.

Response: We appreciate the high opinions and instructive advices from the reviewer. With the help of these advices, the revised manuscript was improved greatly.

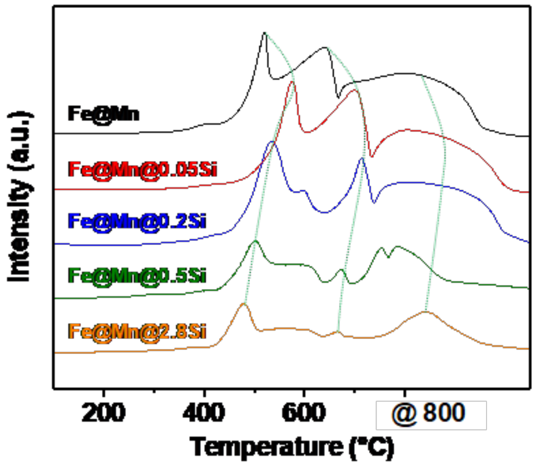
Detailed revisions made according to the comments of reviewer #2

Q1. CO-TPR results suggested that the increase in the thickness of SiO_2 shell inhibited the accessibility and carburization of internal iron species by CO molecules. H_2 is the other component of syngas. Did the thickness of SiO_2 shell influence the accessibility of internal iron species by H_2?

Response: Thanks a lot for your question. We have further added H_2-TPR characterization on these catalysts. As shown in Supplementary Fig. 13, after coating a small amount of SiO_2 (Fe@Mn@0.05Si), the reduction peaks of Fe_2O_3 shifted towards higher temperature, suggesting that the contact of metal with SiO_2 suppressed slightly its reduction, which was related to the metal-support interaction [*Catal. Commun. 2006, 7, 733–738*]. With the further thickening of SiO_2 shell, the reduction peaks shifted towards lower temperature, which may be attributed to that the micropores in shell could adsorb and enrich H_2 [*ACS Catal. 2018, 8, 1218–1226*; *ACS Catal. 2019, 9, 2969–2976*] and thus promote the reduction of Fe_2O_3. These results suggested that the increase of SiO_2 shell thickness did not inhibit the accessibility and reduction of internal iron species by H_2 molecules.

The detailed experimental methodology for the H_2-TPR characterization has been added in the methods section of the revised manuscript, as follows. Besides, the H_2-TPR profiles of catalysts and relevant discussions have been added at Supplementary Fig. 13 in the revised Supplementary Information.

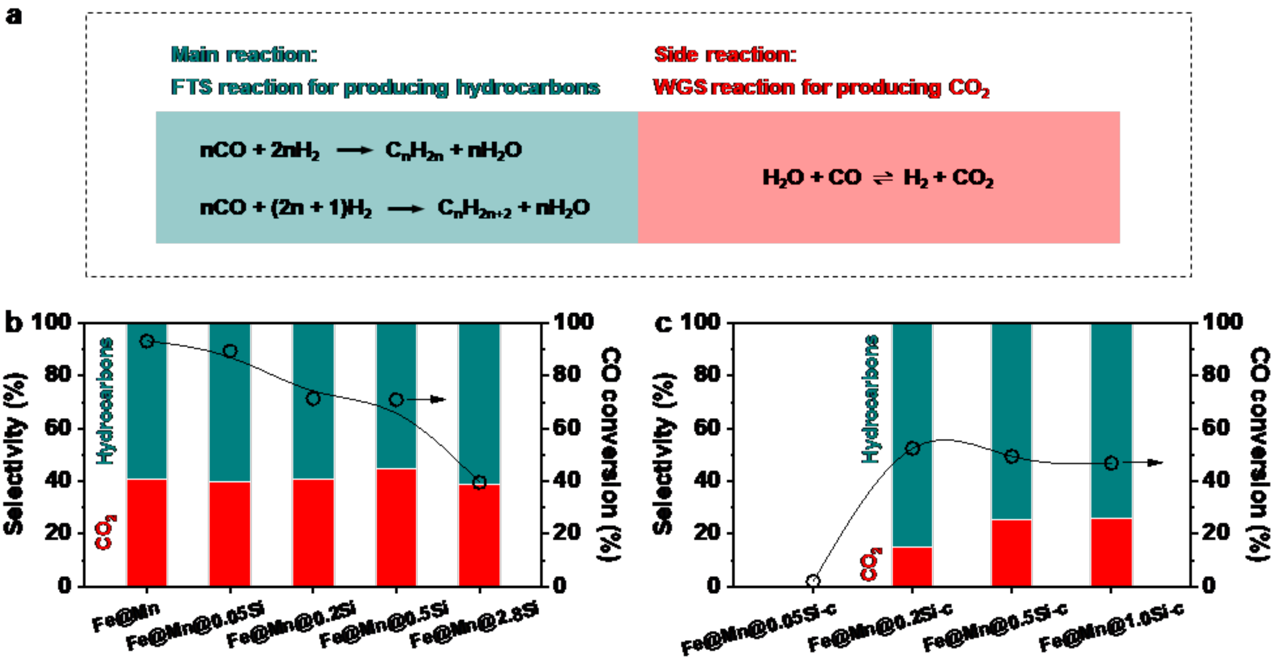
"Hydrogen temperature-programmed reduction (H_2-TPR) experiments were performed on a DAS-7000 chemical adsorption instrument. Prior to each test, 50 mg of sample was packed into the quartz tube and pretreated with N_2 at 350 °C for 1 h. After cooling to 80 °C, 5%H_2/95%N_2 with a flow rate of 30 mL/min was switched into the quartz tube. Then, H_2-TPR was conducted by ramping the temperature to 800 °C with a heating rate of 10 °C/min. The consumption of H_2 during the reduction process was detected by a TCD."



Supplementary Fig. 13. H_2-TPR profiles of catalysts.

Q2. As shown in Supplementary Fig. 14., with the increase of the thickness of SiO_2 shell, the CO_2 selectivity presented different trends on the hydrophilic Fe@Mn@*x*Si and hydrophobic Fe@Mn@*x*Si-c catalysts. The authors are suggested to add some explanations about this phenomenon.

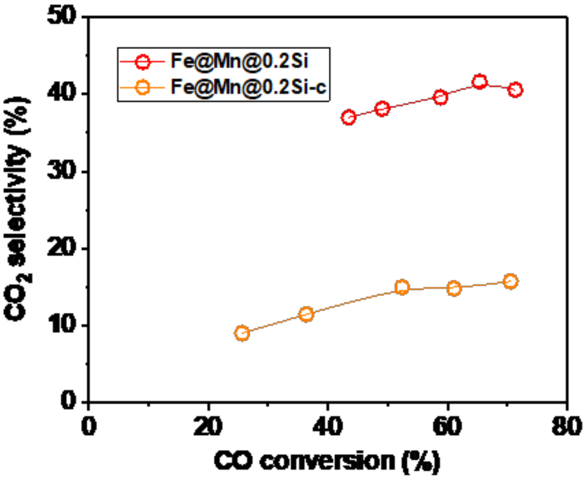
Response: Thanks a lot for the careful reading and insightful suggestion. We have added more explanations about this phenomenon at Supplementary Fig. 14 (Supplementary Fig. 15 in the revised Supplementary Information), as follows.



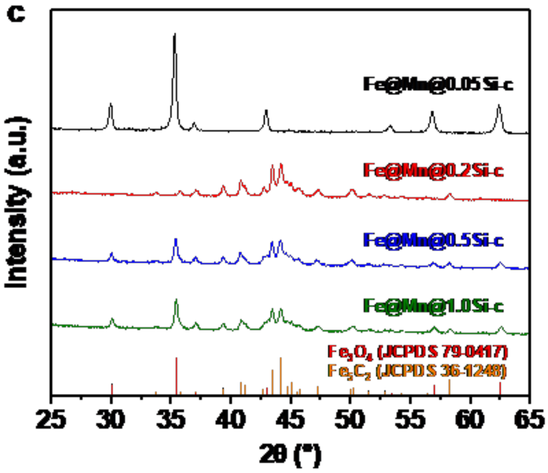
Supplementary Fig. 15. (a) Reactions occurring in the conversion of syngas. CO conversion and products distribution of the (b) Fe@Mn@xSi and (c) Fe@Mn@xSi-c catalysts.

"Because water easily adsorbed on the hydrophilic Fe@Mn@xSi catalysts, serious WGS side reaction occurred and all the Fe@Mn@xSi catalysts exhibited high CO_2 selectivity of about 40%. This was also reflected from Supplementary Fig. 16, in which the CO_2 selectivity on the Fe@Mn@0.2Si catalyst was as high as 37~42% at CO conversion of 43~71%. The hydrophobic SiO_2 shell could reduce the water concentration in the core vicinity of catalyst, thereby suppressing the WGS side reaction. As a result, the hydrophobic Fe@Mn@xSi-c catalysts exhibited much lower CO_2 selectivity than the hydrophilic Fe@Mn@xSi catalysts. However, the increase of shell thickness

inhibited the accessibility and carburization process of internal iron species by CO molecules, leading to the slight oxidation of iron species before water diffused outside the Fe@Mn@0.5Si-c and Fe@Mn@1.0Si-c catalysts (Supplementary Fig. 17c). As Fe_3O_4 phase is very active for the WGS reaction, the CO_2 selectivity on the Fe@Mn@xSi-c catalysts increased with the increase of shell thickness.”



Supplementary Fig. 16. The CO_2 selectivity on the Fe@Mn@0.2Si and Fe@Mn@0.2Si-c catalysts at different CO conversion levels obtained by adjusting the space velocity. Reaction conditions: 320 °C, 2.0 MPa, H_2/CO = 2.

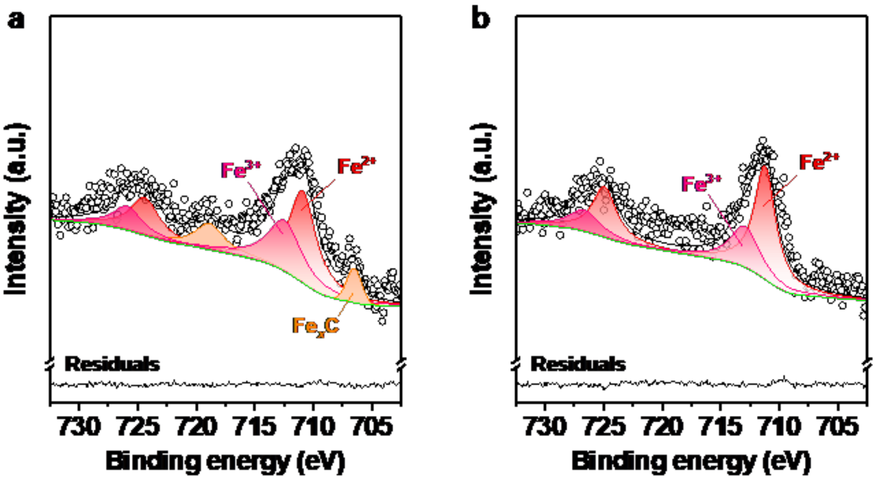


Supplementary Fig. 17. (c) XRD patterns of the spent catalysts.

Q3. As shown in Fig. 3e, the spent Fe@Mn@0.05Si-c catalyst presented in the form of Fe_3O_4 phase without the diffraction peaks related to iron carbide. Did any iron carbide exist on the surface layer of catalyst? The XPS characterization on the spent Fe@Mn@0.05Si-c catalyst should be added and discussed.

Response: According to the advice of reviewer #2, we have added the XPS characterization on the spent Fe@Mn@0.05Si and Fe@Mn@0.05Si-c catalysts. After reaction, a peak at 706.5 eV appeared on the spent Fe@Mn@0.05Si catalyst, which was attributed to the Fe_xC species [*Angew. Chem. Int. Ed. 2016, 55, 9902–9907; Sci. Adv. 2022, 8, eabm3629*]. As for the spent Fe@Mn@0.05Si-c catalyst, no peak related to the Fe_xC species was detected, suggesting that no iron carbide existed on the surface layer of this catalyst.

The XPS characterization and relevant discussions have been added at Supplementary Fig. 19 in the revised Supplementary Information.



Supplementary Fig. 19. XPS spectra of Fe 2p on the spent (a) Fe@Mn@0.05Si and (b) Fe@Mn@0.05Si-c catalysts.

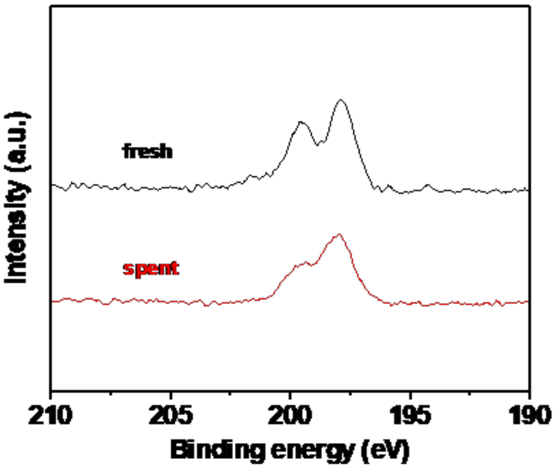
Q4. The authors found the contact of chlorotrimethylsilane with the iron-based catalyst during the hydrophobic modification procedure led to catalyst deactivation, and the increase of SiO_2 shell thickness could protect catalyst from chlorine poisoning. To better illustrate this point, it is suggested to hydrophobic modify the Fe@Mn catalyst without SiO_2 coating and add relevant reaction performance data.

Response: Thanks a lot for this valuable suggestion.

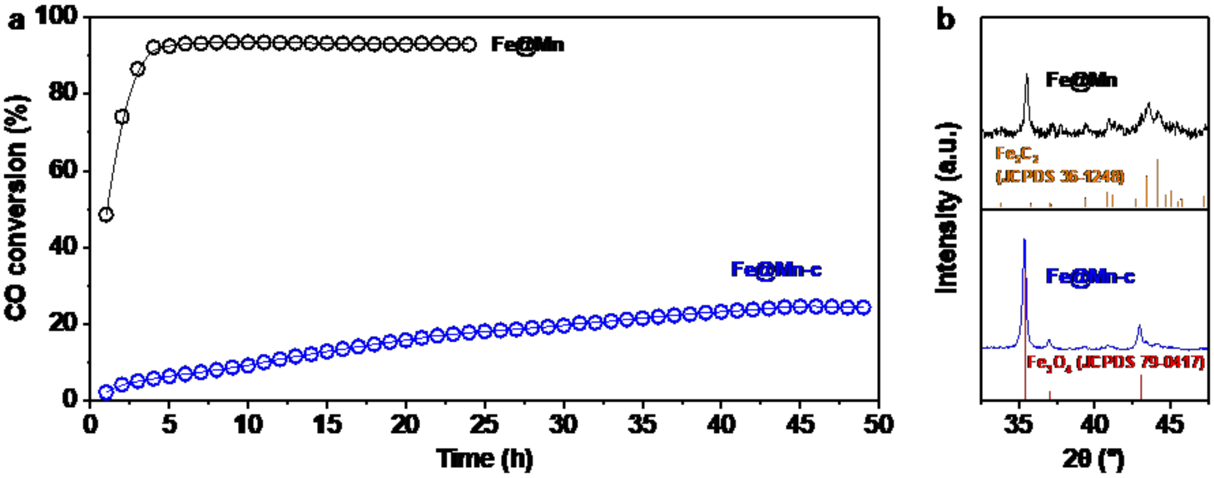
According to the advice of reviewer #2, we have hydrophobic modified the Fe@Mn catalyst without SiO_2 coating and tested the relevant reaction performance of the obtained Fe@Mn-c catalyst. As shown in Supplementary Fig. 20, chlorine existed stably on the surface of the Fe@Mn-c catalyst during reaction, and it suppressed the formation of Fe_xC active phase (Supplementary Fig. 21b). As a result, the Fe@Mn-c catalyst exhibited a much lower CO conversion than the Fe@Mn catalyst without chlorine (Supplementary Fig. 21a). These results further confirmed that the direct contact of chlorotrimethylsilane with the iron-based catalyst during the hydrophobic modification procedure could lead to catalyst deactivation.

The preparation procedure, relevant characterizations, and catalytic test of the Fe@Mn-c catalyst have been added in the methods section of the revised manuscript and Supplementary Figs. 20 and 21 in the revised Supplementary Information, as follows.

"The Fe@Mn-c catalyst was prepared by similar procedures of Fe@Mn@xSi-c. Typically, 0.5 g of Fe@Mn was dried in a vacuum oven at 120 °C for 10 h. After cooling in the vacuum oven, 70 mL of n-hexane was added. Subsequently, 0.5 mL of chlorotrimethylsilane was added. Then, the mixture was ultrasonic treated at room temperature for 1 h. The product was centrifuged, washed with n-hexane, and dried in a vacuum oven at 80 °C for 6 h."



Supplementary Fig. 20. XPS spectra of Cl 2p on the fresh and spent Fe@Mn-c catalysts.

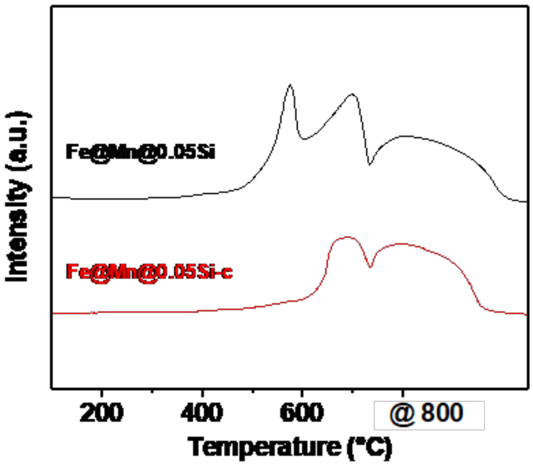


Supplementary Fig. 21. (a) CO conversion on the Fe@Mn and Fe@Mn-c catalysts with time on stream. (b) XRD patterns of the spent Fe@Mn and Fe@Mn-c catalysts.

Q5. It was well demonstrated that chlorine could inhibit the adsorption of CO on catalyst and hinder the carbonization of iron species. Did chlorine influence the reduction process of iron species by H_2?

Response: Thanks a lot for your question. We have further investigated the influence of chlorine on the reduction behavior of iron species by H_2-TPR. As shown in Supplementary Fig. 22, compared with the Fe@Mn@0.05Si catalyst, the reduction peaks of the Fe@Mn@0.05Si-c catalyst shifted towards much higher temperature and the peaks area decreased obviously, suggesting that chlorine inhibited notably the reduction process of iron species by H_2 molecules. Thus, even exposing to the syngas atmosphere at reaction temperature, only Fe_3O_4 without Fe_xC existed in the catalyst containing chlorine, thereby leading to the deactivation of FTS catalyst.

The H_2-TPR characterization and relevant discussions have been added at Supplementary Fig. 22 in the revised Supplementary Information.



Supplementary Fig. 22. H_2-TPR profiles of catalysts.

We thank reviewer #2 again for the careful reading and insightful questions, which are very helpful to improve the scientific quality of this manuscript.

We are pleased that the reviewer has clearly recognized the novelty and merits of this manuscript and hope that our revision work is satisfactory to the reviewer.

Reviewer #3

Overall comment: The authors investigated the effect surface hydrophobization on the phase evolution of iron catalyst during Fischer–Tropsch synthesis. The main conclusion is the reduced water concentration inhibits the oxidation of iron species, resulting the enhanced C-C coupling. The influence of hydrophobic properties of the Fe catalysts in FTS have been investigated a lot recently. And it is well known that the byproduct H_2O as an oxidant usually results in transformation of Fe carbides to oxides. So, I think the novelty of this work is limited. And the characterization is regular and some important information is missing. In addition, the authors used *in-situ* XRD and DRIFTS to discuss the poisoning effect of chlorine on the phase evolution. However, this is not common for Fe-based catalysts, only exits on the Fe@Mn@*x*Si-c because of the special surface modification process. It looks like the authors created a problem, and then tried to explain it. Some of the comments:

Response: We argue that this manuscript contains the novelty and quality, which merit publication in Nature Communications, from the following point of view.

Firstly, we reveal in detail the function of hydrophobic modification on tuning the phase evolution and catalytic performance of the iron-based FTS catalyst. Developing hydrophobic catalyst for syngas conversion has indeed been investigated a lot recently, while researchers mainly focused on the influence of catalyst hydrophobization on the side reactions participated by water.[1-10] As the main oxygen-containing product in the FTS reaction, water not only causes serious side reactions, but also oxidizes the iron carbide active phase, both of which can lead to the deterioration of catalytic performance. As reviewer #2 pointed out, "*Understanding the effect of surface hydrophobization on the phase evolution behavior of iron-based catalyst and its impact on the FTS reaction is highly desirable but still absent*". In this work, we present new insights on the function of hydrophobic modification on regulating the phase structure of the iron-based FTS catalyst.

References in this response

[1] Fellenz, N. A., Bengoa, J. F., Cagnoli, M. V. & Marchetti, S. G. Changes in the surface hydrophobicity degree of a MCM-41 used as iron support: a pathway to improve the activity and the olefins production in the Fischer–Tropsch synthesis. *J. Porous Mat.* 24, 1025–1036 (2017).

[2] Yu, X. et al. Fischer-Tropsch synthesis over methyl modified Fe_2O_3@SiO_2 catalysts with low CO_2 selectivity. *Appl. Catal. B-Environ.* 232, 420–428 (2018).

[3] Wu, P. et al. Hydrophobic SiO_2 supported Fe-Ni bimetallic catalyst for the production of high-calorie synthetic natural gas. *Appl. Catal. A-Gen.* 590, 117302 (2020).

[4] Xu, Y. et al. A hydrophobic FeMn@Si catalyst increases olefins from syngas by suppressing C1 by-products. *Science* 371, 610–613 (2021).

[5] Tan, M. et al. Probing hydrophobization of a Cu/ZnO catalyst for suppression of water–gas shift reaction in syngas conversion. *ACS Catal.* 11, 4633–4643 (2021).

[6] Fang, W. et al. Physical mixing of a catalyst and a hydrophobic polymer promotes CO hydrogenation through dehydration. *Science* 377, 406–410 (2022).

[7] Xu, Y. et al. Insights into the diffusion behaviors of water over hydrophilic/hydrophobic catalysts during the conversion of syngas to high-quality gasoline. *Angew. Chem. Int. Ed.* 62, e202306786 (2023).

[8] Chen, G. et al. Hydrophobic dual metal silicate nanotubes for higher alcohol synthesis. *Appl. Catal. B-Environ.* 334, 122840 (2023).

[9] Liu, P. et al. Tuning cobalt carbide wettability environment for Fischer-Tropsch to olefins with high carbon efficiency. *Chin. J. Catal.* 48, 150–163 (2023)

[10] Shi, Y. et al. Hydrophobic Fe-based catalyst derived from prussian blue for enhanced photothermal conversion of syngas to light olefins. *Adv. Funct. Mater.* 34, 2308670 (2024).

Secondly, we unravel here for the first time that appropriate shell thickness plays a crucial role in stabilizing the iron carbide active phase without Fe_3O_4 formation. Iron carbide, as the active phase for producing multi-carbon hydrocarbons, is easily oxidized into Fe_3O_4 by the water produced during reaction. Protecting iron carbide from oxidation during syngas conversion is highly needed, but still very challenging. In this work, we find that the hydrophobic surface can reduce the water concentration in the core vicinity of catalyst during syngas conversion and inhibit the oxidation of iron species by water. However, the contact of chlorotrimethylsilane with the iron-based catalyst during the hydrophobic modification procedure can poison and deactivate catalyst. The increase of SiO_2 shell thickness protects catalyst from chlorine poisoning, while excessive SiO_2 inhibits the accessibility and carburization of internal iron species by CO molecules. Appropriate shell thickness is needed to stabilize iron carbide without the formation of Fe_3O_4 phase during syngas conversion.

Thirdly, we shed light on the mechanism of chlorine poisoning of the iron-based catalyst. It should be noted that, the poisoning effect of chlorine on the FTS catalyst not only exits in this special hydrophobic catalyst system. Syngas derived from coal, especially biomass, generally contains chlorine impurities, and the poisoning effect of chlorine on the traditional FTS catalysts has also been widely studied for a long time.[1-8] Whereas, the poisoning effect of chlorine on the phase evolution behavior of the iron-based catalyst is still unclear. In this work, combining the information of *in-situ* XRD and *in-situ* DRIFTS characterizations, we disclose that chlorine can hinder the formation of the iron carbide active phase via inhibiting the adsorption of CO molecules, thereby leading to the poisoning and deactivation of FTS catalyst.

References in this response

[1] Gnanamani, M. K. et al. Fischer–Tropsch synthesis: effect of halides and potassium addition on activity and selectivity of cobalt. *Catal. Lett.* 144, 1127–1133 (2014).

[2] Paredes-Nunez, A., Lorito, D., Schuurman, Y., Guilhaume, N. & Meunier, F. C. Origins of the poisoning effect of chlorine on the CO hydrogenation activity of alumina-supported cobalt monitored by operando FT-IR spectroscopy. *J. Catal.* 329, 229–236 (2015).

[3] Ma, W. et al. Fischer–Tropsch synthesis: effects of hydrohalic acids in syngas on a precipitated iron catalyst. *ACS Catal.* 5, 3124–3136 (2015).

[4] Pendyala, V. R. R. et al. Fischer–Tropsch synthesis: XANES investigation of hydrogen chloride poisoned iron and cobalt-based catalysts at the K-edges of Cl, Fe, and Co. *Catal. Lett.* 146, 1858–1866 (2016).

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[6] Ghosh, I. K., Iqbal, Z., van Heerden, T., van Steen, E. & Bordoloi, A. Insights into the unusual role of chlorine in product selectivity for direct hydrogenation of CO/CO_2 to short-chain olefins. *Chem. Eng. J.* 413, 127424 (2021).

[7] Zhang, J. et al. Switching of CO_2 hydrogenation selectivity via chlorine poisoning over Ru/TiO_2 catalyst. *Nano Res.* 16, 4786–4792 (2023).

[8] Li, W. et al. The effect of chlorine modification of precipitated iron catalysts on their Fischer–Tropsch synthesis properties. *Catalysts* 12, 812 (2022).

Finally, this manuscript not just reports several catalysts, but more importantly, it provides new insights on the function of hydrophobic surface working in the syngas chemistry, which can guide the design of efficient iron-based catalysts for converting syngas into gasoline, jet fuel, and aromatics. Moreover, this manuscript is expected to advance the application of hydrophobization strategy in potentially other reactions restricted by water, such as the hydrogenation conversion of CO_2 and the synthesis of dimethyl carbonate.

The above points clearly demonstrate the innovation and importance of this manuscript, which deserves publication in Nature Communications.

In addition, according to the instructive comments of reviewer #3, we have also tried our best to remedy the deficiencies of this manuscript. With the help of these suggestions, the scientific quality of the revised manuscript was improved greatly. We hope that our response and revision work are satisfactory to the reviewer.

Detailed revisions made according to the comments of reviewer #3

Q1. Since the Fe carbides are very sensitive, it is better to characterize the Fe species by *in-situ* technologies (e.g. XRD, Mössbauer).

Response: We thank reviewer #3 for pointing this out. According to the advice of reviewer #3, we have added the characterizations of iron species by *in-situ* XRD technology. To illustrate the protective effect of hydrophobic surface on iron carbide, *in-situ* XRD characterizations on the Fe@Mn@0.2Si and Fe@Mn@0.2Si-c catalysts in the $CO+H_2O$ atmosphere were conducted. Before test, the iron species in the two catalysts were transformed into iron carbide by H_2 reduction and CO carbonization procedures. Then, the two catalysts were exposed to the $CO+H_2O$ atmosphere at 320 °C to observe the influence of H_2O on the iron carbide in the two catalysts. As shown in Fig. 3a, the iron carbide in the hydrophilic Fe@Mn@0.2Si catalyst gradually evolved once introducing H_2O into the reactor chamber. With time on stream, the intensity of diffraction peaks related to iron carbide decreased, while new diffraction peaks at 35.4°, 57.0°, and 62.5° attributed to Fe_3O_4 phase appeared (Fig. 3b). In addition, the phase evolution proceeded rapidly and reached an equilibrium state within one hour (Fig. 3c). These results suggested that H_2O molecules adsorbed easily on the hydrophilic Fe@Mn@0.2Si catalyst and thereby oxidized the internal iron carbide into Fe_3O_4 phase. As for the hydrophobic Fe@Mn@0.2Si-c catalyst, this phase evolution process was not observed (Fig. 3d). With time on stream, the intensity of diffraction peaks related to iron carbide in this hydrophobic catalyst remained stable and no diffraction peak related to Fe_3O_4 phase was detected (Fig. 3e,f). The above results of *in-situ* XRD characterization clearly demonstrated the different phase evolution process of iron carbide in the hydrophilic Fe@Mn@0.2Si and hydrophobic Fe@Mn@0.2Si-c catalysts when exposing to the CO+H_2O atmosphere, confirming that the oxidation of iron carbide by H_2O molecules could be effectively inhibited via surface hydrophobization.

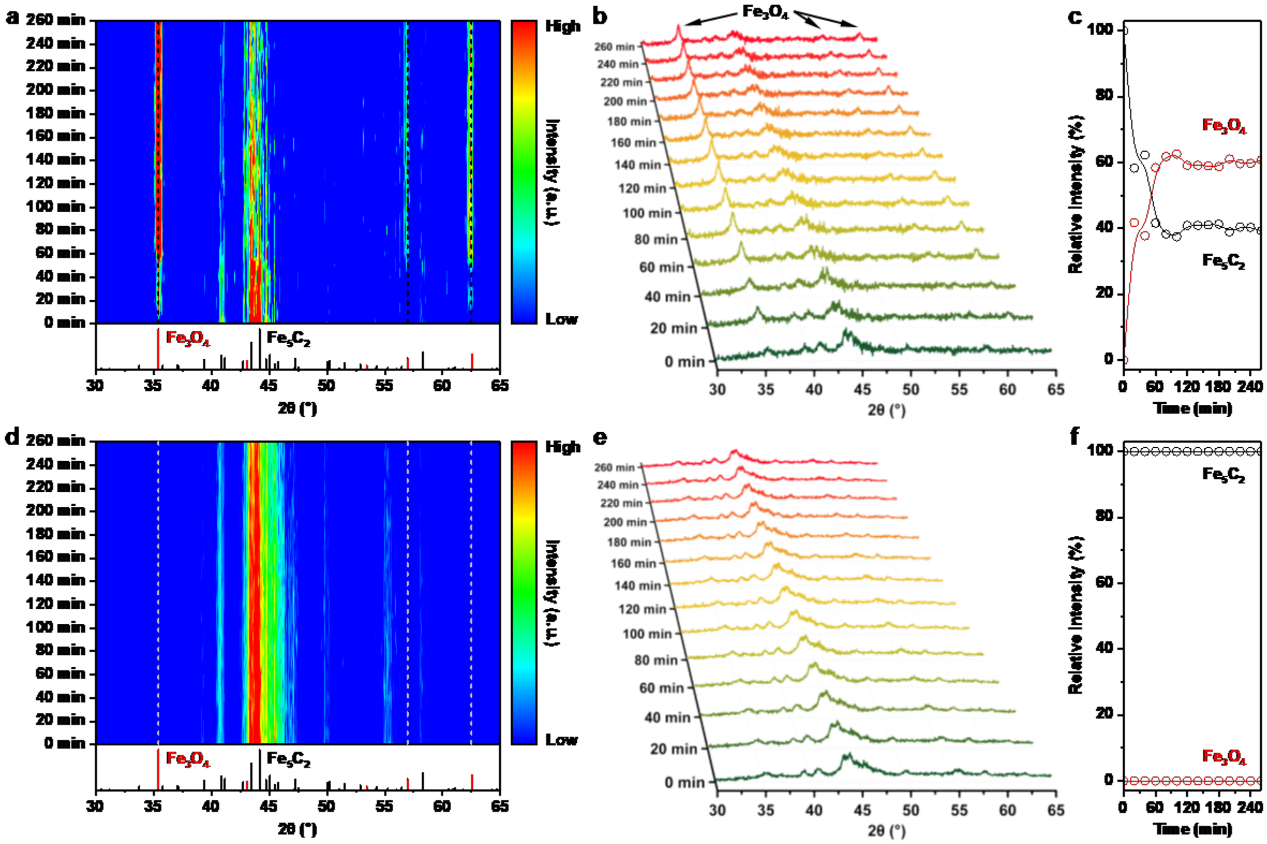

Fig. 3. Inhibiting the oxidation of iron carbide by water via surface hydrophobization. (a-c) Heatmap (a), *in-situ* XRD patterns (b), and the relative intensity between the diffraction peak of Fe_5C_2 at 44.2° and the diffraction peak of Fe_3O_4 at 35.4° (c) of the Fe@Mn@0.2Si catalyst when exposing to the CO+H_2O atmosphere at 320 °C. **(d-f)** Heatmap (d), *in-situ* XRD patterns (e), and the relative intensity between the diffraction peak of Fe_5C_2 at 44.2° and the diffraction peak of Fe_3O_4 at 35.4° (f) of the Fe@Mn@0.2Si-c catalyst when exposing to the CO+H_2O atmosphere at 320 °C.

The above results and discussions of *in-situ* XRD characterization have been added at Page 9 and Fig. 3 in the revised manuscript.

It should be noted that, *in-situ* Mössbauer spectroscopy is not suitable for characterizing the iron species during the FTS reaction, for the following reasons. First, the Mössbauer spectrum is generally collected at low temperature of 4.2 K ~ 300 K (−268.8 °C ~ 27 °C), because the superparamagnetic phenomenon of iron species is very serious at higher temperature, resulting in the failure to identify iron carbide and iron oxide. Second, collecting one Mössbauer spectrum usually needs 12 h ~ 24 h to achieve a satisfactory signal-to-noise ratio, thus it is unable to observe the phase evolution with time like the *in-situ* XRD technology.

As far as we know, almost all of the previous works used *ex-situ* Mössbauer spectroscopy performed at −268.8 °C ~ 27 °C to characterize the iron species in FTS catalyst.[1-12]

References in this response

[1] Lyu, S. et al. Stabilization of ε-iron carbide as high-temperature catalyst under realistic Fischer–Tropsch synthesis conditions. *Nat. Commun.* **11**, 6219 (2020).

[2] Qian, F. et al. Stabilized ε-Fe_2C catalyst with Mn tuning to suppress C1 byproduct selectivity for high-temperature olefin synthesis. *Nat. Commun.* **15**, 5128 (2024).

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[4] Zhu, J. et al. Dynamic structural evolution of iron catalysts involving competitive oxidation and carburization during CO_2 hydrogenation. *Sci. Adv.* **8**, eabm3629 (2022).

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[7] Liang, J. et al. CO_2 hydrogenation over Fe-Co bimetallic catalysts with tunable selectivity through a graphene fencing approach. *Nat. Commun.* **15**, 512 (2024).

[8] Li, Z. et al. Ambient-pressure hydrogenation of CO_2 into long-chain olefins. *Nat. Commun.* **13**, 2396 (2022).

[9] Wei, J. et al. Directly converting CO_2 into a gasoline fuel. *Nat. Commun.* **8**, 15174 (2017).

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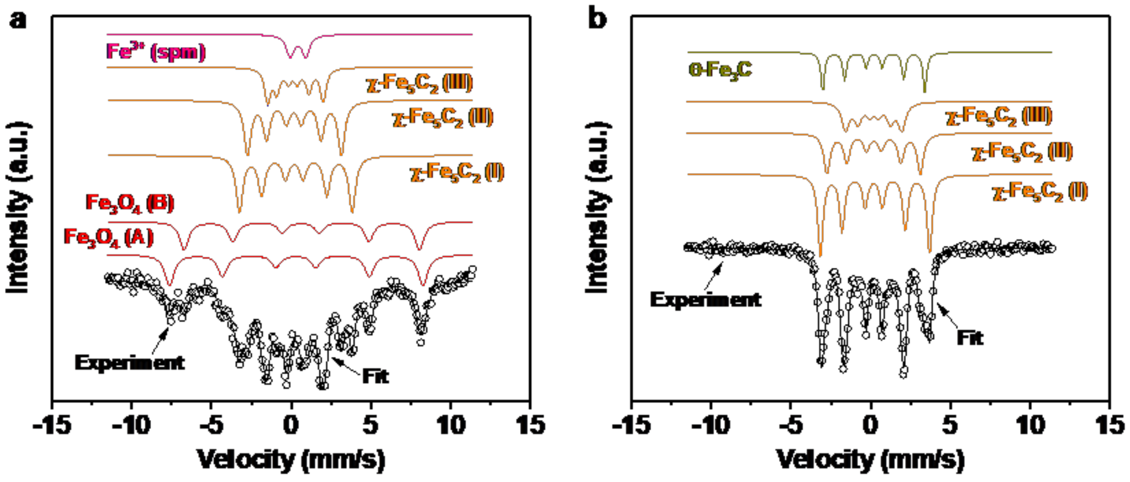
[11] Xu, K. et al. ε-Iron carbide as a low-temperature Fischer–Tropsch synthesis catalyst. *Nat. Commun.* **5**, 5783 (2014).

[12] Torres Galvis, H. M. et al. Supported iron nanoparticles as catalysts for sustainable production of lower olefins. *Science* **335**, 835–838 (2012).

In this work, we also use *ex-situ* Mössbauer spectroscopy to characterize the iron species in FTS catalyst. As shown in Supplementary Fig. 9 and Supplementary Table 3, after reaction, the iron species in the hydrophilic Fe@Mn@0.2Si catalyst was transformed into a mixture of 59.7% χ-Fe_5C_2, 34.3% Fe_3O_4 and 6.0% Fe^{3+}(spm), while that in the hydrophobic Fe@Mn@0.2Si-c catalyst was converted into 74.1% χ-Fe_5C_2 and 25.9% θ-Fe_3C, suggesting that the surface hydrophobization could inhibit the oxidation of iron species by water. The results of Mössbauer spectroscopy were consistent with the *in-situ* XRD characterization mentioned above.



Supplementary Fig. 9. Mössbauer spectra of the (a) spent Fe@Mn@0.2Si and (b) spent Fe@Mn@0.2Si-c catalysts.

Supplementary Table 3. Detailed Mössbauer parameters.

Catalyst	Assignment	Mössbauer parameters			
		IS (mm/s)	QS (mm/s)	Hhf (kOe)	Spectral contribution (%)
Fe@Mn@0.2Si	Fe^{3+} (spm)	0.37	0.97	/	6.0
	Fe_3O_4 (A)	0.30	-0.02	492	18.4
	Fe_3O_4 (B)	0.63	-0.05	457	15.9
	χ-Fe_5C_2 (I)	0.24	-0.09	219	23.9
	χ-Fe_5C_2 (II)	0.18	-0.03	182	23.6
	χ-Fe_5C_2 (III)	0.18	-0.15	108	12.2
Fe@Mn@0.2Si-c	χ-Fe_5C_2 (I)	0.23	-0.08	212	36.9
	χ-Fe_5C_2 (II)	0.19	0.03	179	15.5
	χ-Fe_5C_2 (III)	0.20	0.03	111	21.7
	θ-Fe_3C	0.19	0.00	198	25.9

In summary, we believe that we have clearly demonstrated the influence of surface hydrophobization on the phase composition of catalyst via combining the *in-situ* XRD, *ex-situ* XRD, and *ex-situ* Mössbauer spectroscopy technologies.

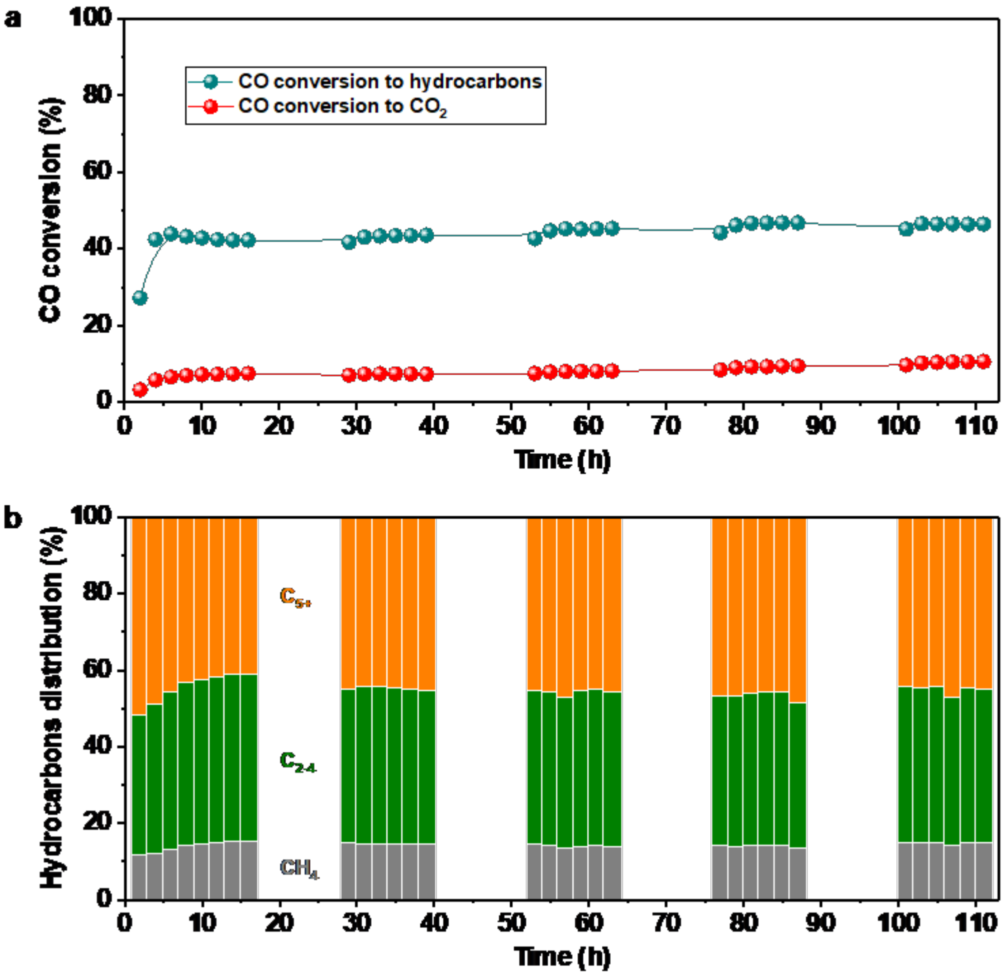
We sincerely thank reviewer #3 again for this valuable suggestion, which is very helpful to improve the scientific quality of this manuscript. We hope that our response and revision for this question are satisfactory to the reviewer.

Q2. The authors didn't present the catalytic performance with time. What time for the spent catalysts? Is there any induction or deactivation period?

Response: We apologize for forgetting to mention the reaction time and thank reviewer #3 for pointing this out. The syngas conversion reactions were generally carried out for 24 hours, and the catalytic data at the stable state after 12 hours of reaction were collected for comparison. This description has been added in the methods section of the revised manuscript.

In addition, we have also added a stability test on the Fe@Mn@0.2Si-c catalyst. As shown in Supplementary Fig. 10, this catalyst rapidly reached a relatively stable state within 4 hours. Besides, during 110 hours of continuous reaction, the CO conversion to hydrocarbons and CO_2 on the Fe@Mn@0.2Si-c catalyst remained at about 45% and 8%, respectively. Meanwhile, the selectivity for CH_4 in hydrocarbons was stable at around 14%. These results suggested that the hydrophobic Fe@Mn@0.2Si-c catalyst possessed a good catalytic stability for syngas conversion.

The stability test and relevant discussions have been added at Supplementary Fig. 10 in the revised Supplementary Information.



Supplementary Fig. 10. (a) CO conversion and (b) hydrocarbons distribution during the stability test of the Fe@Mn@0.2Si-c catalyst. The reaction data corresponding to the blank space in the figure was not collected, because the gas chromatograph was switched to another reactor at this time.

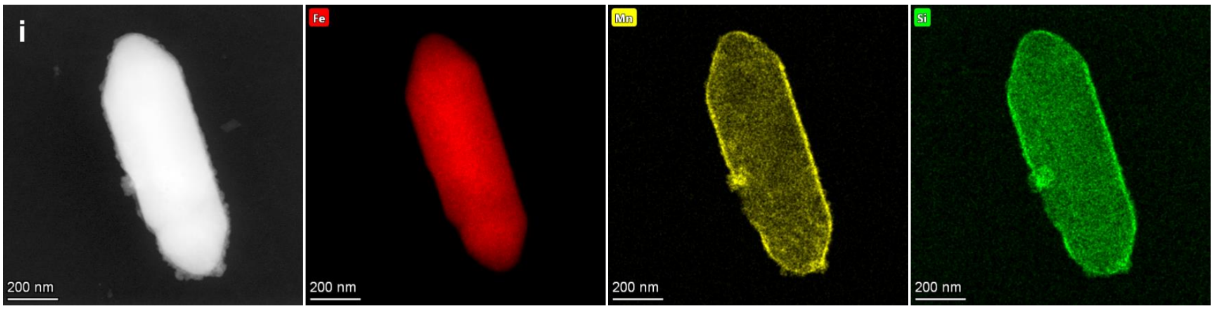
Q3. The authors supposed several diffusion behaviors in different catalysts, such as Fig. 2f and 2g, but lacked solid evidence.

Response: We thank reviewer #3 for pointing this out. These diffusion behaviors in different catalysts shown in Fig. 2f and 2g were supposed based on the results of molecular dynamic simulation in our previous work [*Angew. Chem. Int. Ed. 2023, 62, e202306786*]. As reviewer #3 commented, there is indeed no solid evidence in this manuscript. Thus, in order to avoid the ambiguity to readers and make this work more rigorous, we have deleted Fig. 2f and 2g in the revised manuscript.

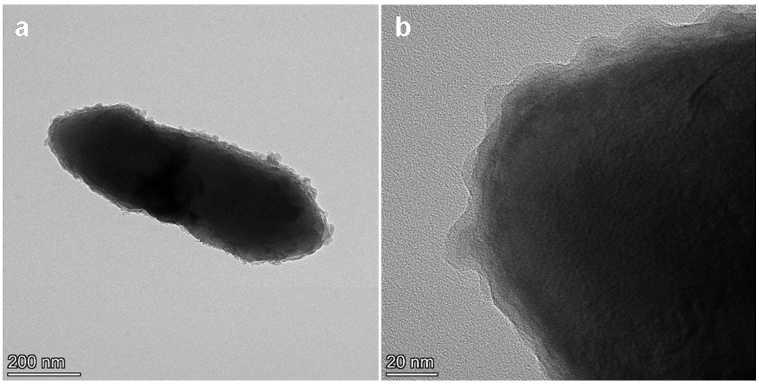
Q4. The authors proposed that the core of the Fe catalyst would shrink because of the density difference between Fe oxides and carbides. However, it is hard to get this conclusion from Fig. 1.

Response: Thanks a lot for your question.

As shown in Supplementary Fig. 2i and Supplementary Fig. 6, the core of the fresh Fe@Mn@0.2Si and Fe@Mn@0.2Si-c catalysts were solid. After reaction, many voids appeared in the core of the two catalysts, especially the Fe@Mn@0.2Si-c catalyst (Fig. 1), suggesting that the core of catalyst shrank and the volume of iron species decreased.



Supplementary Fig. 2. (i) HAADF-TEM image and EDS elemental mapping of Fe@Mn@0.2Si.



Supplementary Fig. 6. TEM images of the Fe@Mn@0.2Si-c catalyst.

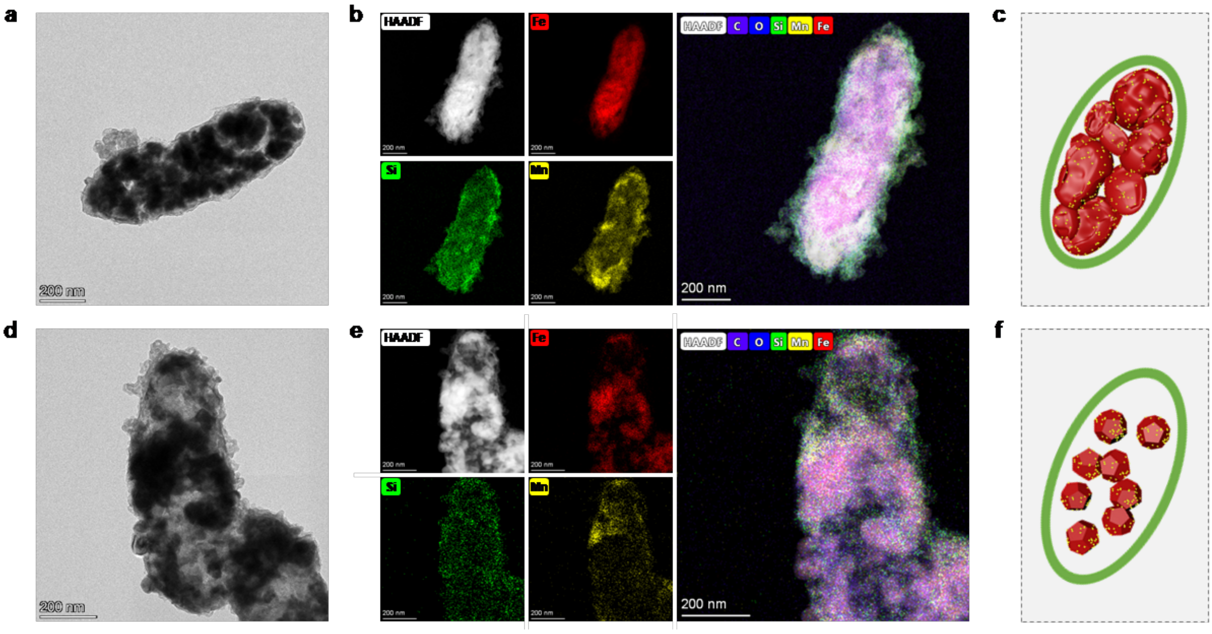
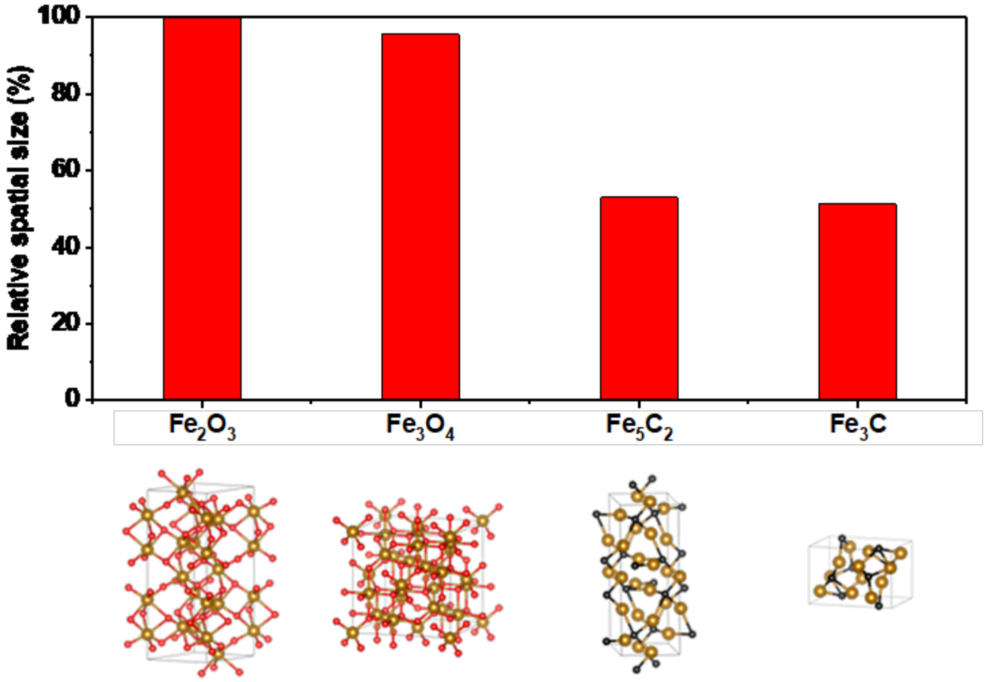


Fig. 1. (a-c) TEM image (a), EDS elemental mapping (b), and structural model (c) of the spent Fe@Mn@0.2Si catalyst. (d-f) TEM image (d), EDS elemental mapping (e), and structural model (f) of the spent Fe@Mn@0.2Si-c catalyst.

We have further quantitatively calculated the relative spatial size of iron oxides and iron carbides based on the volume of unit cell (Supplementary Fig. 7). First, the volume of each iron phase with 120 Fe atoms was calculated. Then, the volume ratios of different iron phases to Fe_2O_3 phase with the same number of Fe atoms were calculated. Detailed data were shown in Supplementary Table 2. The order of the relative spatial size of different iron phases is $Fe_2O_3 > Fe_3O_4 > Fe_5C_2 > Fe_3C$, implying that the transformation of iron oxides to iron carbides is a volume-decreasing process, which is consistent with the TEM images above.



Supplementary Fig. 7. Relative spatial size of different iron phases.

Supplementary Table 2. Calculation of the relative spatial size of different iron phases.

Iron phase	V_0 (Å^3) [a]	n_{Fe} [b]	V (Å^3) [c]	Relative spatial size [d]
Fe_2O_3	301.3	12	3012.8	100.0%
Fe_3O_4	575.9	24	2879.7	95.6%
Fe_5C_2	266.0	20	1595.9	53.0%
Fe_3C	154.6	12	1546.2	51.3%

[a] Volume of unit cell.

[b] Number of Fe atom in unit cell.

[c] Volumes of different iron phases with 120 Fe atoms.

[d] The volume ratios of different iron phases to Fe_2O_3 phase with the same number of Fe atoms.

In addition, the density difference between iron oxides and iron carbides has also been well confirmed in our previous work [*Applied Catalysis B: Environment and Energy 2024, 353, 124067*]. As shown in Figure R1, after transforming Fe_2O_3@SiO_2 into Fe_5C_2@SiO_2 by reduction and carbonization treatments, the core of catalyst shrunk obviously. By further treating Fe_5C_2@SiO_2 with water vapor, Fe_3O_4@SiO_2 was obtained and the core of catalyst increased again. Because the SiO_2

shell was stable during these processes, the volume change of core was attributed to the density difference between iron oxides and iron carbides.

[Redacted]

Figure R1. (*Figure 3 in Applied Catalysis B: Environment and Energy 2024, 353, 124067*)

(d) XRD patterns of Fe_2O_3@SiO_2, Fe_5C_2@SiO_2 and Fe_3O_4@SiO_2. TEM images of (e) Fe_5C_2@SiO_2 and (f) Fe_3O_4@SiO_2. (g) Structural model of the volume change of iron species during the carbonization and oxidation processes.

We especially thank reviewer #3 for the careful reading and insightful questions, which are very helpful to improve the scientific quality of this manuscript.

We hope that our revision work is satisfactory to the reviewer.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

I read the answer to my questions and checked the corresponding correction in the revised manuscript. It is now acceptable with its present status.

Reviewer #2 (Remarks to the Author):

All the comments and suggestions have been addressed. I recommend this manuscript for publication in Nature Communications.

Reviewer #3 (Remarks to the Author):

I think all the technical problems have been addressed well now. But I still care about the novelty of this work. As stated by the authors in response, the report about influence of catalyst hydrophilicity on phase evolution is limited. But there is actually a lot of consensus on the effect of H2O on the formation of iron carbide. For example, the oxidation of H2O results in the easier formation of Fe3O4. Therefore, I think that the influence of hydrophilicity on iron phase can be predicted, and the conclusions in this paper are consistent with these predictions. On the other hand, Although the study on the poisoning effect of chlorine on catalysts is of significance in industry, it is important to point out whether the form of chlorine studied in this work is similar to those in real process.

Point-by-point response to the reviewer comments

Reviewer #1

Comments: I read the answer to my questions and checked the corresponding correction in the revised manuscript. It is now acceptable with its present status.

Response: Thank you very much for reviewing our manuscript and providing helpful suggestions for us to improve the quality of this manuscript.

Reviewer #2

Comments: All the comments and suggestions have been addressed. I recommend this manuscript for publication in Nature Communications.

Response: Thanks a lot for the professional review work, constructive comments, and valuable suggestions on our manuscript.

Reviewer #3

Comments: I think all the technical problems have been addressed well now. But I still care about the novelty of this work. As stated by the authors in response, the report about influence of catalyst hydrophilicity on phase evolution is limited. But there is actually a lot of consensus on the effect of H_2O on the formation of iron carbide. For example, the oxidation of H_2O results in the easier formation of Fe_3O_4. Therefore, I think that the influence of hydrophilicity on iron phase can be predicted, and the conclusions in this paper are consistent with these predictions.

Response: We thank reviewer #3 for the recognition of the technical aspects of our manuscript.

It is well known that the iron carbide active phase is easily oxidized into Fe_3O_4 by the H_2O

produced during reaction, leading to the deterioration of catalytic performance. However, the phase transformation of iron species during syngas conversion is complex, and the effects of surface hydrophobization on the phase evolution behavior of iron-based catalyst are still elusive. In this work, we reveal in detail the function of hydrophobic modification on tuning the phase evolution of iron-based FTS catalyst via combining the CO+H_2O model experiments and multiple characterizations, such as the *in-situ* XRD, *ex-situ* XRD, and *ex-situ* Mössbauer spectroscopy.

More importantly, we unravel here for the first time that appropriate thickness of hydrophobic shell plays a crucial role in stabilizing the iron carbide active phase without Fe_3O_4 formation. The hydrophobic surface can reduce the H_2O concentration in the core vicinity of catalyst during syngas conversion and inhibit the oxidation of iron species by H_2O. However, the contact of chlorine with the iron-based catalyst during the hydrophobic modification procedure can poison and deactivate catalyst by inhibiting the carbonization of iron species. The increase of SiO_2 shell thickness protects catalyst from chlorine poisoning, while excessive SiO_2 inhibits the accessibility and carburization of internal iron species by CO molecules. Appropriate shell thickness is needed to stabilize the iron carbide active phase without Fe_3O_4 formation and achieve good catalytic performance, which has not been reported previously.

Besides, these findings in our manuscript about the function of hydrophobic catalysts working in the syngas chemistry are expected to advance the application of hydrophobization strategy in potentially many other reactions restricted by water, such as the hydrogenation conversion of CO_2, the oxidation of methane into methanol, and the synthesis of dimethyl carbonate.

Thus, we believe that this manuscript contains the novelty and importance, which deserve publication in Nature Communications.

Comments: On the other hand, Although the study on the poisoning effect of chlorine on catalysts is of significance in industry, it is important to point out whether the form of chlorine studied in this work is similar to those in real process.

Response: We thank reviewer #3 for pointing this out.

In industry, syngas derived from coal, especially biomass, generally contains chlorine impurity, which presents in the form of hydrogen chloride.[1-4] The previous works generally investigated the poisoning effect of chlorine on catalyst by adding hydrogen chloride[1,5,6] or trichloroethylene[7]. In this work, the chlorine existed on catalyst is attributed to hydrogen chloride produced during the hydrophobic modification procedure. Thus, the form of chlorine studied in this work is similar to those in real process.

The following explanations have been added in Page 13 of the revised manuscript.

"In industry, syngas derived from coal, especially biomass, generally contains chlorine impurity, which presents in the form of hydrogen chloride [ACS Catal. 5, 3124–3136 (2015); Chem. Eng. Technol. 31, 655–666 (2008); Powder Technol. 180, 265–270 (2008)]. Thus, the form of chlorine studied in this work is similar to those in real process, and understanding the poisoning mechanism of chlorine on catalyst is also important for the industrial application."

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[1] Ma, W. et al. Fischer–Tropsch synthesis: effects of hydrohalic acids in syngas on a precipitated iron catalyst. *ACS Catal.* 5, 3124–3136 (2015).

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[6] Pendyala, V. R. R. et al. Fischer–Tropsch synthesis: XANES investigation of hydrogen chloride poisoned iron and cobalt-based catalysts at the K-edges of Cl, Fe, and Co. *Catal. Lett.* 146, 1858–1866 (2016).

[7] Paredes-Nunez, A., Lorito, D., Schuurman, Y., Guilhaume, N. & Meunier, F. C. Origins of the poisoning effect of chlorine on the CO hydrogenation activity of alumina-supported cobalt monitored by operando FT-IR spectroscopy. *J. Catal.* 329, 229–236 (2015).